Avakening to Reality

Available online at www.elixirpublishers.com (Elixir International Journal)

Vibrational Spectroscopy



Elixir Vib. Spec. 90 (2016) 37416-37430

# Vibrational and Optical Characterization Studies of Diphenyl Ketone by Single Crystal

D.Cecily Mary Glory<sup>1</sup>, R.Madivanane<sup>2</sup>, K.Sambathkumar<sup>3,\*</sup>, A.Claude<sup>3</sup> and K.Settu<sup>3</sup>

<sup>1</sup>R& D centre, Bharathar University.

<sup>2</sup>Department of Physics, Mahatma Government College, Maye, Puducherry,India.

<sup>3</sup>P.G.&Research Department of Physics, A.A.Govt.Arts College, Villupuram-605602, Tamil Nadu, India.

ARTICLE INFO Article history: Received: 16 November 2015; Received in revised form: 28 December 2015; Accepted: 4 January 2016;

Keywords DPK, HOMO- LUMO, UV, NBO, Mullikan, MEP.

# ABSTRACT

Diphenyl ketone (DPK), a semi-organic nonlinear optical material, has been synthesized and single crystals were grown from alcohol – ethanol solution at room temperature up to dimensions of 4.5cm×4.5cm×4cm. The unit cell parameters were determined from single crystal and powder X-ray diffraction studies. The structural perfection of the grown crystal has been analyzed by X-ray diffraction (XRD) study. The variation of dielectric properties of the grown crystal with respect to frequency has been investigated at different temperatures. Microhardness measurements revealed the mechanical strength of grown crystal. The relative second harmonic efficiency of the compound is found to be 1.4 times greater than that of KDP. And the theoretical studies were conducted on the molecular structure and vibrational spectra of diphenyl ketone (DPK). The FT-IR and FT-Raman spectra of DPK were recorded in the solid phase. The molecular geometry and vibrational frequencies of DPK in the ground state have been calculated by using the density functional methods (B3LYP) invoking 6-311++G(d,p) and 6-311+G(d,p) basis set. The optimized geometric bond lengths and bond angles obtained by DFT method show best agreement with the experimental values. A detailed interpretation of the FT-IR and FT- Raman, Mullikan spectra of DPK was also reported. NBOs are localized electron pair orbitals for bonding pairs and lone pairs. UV-VIS spectrum of the compound was recorded and the electronic properties, such as HOMO and LUMO energies, were performed by time dependent density functional theory (TD-DFT) approach. Finally the calculations results were applied to simulated infrared and Raman spectra of the title compound which show good agreement with observed spectra. And the temperature dependence of the thermodynamic properties of constant pressure (Cp), entropy (S) and enthalpy change ( $\Delta H0 \rightarrow T$ ) for DPK were also determined.

© 2016 Elixir All rights reserved.

# Introduction

Diphenyl ketone (DPK), an aromatic ketone is an important compound in organic photochemistry and perfumery as well as in organic synthesis. It is a white crystalline substance with rose-like odor; insolube in water; melting point 49° C; boiling point 305 - 306 C. Diphenyl ketone is used as a constituent of synthetic perfumes and as a starting material for the manufacture of dyes, pesticides and drugs (especially anxiolytic and hypnotic drugs). Diphenyl ketone is used as a photoinitiator of UV-curing applications in inks, adhesive and coatings, optical fiber as well as in printed circuit boards. Photoinitiators are compounds that break down into free radicals upon exposure to ultraviolet radiation. Photoinitiators undergo a unimolecular bond cleavage upon irradiation to yield free radicals (benzoin esters; benzil ketals; alpha-dialkoxy acetophenones; alphahydroxy alkylphenones; alpha-amino alkylphosphine; acylphosphine oxides). Another type of photoinitiators undergoes a bimolecular reaction where the excited state of the photoinitiator interacts with a second molecule (a co-initiator) to generate free radicals (benzophenones, amines; thioxanthones, itanocenes). So

<sup>⊉</sup>yahoo.co.in © 2016 Elixir All rights reserved

Diphenvl ketone derivatives are known to be pharmacologically active. From a molecular chemistry point of view interaction of diphenyl ketone with B-DNA has been clearly demonstrated both experimentally and theoretically. The interaction with DNA and the successive photo-induced energy transfer is at the base of the diphenyl ketone activity as DNA photo sensitizers and may explain part of its therapeutic potentialities. Ultraviolet radiation has more energy than visible light and thus degrades the physical properties such as the appearance of organic substances and plastics. Diphenyl ketone can act as optical filters or deactivate substrate molecules that have been excited by light for the protection polymers and organic substances. There, cosmetic grades are used as sunscreen agents to reduce skin damage by blocking UV [1-3]. The substituted benzene derivatives with high optical non-linearity are very promising materials for future optoelectronics and non-linear optical applications. Non-linear optical effects of compound depend on the polarizability of organic material is generally contribution from the lattice components because of the weak intermolecular bonding and hence posses the high degree of

delocalization. By combining all these facts into account, the present study has been aimed, to investigate the vibrational spectra of DPK. Investigations have also been carried out to identify the HOMO-LUMO energy gap, first NLO property (first-hyperpolarizability), chemical hardness, chemical potential and delocalization activity of the electron clouds in the optimized molecular structure.

All these investigations have been done on the basis of the optimized geometry by using the density functional theory (DFT) at B3LYP/6-311+G(d,p) and 6-311++G(d,p) level. Theoretical studies of bioactive compounds are of interest in order to gain a deeper insight on their action and thus helping in the design of new compounds with therapeutic effects. The knowledge of physico-chemical properties and sites of reaction of investigated compound will provide a deeper insight of its probable action. Particularly, molecular electrostatic potential (MEP) is related to the electronic density and is a very useful descriptor in understanding sites for electrophilic attack and nucleophilic reactions as well as hydrogen bonding interactions. For the investigated compound, molecular electrostatic potential (MEP) is calculated at B3LYP/6-311++G(d,p).

#### Experimental procedure

#### Synthesis and crystal growth

The all the chemicals obtained from Lancaster chemical Company, UK and were used without any further purification. The Diphenyl ketone is taken as a solid flaky salt and dissolved in ample amount of alcohol till it reaches saturation state. Then the solution is heated gently in order to obtain the supersaturated state beyond which the salt becomes unsoluble in the solvent viz., alcohol. The solubility and supersolubility of Diphenyl ketone was observed to be 10 grams and 15 grams per 100ml of ethanol solvent. Then the supersaturated solution is then filtered using Schott Duran Filter paper (pore size 5 micron) and left inside the constant temperature solution growth process for nucleation and subsequent crystallization. The nucleation time was measured for repeatability and was observed to be 452 seconds. The solution was left for crystallization in a constant temperature water bath where the ambient temperature of the bath was optimally kept at 35°C for complete solute utilization where the solvent was found to evaporate fully forming Diphenyl ketone Crystals in the beaker in which it was kept to grow. The DPK crystal is sown in Fig 1.



Fig 1. Cleaved Crystal of Diphenyl ketone.

#### **Characterization techniques**

Single-crystal X-ray diffraction analysis of DPK was carried out using ENRAF NONIUS CAD-4 diffractometer with Mo Kα (0.71073 Å) radiation. Powder X-ray diffraction has been recorded using a Rich Seifert diffractometer (model 2002) with Cu Ka ( $\lambda$ =1.5045 Å) and powdered sample was scanned over the range 10-70° at the rate of 1°/min. A PANalytical X'Pert PRO MRD high-resolution XRD system. with Cu K $\alpha_1$  radiation, was employed to assess the crystalline perfection of grown crystal. The rocking curves of the crystals for the (200) diffraction planes were recorded in symmetrical Bragg geometry using the (100) natural facets by performing a x scan with triple-axis geometry. The monochromated X-ray beam incident on the specimen was obtained using a hybrid two-bounce Ge (220) monochromator with a parabolic multilayer mirror assembly. The diffracted beam from the specimen was detected using a scintillation detector with a triple- axis three bounce Ge(220) analyzer. FTIR and FT-Raman spectrum were recorded using the Perkin Elmer spectrum one FTIR spectrometer by KBr pellet technique and Bruker RFS 27 in the region 4000–400 cm<sup>-1</sup>. The experiment was carried out in the frequency range 100 Hz-5 MHz at room temperature. The grown crystals were tested for their microhardness property using Shimadzu HMV Vickers's microhardness tester fitted with a diamond indenter. UV-Vis spectrum was recorded in the range of 200-2000 nm using Perkin Elmer Lambda35 spectrophotometer.

#### X-ray diffraction analysis

Single crystal X-ray diffraction analysis for the grown DPK crystal has been carried out to confirm the crystallinity and also to identify the unit cell parameters. Diphenyl ketone exhibited as a face centered monoclinic structure with space group C212121. The lattice parameters were calculated from single crystal data and the calculated values are given in Table 1 and the final atomic coordinates are listed in Table 2 with values reported in the literature for the sake of comparison. The results are in agreement with the earlier reported values [4].

Molecular formula	C13H10O
Formula weight	136.4
Temperature	293
Wavelength	1.5045 Å
Crystal system	monoclinic
Space group	'P 21 21 21'
Unit cell dimensions a	9.751Å
b	10.671 Å
с	24.813 Å
α	87.47
β	83.80
υ	63.154
Volume	1001.71Å3
Z	4
Calculated density	1.208
Absorption correction	1.208
F(000)	200
Crystal size	4.5 cm x4.5 cm x 4 cm
Completeness to theta=30.05°	100.0%
Theta rang for data collection	1.53-30.05°
Refinement method	Full-matrix least-squares on F <sup>2</sup>
R indices (all data)	$0.0478, wR_2 = 0.0478$

 Table 1. Crystal data and structure refinement for the

 Diphenvl Ketone.

Atom	X	У	Z
C1	0.1940(3)	0.4979(2)	0.89906(17)
C2	0.2203(3)	0.3664(2)	0.91343(19)
C3	0.3107(3)	0.2974(2)	0.8381(2)
C4	0.3740(3)	0.3583(3)	0.7468(2)
C5	0.3461(3)	0.4887(2)	0.7303(2)
C6	0.2558(3)	0.5608(2)	0.80679(16)
C7	0.2199(3)	0.7001(2)	0.78224(18)
C8	0.1982(3)	0.7968(2)	0.87218(17)
C9	0.1001(3)	0.9054(2)	0.8519(2)
C10	0.0822(3)	1.0011(2)	0.9291(3)
C11	0.1636(3)	0.9903(2)	1.0284(3)
C12	0.2631(3)	0.8833(2)	1.05006(18)
C13	0.2791(3)	0.7863(2)	0.2791(3)
H13	0.1345	0.5446	0.9515
H14	0.1764	0.3246	0.9747
H15	0.3293	0.2091	0.8487
H16	0.4359	0.3111	0.6960
H17	0.3879	0.5290	0.6676
H18	0.0457	0.9133	0.7847
H19	0.0154	1.0731	0.9146
H20	0.1516	1.0551	1.0811
H21	0.3191	0.8767	1.1168
H22	0.3443	0.7137	0.9876
O24	0.2096(3)	0.73555(16)	0.68655(12)

Table 2. Atomic coordinates and equivalent parameters  $(A^2 x \ 10^3)$  of Diphenyl Ketone.

#### X-ray powder diffraction analysis

From the X-ray powder diffraction data, the various planes of reflection were indexed using XRDA 3.1 program and the lattice parameters have been evaluated. The lattice parameters are in good agreement with the reported values [4]. The indexed X-ray powder diffraction pattern is shown in Fig. 2. The observed d values for different 2h with (h k l) indices of the corresponding planes are given in Table 3.

l'able 3.	Indexed	X-ray	powder	diffraction	data of

Dipheny	l Ketone	crystal.
---------	----------	----------

<b>F</b> J J ~ J ~							
h	k	l	d cal.(Å)	2θ cal.(°)			
2	0	0	7.5888	11.652			
2	1	1	7.1767	12.323			
1	1	2	4.9094	18.054			
2	2	0	4.0103	22.148			
3	2	1	3.7313	23.828			
1	0	3	3.4953	25.463			
3	2	1	3.7679	26.564			

## **Microindentation Tests**

Among the various method of hardness measurements, the most common and reliable method is the Vicker's hardness test method. Smith and Sand land have proposed that a pyramid be substituted for a ball in order to provide geometrical similitude under different values of load. The Vicker's pyramid indentor where opposite faces contain an angle ( $\alpha = 136^\circ$ ) is the most widely accepted pyramid indentor. Pyramid indentors are said to be best suited for hardness tests due to two reasons namely

i. The contact pressure for a pyramid indentor is independent of indent size.

ii.Pyramid indenters are less affected by elastic release than other indentors.

The base of the Vicker's pyramid is a square and the depth of indentation corresponds to 1/7th of the indentation diagonal. The Vicker's hardness number HV or Diamond Pyramid Number (DPN) is defined as.

 $H_v = \frac{2WSin\alpha/2}{2}$ 

Where a is the apex angle of the indentor (a  $=136^{\circ}$ ). The Vicker's hardness number is therefore calculated from the relation

Hv = W / Pyramid area  
= 
$$\frac{1.8544 \times W}{1.8544 \times W}$$
 kg/mm<sup>2</sup>

Diphenyl ketone crystal had a maximum Vickers microhardness value of 206 for 20grams and a minimum of 162 for 90 grams load. The variation of microhardness with the applied load is shown in Fig.3.



Fig 2. Powder XRD of Diphenyl ketone.



Fig 3. Vickers Microhardness tests for Diphenyl ketone. Computational details

The initial geometry of DPK is optimized using the B3LYP/6-311+G(d,p) and 6-311++G(d,p) level of Gaussian 09W programme package [5]. The vibrational frequency analysis is computed using B3LYP/6-311++G(d,p) method to determine the nature of a stationary point found by geometry optimization. The first hyperpolarizability and the chemical shift of the atoms of DPK have been calculated using B3LYP/6-311++G(d,p) method. The HOMO-LUMO analysis has been carried out to explain the charge transfer within the compound. The chemical hardness  $(\eta)$  and chemical potential  $(\mu)$  have been calculated using the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). NBO analysis has been performed on DPK using B3LYP/6-31++G(d,p) level in order to elucidate the intermolecular hydrogen bonding, intermolecular charge transfer (ICT), rehybridization, delocalization of electron density. The comparison between the calculated and the observed vibrational spectra helps us to understand the observed spectral features. In order to improve the agreement of theoretically calculated frequencies with experimentally calculated frequencies, it is necessary to scale down the theoretically calculated harmonic frequencies. Hence, the vibrational frequencies theoretically calculated at B3LYP/6-311+G(d,p) and 6-311++G(d,p) are scaled down by using MOLVIB 7.0 version written by Tom Sundius [6-7].

#### **Prediction of Raman Intensities**

The Raman activities (S<sub>i</sub>) calculated by GaUssian 09W package have been suitably adjusted by the scaling procedure with MOLVIB and subsequently converted to relative Raman intensities (I<sub>i</sub>) using the following relationship derived from the basic theory of Raman scattering [8-10].

$$I_{i} = \frac{f(v_{0} - v_{i})^{4}Si}{v_{i} \left[1 - \exp{\frac{-hcv_{i}}{kT}}\right]}$$

where  $v_0$  is the exciting frequency (in cm<sup>-1</sup> units).  $v_i$  is the vibrational wave number of the i<sup>th</sup> normal mode, h, c and k are universal constants, and f is the suitably chosen common scaling factor for all peak intensities.

# **Results and discussion**

#### Molecular geometry

The optimized molecular structure and numbering scheme of DPK are shown in Fig. 4. The geometry of the compound under investigation is considered by possessing  $C_1$  point group symmetry. The calculated optimized geometrical parameters of DPK are presented in Table 4.

Detailed description of vibrational modes can be given by means of normal coordinate analysis. The internal coordinates describe the position of the atoms in terms of distances, angles and dihedral angles with respect to an origin atom. The symmetry coordinates are constructed using the set of internal coordinates. In present investigation, the full sets of 96 standard internal coordinates (containing 30 redundancies) for DPK are defined in Table 5. From these, a non-redundant set of local symmetry coordinates are constructed by suitable linear combinations of internal coordinates following the recommendations of Fogarasi et al. [11,12] are summarized in Table 6. Several authors have explained the changes in bond length of the C-H bond on the substitution due to a change in charge distribution on the carbon of the benzene ring. The substituent may be either of the electrons withdrawing type of oxygen. The carbon atoms are bonded to the hydrogen atoms with an  $\sigma$  bond in the benzene and the substitution of a halogen for hydrogen reduces the electron density at the ring carbon atom. The ring carbon atoms in substituted benzenes exert a larger attraction on the valence electron cloud of the hydrogen atom resulting in an increase in the C-H force constant and a decrease in the corresponding bond length. It would be influenced by the combined effects of the inductivemesomeric interaction and the electric dipole field of the polar substituent. From theoretical values, it is found that most of the optimized bond lengths are slightly larger than the experimental values, due to the fact that the theoretical calculations belong to isolated molecule in gaseous phase and the experimental results belong to molecule in solid state. The computed bond length and bond angles are compared with Xray diffraction data of similar compound. For DPK, the benzene ring appears a little distorted with larger C7-C8 bond length and shorter C5-C6 bond length and angles slightly out

of the regular hexagonal structure. It is due to the substitutions of the oxygen and carbon atom in the place of H atoms. The C-H bonds are found to be shorter than the other bonds for DPK. These distortions are explained in terms of the change in hybridisation effect by the substituent at the



#### Fig 4. Molecular structure of Diphenvl ketone.

Carbon site to which it is appended. The C-C bond lengths adjacent to the C4-C3, C7-O22 bonds are increases and the angles C2-C1-C6, C3-C4-C5, C5-C4-C7, C7-C8-C14,C9-C10-C4 are smaller than typical hexagonal angle of 120° by B3LYP method. This is because of the effect of substitution of O–C group attached to the C7 of the benzene ring. The variation in torsional angles C5-C4-O14-H15 =162.48°(B3LYP) is due to charge delocalization of the title compound. Comparing bond angles and bond lengths by calculated B3LYP method with experimental data, the B3LYP\6-311++G(d,p) calculated values correlates well with the experimental data. Also, it should be noted that the experimental results belong to solid phase and theoretical calculations belong to gaseous phase. The calculated geometric parameters can be used as foundation to calculate the other parameters of the molecule. In order to find the most optimized geometry, the energy calculations are carried out.

#### First hyperpolarizability

The potential application of the title compound in the field of nonlinear optics demands, the investigation of its structural and bonding features contribution to the hyperpolarizability enhancement, by analysing the vibrational modes using IR and Raman spectroscopy. Many organic molecules, containing conjugated  $\pi$  electrons are characterized by large values of molecular first hyper polarizabilities, were analysed by means of vibration spectroscopy [13]. In most of the cases, even in the absence of inversion symmetry, the strongest band in the IR spectrum is weak in the Raman spectrum and vice-versa. But the intramolecular charge from the donor to acceptor group through a  $\pi$ -bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making IR and Raman activity strong at the same time. The experimental spectroscopic behavior described above is well accounted for a calculations in  $\pi$  conjugated systems that predict exceptionally infrared intensities for the same normal modes. The first hyperpolarizability ( $\beta$ ) of this novel molecular system is calculated using the *ab initio* quantum mechanical method, based on the finite-field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. The first hyperpolarizability is a third-rank tensor that can be described by a 3x3x3 matrix.

calculations							
Parameters	Parameters Bond Length (Å)		Exp Parameters		Bond Angle Value ( <sup>0</sup> )		Exp
	B3LYP/6-	B3LYP/6-	_		B3LYP/6-	B3LYP/6-311++G(d,p)	
	311+G(d,p)	311 + + G(d,p)			311+G(d,p)		
C1-C2	1.3970	1.3972	1.390	C2-C1-C6	119.2856	119.2858	116.7
C1-C6	1.4003	1.4005	1.396	C2-C1-H15	120.2973	120.2979	-
C1-H15	1.0851	1.0854	-	C6-C1-H15	120.4165	120.4169	-
C2-C3	1.3990	1.3992	-	C1-C2-C3	120.5623	120.5627	-
C2-H16	1.0852	1.0855	-	C1-C2-H16	120.1325	120.1329	-
C3-C4	1.4081	1.4086	1.391	C3-C2-H16	119.3044	119.3048	-
C3-O22	1.0769	1.0771		C2-C3-C4	121.0310	121.0316	-
C4-C5	1.4140	1.4145	1.369	C2-C3-O22	117.1524	117.1529	-
C4-C7	1.5090	1.5097	-	C4-C3-O22	121.8150	121.8154	-
C5-C6	1.3923	1.3929	-	C3-C4-C5	117.4439	117.4443	-
C5-H17	1.0822	1.0825	1.215	C3-C4-C7	127.6770	127.6778	119.7
C6-H18	1.0850	1.0853	1.090	C5-C4-C7	114.8787	114.8787	-
C7-C8	1.5193	1.5197	-	C4-C5-C6	121.5672	121.5679	-
C7-H24	1.2572	1.2577	1.090	C4-C5-H17	117.6760	117.6767	-
C8-C9	1.4083	1.4088	-	C6-C5-H17	120.7560	120.7563	-
C8-H14	1.4141	1.4145	1.090	C1-C6-C5	120.1084	120.1087	122.1
C9-C10	1.3990	1.3992	-	C1-C6-H18	120.1811	120.1813	-
C9-H23	1.0771	1.0774	1.090	C5-C6-H18	119.7101	119.7107	-
C10-H11	1.2850	1.2853	-	C4-C7-C8	127.4870	127.4874	-
C10-C12	1.3971	1.3975	-	C4-C7-H24	116.2561	116.2565	-
C12-C13	1.4005	1.4009	-	C8-C7-H24	116.2562	116.2566	-
C12-H19	1.0850	1.0854	1.090	C7-C8-C9	127.6770	127.6771	119.2
C13-C14	1.3927	1.3929	-	C7-C8-C14	114.8782	114.8785	-
C13-H20	1.0851	1.0853	1.090	C9-C8-H14	117.4443	117.4446	-
C14-H21	1.0823	1.0825	1.090	C8-C9-C10	121.0312	121.0316	-
O22-H23	1.6962	1.6967	-	C8-C9-H23	121.8152	121.8156	-
				C10-C9-H23	117.1523	117.1528	-
				C9-C10-C11	119.3044	119.3048	11.10
				C9-C10-C12	120.5621	120.5627	-
				C11-C10-C12	120.1320	120.1325	-
				C10-C12-C13	129.2851	129.2856	-
				C10-C12-H19	120.2973	120.2979	-
				C13-C12-H19	120.4165	120.4169	-
				C12-C13-H14	120.1083	120.1087	-
				C12-C13-H20	120.1810	120.1815	-
				H14-C13-H20	119.7102	119.7109	-
				C8-H14-C13	121.5674	121.5676	-
				C8-H14-H21	117.6763	117.6767	-
				C13-H14-H21	120.7560	120.7563	-
				С3-О22-Н23	136.7633	136.7637	-
				С9-Н23-О22	136.7632	136.7637	-

# Table 4. Optimized geometrical parameters of Diphenyl Ketone by B3LYP /6-311+G(d,p) and B3LYP/6-311++G(d,p) calculations

<sup>a</sup>For numbering of atoms refer Fig. 4

<sup>a</sup>Experimental values are taken from Ref.[27].

Table 5. Definition of internal	l coordinates o	of Diphenyl
Keton	e	

No.	Symbol	Туре	<b>Definition</b> <sup>a</sup>				
(i)							
Stretching							
1-10	R <sub>i</sub>	C-H	$C_1$ - $H_{23}$ , $C_2$ - $H_{24}$ , $C_3$ - $H_{20}$ , $C_5$ - $H_{21}$ , $C_6$ -				
			$H_{22}, C_9 - H_{19},$				
		<i></i>	$C_{10}$ - $H_{18}$ , $C_{11}$ - $H_{17}$ , $C_{16}$ - $H_{12}$ , $C_{13}$ - $H_{15}$				
11	Xi	C-0	C <sub>7</sub> -O <sub>14</sub>				
12-	r <sub>i</sub>	C-C	$C_1 - C_2, C_2 - C_3, C_3 - C_4, C_4 - C_5, C_5 - C_6, C_6, C_6, C_6, C_6, C_6, C_6, C_6,$				
25			$C_{6}, C_{4}-C_{7}, C_{7}-C_{8},$				
			$C_8 - C_9, C_9 - C_{10}, C_{10} - C_{11}, C_{11} - C_{12}, C_{12} - C_{10}$				
In plan	a handing		$C_{13}, C_{13}, C_{8}$				
111-pian		Ding1					
20-	α <sub>i</sub>	Kingi	$C_1 - C_2 - C_3, C_2 - C_3 - C_4, C_3 - C_4 - C_5, C_4 - C_5 - C$				
32	<i>a</i> .	Ring?	$C_{6}, C_{5}, C_{6}, C_{1}, C_{6}, C_{1}, C_{2}$				
36	ui	King2	$C_3 - C_4 - C_7, C_4 - C_7 - C_8, C_7 - C_8 - C_9, C_8 - C_9$				
37-	a.	Ring3					
42	u <sub>1</sub>	King.					
43-	ß.	C-C-H	$H_{22}-C_1-C_2$ $H_{22}-C_1-C_2$ $H_{22}-C_2-C_3$ $H_{22}-C_3-C_3$				
62	p <sub>1</sub>	e e n	Ce-Ce-H24-C2-C1-H24-C2-C2-H20-C2-				
			C4 H20-C2-C2 H21-C5-C4 H21-C5-				
			$C_{6}$ , $H_{10}$ - $C_{0}$ - $C_{8}$ , $H_{10}$ - $C_{0}$ - $C_{10}$ , $H_{18}$ - $C_{10}$ -				
			$C_{9}$ , $H_{18}$ - $C_{10}$ - $C_{11}$ , $H_{17}$ - $C_{11}$ - $C_{10}$ , $H_{17}$ - $C_{11}$ -				
			$C_{12}$ , $H_{16}$ - $C_{2}$ - $C_{13}$ , $H_{16}$ - $C_{12}$ - $C_{11}$ , $H_{15}$ - $C_{13}$ -				
			$C_{12}$ , $H_{15}$ - $C_{13}$ - $C_8$				
63,64	Zi	O-C-C	O <sub>14</sub> - C <sub>7</sub> -C <sub>8</sub> ,O <sub>14</sub> -C <sub>7</sub> -C <sub>4</sub>				
Out-of-	-plane bend	ling					
65-	ψi	C-H	$H_{21}-C_5-C_6-C_4, H_{22}-C_6-C_1-C_5, H_{23}-C_1-C_5, H_{23}-C_5, H_{23}-C_5-C_5, H_{23}-C_5-C_5-C_5, H_{23}-C_5-C_5-C_5-C_5-C_5-C_5-C_5-C_5-C_5-C_5$				
74			C <sub>2</sub> -C <sub>6</sub> ,H <sub>24</sub> -C <sub>2</sub> -C <sub>1</sub> -C <sub>3</sub> ,H <sub>20</sub> -C <sub>3</sub> -C <sub>4</sub> -				
			$C_2, H_{18}-C_{10}-C_9-C_{11}, H_{19}-C_9-C_{10}-C_8, H_{17}-C_9-C_{10}-C_8, H_{17}-C_9-C_{10}-C_8, H_{17}-C_9-C_{10}-C_8, H_{17}-C_{10}-C_{$				
			$C_{11}$ - $C_{12}$ - $C_{10}$ , $H_{16}$ - $C_{12}$ - $C_{11}$ - $C_{13}$ , $H_{15}$ - $C_{13}$ -				
			C <sub>12</sub> -C <sub>8</sub> ,				
75	χi	C-0	$O_{14}$ - $C_7$ - $C_8$ - $C_4$				
Torsio	1	I	1				
76–	$ au_i$	t Ring	$C_1 - C_2 - C_3 - C_4, C_2 - C_3 - C_4 - C_5, C_3 - C_4 - C_5$				
81			$C_6, C_4 - C_5 - C_6 - C_1, C_5 - C_6 - C_1 - C_2, C_2, C_2, C_2, C_2, C_2, C_2, C_2,$				
			C <sub>2</sub> -C <sub>3</sub>				
82-	τi	t Ring	$C_3 - C_4 - C_7 - C_8, C_4 - C_7 - C_8 - C_9, C_7 - C_8 - C_9$				
86			$C_3, C_8 - C_9 - C_3 - C_4, C_9 - C_3 - C_4 - C_7$				
87-	$ au_i$	t Ring	$C_8-C_9-C_{10}-C_{11},C_9-C_{10}-C_{11}-C_{12},C_{10}-C_$				
92			$C_{11}$ - $C_{12}$ - $C_{13}$ , $C_{11}$ - $C_{12}$ - $C_{13}$ - $C_8$ , $C_{12}$ - $C_{13}$ -				
			$C_8-C_9, C_{13}-C_8-C_9-C_{10}$				
93-	τι	Butterfly	$C_{13}$ - $C_8$ - $C_9$ - $H_{19}$ , $C_7$ - $C_8$ - $C_9$ - $C_{10}$ , $C_5$ - $C_4$ -				
96			$C_3-H_{20}, C_7-C_4-C_3-C_2$				

<sup>a</sup>For numbering of atoms refer Fig.4

The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [14]. The components of  $\beta$  are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the electrical field is weak and homogeneous, this expansion becomes

$$E = E_0 - \sum_{i} \mu_i F^i - \frac{1}{2} \sum_{ij} \alpha_{ij} F^i F^j - \frac{1}{6} \sum_{ijk} \beta_{ijk} F^i F^j F^k - \frac{1}{24} \sum_{ijkl} v_{ijkl} F^i F^j F^k F^l$$

Where E<sub>0</sub> is the energy of the unperturbed molecule;  $F^i$  is the field at the origin; and  $\mu_i$ ,  $\alpha_{ij}$   $\beta_{ijk}$  and  $\gamma_{ijkl}$  and are the components of dipole moment, polarizability, the first hyperpolarizabilities and second hyperpolarizibilities, respectively. The calculated total dipole moment ( $\mu$ ) and mean first hyperpolarizability ( $\beta$ ) of DPK are 2.961 Debye and 6.821x10<sup>-30</sup> esu, respectively, which is comparable with the reported values of similar derivatives. The large value of hyperpolarizibilities,  $\beta$  which is a measure of the non-linear optical activity of the molecular system, is associated with the intramolecular charge transfer, resulting from the electron

cloud movement through  $\pi$  conjugated frame work from electron donor to electron acceptor groups. The physical properties of these conjugated molecules are governed by the high degree of electronic charge delocalization along the charge transfer axis and by the low band gaps. So we conclude that the title compound is an attractive object for future studies of nonlinear optical properties.

Table 6. Definition of local symmetry coordinates of
Diphenyl Ketone

[	No.	Туре	Definition <sup>a</sup>
	(i)		
	1-10	СН	$R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10}$
ΙL	11	CO	X <sub>11</sub>
1 L	12-25	CC	$\mathbf{r}_{12}$ , $\mathbf{r}_{13}$ , $\mathbf{r}_{14}$ , $\mathbf{r}_{15}$ , $\mathbf{r}_{16}$ , $\mathbf{r}_{17}$ , $\mathbf{r}_{18}$ , $\mathbf{r}_{19}$ , $\mathbf{r}_{20}$ , $\mathbf{r}_{21}$ , $\mathbf{r}_{22}$ , $\mathbf{r}_{23}$ , $\mathbf{r}_{24}$ , $\mathbf{r}_{25}$
		R <sub>1</sub> trigd	$(\alpha_{26}$ - $\alpha_{27}$ + $\alpha_{28}$ - $\alpha_{29}$ + $\alpha_{30}$ - $\alpha_{31})/\sqrt{6}$
	27	R <sub>1</sub> symd	$(-\alpha_{26} - \alpha_{27} + 2\alpha_{28} - \alpha_{29} - \alpha_{30} - 2\alpha_{31}) / \sqrt{12}$
	28	R <sub>1</sub> asymd	$(\alpha_{26} - \alpha_{27} + \alpha_{29} - \alpha_{30}) / \sqrt{2}$
	29	R bend1	$\alpha_{32}+a(\alpha_{33}+\alpha_{34})+b(\alpha_{35}-\alpha_{36})$
	30	R bend2	$(a-b)\alpha_{32}-\alpha_{36}+(1-a)\alpha_{34}-\alpha_{35}$
	31	R <sub>2</sub> trigd	$(\alpha_{37}\text{-}\alpha_{38}\text{+}\alpha_{39}\text{-}\alpha_{40}\text{+}\alpha_{41}\text{-}\alpha_{42})/\sqrt{6}$
	32	R <sub>2</sub> symd	$(-\alpha_{37}-\alpha_{38}+2\alpha_{39}-\alpha_{40}-\alpha_{41}-2\alpha_{42})/\sqrt{12}$
	33	R <sub>2</sub> asymd	$(\alpha_{37}-\alpha_{38}+\alpha_{40}-\alpha_{41})/\sqrt{2}$
	34-43	b C H	$(\beta_{43}-\beta_{44})/\sqrt{2}, (\beta_{45}-\beta_{46})/\sqrt{2}, (\beta_{47}-\beta_{48})/\sqrt{2}, (\beta_{49}-\beta_{48})/\sqrt{2}$
			$\beta_{50}$ / $\sqrt{2}$ , $(\beta_{51}$ - $\beta_{52}$ )/ $\sqrt{2}$ , $(\beta_{53}$ - $\beta_{54}$ )/ $\sqrt{2}$ , $(\beta_{55}$ -
			$\beta_{56}$ // $\sqrt{2}$ ,( $\beta_{57}$ - $\beta_{58}$ )/ $\sqrt{2}$ ,( $\beta_{59}$ - $\beta_{60}$ )/ $\sqrt{2}$ ,( $\beta_{61}$ -
			$\beta_{62})/\sqrt{2}$
	44	b OC	$(Z_{63}-Z_{64}) / \sqrt{2}$
	45-55	ωCΗ	Ψ65 ,Ψ66,Ψ67,Ψ68,Ψ69,Ψ70,Ψ71,Ψ72,Ψ73,Ψ74,Ψ75
	56	ωCO	χ <sub>75</sub>
	57	1Ring trigd	$(\tau_{76} - \tau_{77} + \tau_{78} - \tau_{79} + \tau_{80} - \tau_{81}) / \sqrt{6}$
	58	1Ring symd	$(\tau_{76} - \tau_{78} + \tau_{79} - \tau_{81}) / \sqrt{2}$
	59	1Ring asymd	$(-\tau_{76} + 2\tau_{77} - \tau_{78} - \tau_{79} + 2\tau_{80} - \tau_{81}) / \sqrt{12}$
	60	Torsion1	$\tau_{a,c}$ b( $\tau_{aa} + \tau_{a,c}$ ) $2(\tau_{aa} + \tau_{a,c})$
୲┝	61	Torsion?	$(a_{2}b)(\tau_{22}+\tau_{36})+a(\tau_{32}+\tau_{35})$
╵┝	62	3Ring	(a-b)(182+186+(1-a)(183+185))
	02	trigd	$(\tau_{87} - \tau_{88} + \tau_{89} - \tau_{90} + \tau_{91} - \tau_{92}) / \sqrt{6}$
	63	3Ring	
		symd	$(\tau_{87} - \tau_{89} + \tau_{90} - \tau_{92}) / \sqrt{2}$
	64	3Ring asymd	$(\text{-}\tau_{87} + 2\tau_{88} \text{-} \tau_{89} \text{-} \tau_{90} + 2\tau_{91} \text{-} \tau_{92}) \; / \; \sqrt{12}$
	65-66	Butterfly	$(\tau_{93} - \tau_{94}) / \sqrt{2} (\tau_{95} - \tau_{96}) / \sqrt{2}$
L	9		

<sup>a</sup>The internal coordinates used here are defined in Table 5.

# **HOMO-LUMO** analysis

Many organic molecules that contain conjugated  $\pi$  electrons are characterized hyperpolarizabilities and were analyzed by means of vibrational spectroscopy. In most cases, even in the absence of inversion symmetry, the weakest bands in the Raman spectrum are strongest in the IR spectrum and vice versa. But the intramolecular charge transfer from the donor to accepter group through a single–double bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making IR and Raman activity strong at the same time. It is also observed in the title compound the bands in FT-IR spectrum have their counterparts in Raman shows that the

relative intensities in IR and Raman spectra are comparable resulting from the electron cloud movement through  $\pi$ conjugated frame work from electron donor to electron acceptor groups. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important parameters for quantum chemistry. We can determine the way the molecule interacts with other species; hence, they are called the frontier orbitals. HOMO, which can be thought the outermost orbital containing electrons, tends to give these electrons such as an electron donor. On the other hand; LUMO can be thought the innermost orbital containing free places to accept electrons [15]. Owing to the interaction between HOMO and LUMO orbital of a structure, transition state transition of  $\pi^*$  type is observed with regard to the molecular orbital theory. The calculated self- consistent field (SCF) energy of DPK is -576.4838 a.u. Therefore, while the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. Energy difference between HOMO and LUMO orbitals is called as energy gap that is an important stability for structures. In addition, the pictorial scheme of few MOs of DPK is shown in Fig. 5. HOMO is localized on the central ring and has partially contribution from the substitution groups such as oxygen and amino group. LUMO is guite localized on the central ring and has strong contribution from the substituted electronegative oxygen and amino group. The energy gap between HOMO and LUMO is 0.1868 a.u., which shows that charge transfer may be taking place from the ring to oxygen atom. As seen from the Fig. 5 HOMO-1 is very similar to HOMO, rotated by 90°. HOMO-3 is mainly localized on ring carbon atom where as LUMO+3 is localized on ring carbon atoms and oxygen atom.

## Global and local reactivity descriptors

Based on density functional descriptors global chemical reactivity descriptors of molecules such as hardness, chemical potential, softness, electronegativity and electrophilicity index as well as local reactivity have been defined [16-20]. Pauling introduced the concept of electronegativity as the power of an atom in a molecule to attract electrons to it. Hardness (n), chemical potential ( $\mu$ ) and electronegativity ( $\chi$ ) and softness are defined follows.

$$\eta = \frac{1}{2}(\partial 2E/\partial N2)V(r) = \frac{1}{2}(\partial \mu/\partial N)V(r)$$

 $= (\partial E / \partial N) V(r)$ μ

 $= -\mu = -(\partial E/\partial N)V(r)$ χ 🗆

where E and V(r) are electronic energy and external potential of an N-electron system respectively. Softness is a property of molecule that measures the extent of chemical reactivity. It is the reciprocal of hardness.

S = 1/n

Using Koopman's theorem for closed-shell molecules, n,  $\mu$  and  $\chi$  can be defined as

= (I-A)/2η

$$\mu = -(I+A)/$$

$$\chi = (I+A)/2$$

where A and I are the ionization potential and electron affinity of the molecules respectively. The ionization energy and electron affinity can be expressed through HOMO and LUMO orbital energies as  $I = -E_{HOMO}$  and  $A = -E_{LUMO}$ . Electron affinity refers to the capability of a ligand to accept precisely one electron from a donor. However in many kinds of bonding viz covalent hydrogen bonding, partial charge transfer takes places. Recently Parr et al [16] have defined a new descriptor to quantify the global electrophilic power of the molecule as electrophilicity index  $(\omega)$ , which defines a quantitative classification of the global electrophilic nature of a molecule Parr *et al* [16] have proposed electrophilicity index ( $\omega$ )  $\Box$  as a measure of energy lowering due to maximal electron flow between donor and acceptor. They defined electrophilicity index  $(\omega)$  as follows





Lumo energy= -0.1871a.u.

Fig 5. Frontier orbital energy of Diphenyl ketone

The usefulness of this new reactivity quantity has been recently demonstrated in understanding the toxicity of various pollutants in terms of their reactivity and site selectivity [21-23]. The calculated value of electrophilicity index describes the biological activity of DPK. All the calculated values of hardness, potential, softness and electrophilicity index are shown in Table 7.

B3LYP/6-311++G(d,p)	
-0.3739a.u	
-0.1871a.u.	
-0.1868 a.u.	
0.3739 a.u.	
0.1871a.u.	
10.7066 a.u.	
0.0934 a.u.	
-0.2805 a.u.	
0.4207 a.u.	

#### Table 7. HOMO - LUMO energy gap and related molecular properties of Diphenvl Ketone

#### **UV-spectral analysis**

The Absorption spectra of Diphenyl ketone was taken in a Lambda 35 UV-VIS spectrophotometer where two prominent absorption maxima were observed at 225nm and 255nm respectively. It also has two additional maxima, one at 285nm and another at 345nm. It is observed that Diphenyl ketone gives some UVB protection but is particularly useful in the UVA region, the region that is the principle cause of colour loss and perfume degradation. A transmission peak at 255nm signifies a  $\pi$  to  $\pi^*$  transition and identification of the presence of the benzene rings in the radical. Aromatic systems, which contain p electrons, absorb strongly in the ultraviolet. This is evident by a previous transmission peak at 245nm. Two more prominent peaks were observed at 328nm and 382 nm of the transmission spectra in addition to the 225nm and 255nm peaks observed earlier. These values may be slightly shifted by solvent effects. The role of substituents and of the solvent influences on the UV spectrum.

Excited state	EE(ev)	Oscillator strength f	Configuratio n	CI expansion coefficient	Wavelengt h (nm)
1	-2.3809	0.0000	45 →48	0.10436	225
			46 →47	-0.67862	
			$46 \rightarrow 47$	0.67862	
2	-2.0965	0.0055	$42 \rightarrow 47$	0.19440	245
			$45 \rightarrow 47$	-0.41471	
			$46 \rightarrow 48$	0.44417	
			$42 \rightarrow 47$	-0.19440	
			$45 \rightarrow 48$	0.19845	
3	1.9979	0.0000	$42 \rightarrow 48$	0.13036	255
			$45 \rightarrow 47$	0.34885	
			$45 \rightarrow 48$	0.30215	
			$46 \rightarrow 48$	0.47218	
			$45 \rightarrow 47$	-0.34885	
			$45 \rightarrow 48$	-0.30215	
			$46 \rightarrow 48$	-0.47218	
4	3.3644	0.1788	$42 \rightarrow 48$	0.16992	285
-			$43 \rightarrow 47$	-0.18248	
			$43 \rightarrow 48$	0.14568	
			$44 \rightarrow 47$	-0.13277	
			$45 \rightarrow 47$	-0.40187	
			$45 \rightarrow 48$	0.43448	
			$43 \rightarrow 48$	-0.14568	
			$44 \rightarrow 46$	0.13277	
			$45 \rightarrow 48$	-0.43448	
5	3.4654	0.0000	$43 \rightarrow 47$	0.18827	345
0	511001	0.0000	$43 \rightarrow 48$	0.18081	0.0
			$44 \rightarrow 47$	-0.51423	
			$44 \rightarrow 48$	-0.36935	
			$44 \rightarrow 47$	0.51423	
			$44 \rightarrow 48$	0.36935	
6	3,5005	0.0345	$42 \rightarrow 47$	0.10409	382
~	2.2000	0.00.0	$43 \rightarrow 47$	-0.50595	50-
			$43 \rightarrow 48$	0.27885	
		1	$43 \rightarrow 47$	0.50595	
			$43 \rightarrow 48$	-0.27885	
		1	$44 \rightarrow 47$	0.19475	
		1	$44 \rightarrow 48$	-0 19981	
			11 / 10	0.17701	I

 Table 8. The computed excitation energies, oscillator strength, electronic transition configuration wavelength of Diphenyl Ketone using TD-DFT/B3LYP/6-311++G(d,p)

This band may be due to electronic transition of the ring 2 to ring 1 through bridge (transition of  $\pi$ - $\pi$ \*). The calculated results involving the vertical excitation energies, oscillator strength (*f*) and wavelength are carried out and compared with measured experimental wavelength are reported in Table 8.

TD-DFT/B3LYP/6-311+G(d,p) predict one intense electronic transition at eV (382 nm) with an oscillator strength f = 0.0055, in good agreement with the measured experimental data ( $\lambda_{exp} = 382$ nm) as shown in Fig. 6. The transmission Spectra of Diphenyl ketone are shown in Fig 7.

#### NBO analysis

The NBO analysis is carried out by examining all possible interactions between 'filled' (donor) Lewis-type NBOs and 'empty' (acceptor) non-Lewis NBOs, and estimating their energetic important by 2nd order perturbation theory. Since these interactions lead to loss of occupancy from the localized NBOS of the idealized Lewis structure into the empty non-Lewis orbitals, they are referred to as delocalization corrections to the zeroth-order natural Lewis structure. For each donor NBO (i) and acceptor NBO (j) with delocalization  $i \rightarrow j$  is estimated as

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\epsilon_j - \epsilon_i}$$

Where  $q_i$  is the donor orbital occupancy  $\varepsilon_i$  and  $\varepsilon_i$  are diagonal elements orbital energies and F(i, j) is the off diagonal NBO Fock matrix element. The larger  $\dot{E}^{(2)}$  value, the more intensive is the interaction between electron donors and acceptors, i.e., the more donation tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system. DFT (B3LYP/6-311++G(d,p) level computation is used to investigate the various second-order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem, which is a measure of the delocalization or hyper-conjugation [24]. NBOs are localized electron pair orbitals for bonding pairs and lone pairs. The hybridization of the atoms and the weight of each atom in each localized electron pair bond are calculated in the idealized Lewis structure. A normal Lewis structure would not leave any antibonding orbitals, so the presence of antibonding orbitals.



Fig 6. UV-VIS Absorption Spectra of Diphenyl ketone



Shows deviations from normal Lewis structures. Anti bonding localized orbitals are called non-Lewis NBOs. If the occupancy is not 8.0, then there are deviations from an ideal Lewis structure. In order to study the small deviations from idealized Lewis structure, the Donor-Acceptor interaction approach is adopted. In DPK,  $\pi$ (C3- C4) $\rightarrow \pi^*$ (C5-C6) interaction is seen to give a strong stabilization 69.19 kJ/mol. This strong stabilization denotes the larger delocalization. The interesting interactions in DPK molecule are LP2O1 and LP1O24 with that of antibonding C7-C10 and C4-C7. These two interactions result the stabilization energy of 73.87 and 77.82 kJ/mol respectively. This highest interaction around the ring can induce the large bioactivity in the molecule. The p character of oxygen lone pair orbital LP1O24 and LP2O24 are 99.99% and 99.98%, respectively. This shows that the lone pair orbital participates in electron donation in the molecule. The calculated values of  $E^{(2)}$  are shown in Table 9. And NBO charge values are shown in Fig 8.

#### **Mulliken Population analysis**

The charge distributions calculated by the Mulliken method for the equilibrium geometry of DPK with DFT/6-311++G(d,p) are listed in Table 10.The charge distribution on the molecule has an important influence on the vibrational spectra. The corresponding Mulliken's plot is shown in Fig. 9. From the results it is clear that the substitution of C-O atoms in the aromatic ring leads to a redistribution of electron

density. The  $\sigma$ -electron withdrawing character of the chlorine atom in this title compound is demonstrated by the decrease of electron density on O<sub>22</sub> atom. The atomic charges in the CH<sub>2</sub> group are almost identical. The atomic charges obtained from 6-311++G(d,p) basis set shows that C<sub>7</sub> atom is more acidic due to more positive charge whereas H are more negative (Table10).

#### Analysis of Molecular Electrostatic Potential (Mesp)

The molecular electrostatic potential surface (MESP) is a method of mapping electrostatic potential onto the iso-electron density surface. It simultaneously displays electrostatic potential (electron + nuclei) distribution, molecular shape, size and dipole moments of the molecule and it provides a visual method to understand the relative polarity. Electrostatic potential maps illustrate the charge distributions of molecule three dimensionally. These maps allow us to visualize variably charged regions of a molecule. The knowledge of the charge distributions can be used to determine how molecules interact with one another. One of the



Fig 8. NBO charge values of Diphenyl ketone



Fig 9. Mulliken plot of Diphenyl ketone

Purposes of finding the electrostatic potential is to find the reactive site of a molecule. In the electrostatic potential map, the semi–spherical blue shapes that emerge from the edges of the electrostatic potential map are hydrogen atoms [24]. The molecular electrostatic potential at a point *r* in the space around a molecule (in atomic units) can be expressed as,  $V(r) = \sum Z_A / |R_A - r| - \int \rho(r^2) / |r^2 - r| dr^2$ 

where  $Z_A$  is the charge on nucleus A located at  $R_A$  and  $\rho(r')$  is the electronic density function for the molecule.

JII++G(u,p) Dasis set									
Donor(i)	Hybrid(%S)	Туре	Occupancy	Acceptor (j)	Туре	E(2) <sup>a</sup> (kJ/mol)	$E(j)-E(i)^{a}(a.u)$	$F(i,j)^{c}(a.u)$	
C1-C 2	49.96/50.04	π	0.98964	C2-C3	π*	11.66	1.30	0.059	
C1-C2	48.62/51.38	σ	0.6973	C3-C4	σ*	10.18	0.28	0.069	
C1-H16	62.22/49.87	σ	0.7888	C2-C3	π*	2.09	1.11	0.061	
C3-C4	48.43/51.57	σ	0.6959	C4-C5	σ*	2.17	1.27	0.066	
C3-C4	49.76/52.63	π	0.6883	C1-C2	$\pi^*$	8.57	0.29	0.064	
C3-H18	59.75/40.25	σ	0.7730	C3-H18	σ*	4.34	1.32	0.096	
C5-C6	50.04/49.96	π	0.7074	C1 -C2	π*	10.12	0.29	0.069	
C5-C 6	47.59/52.41	π	0.6899	C3 - C4	π*	9.55	0.28	0.066	
C7- O24	38.41/67.86	π	0.6198	C3 - C4	π*	4.70	0.32	0.053	
C8-C9	51.57/48.43	π	0.7181	C7 - O24	π*	17.74	0.22	0.081	
C8-C13	54.89/45.11	σ	0.7203	C8 - C9	σ*	2.43	1.26	0.070	
C9-H19	59.75/40.25	σ	0.7730	C3 - H18	σ*	59.95	1.32	0.356	
C10-C11	50.04/49.96	π	0.7074	C8 - C9	π*	10.18	0.28	0.069	
C12-C13	49.96/50.04	π	0.7068	C8-C9	π*	9.55	0.28	0.066	
O 24		LP(1)	0.00554	C 7-C10	π*	73.87	1.60	0.099	
O 24		LP(2)	0.01325	C4 - C7	π*	77.82	0.80	0.070	
C3-C 4	51.57/48.43	π*	0.14467	C1 - C2	π*	118.52	0.01	0.081	
C3-C4	52.63/47.37	π*	0.01445	C5 - C6	π*	69.19	0.02	0.082	
C7-O24		π*	0.01325	C8 - C 9	π*	24.53	0.06	0.083	
C8 - C 9		π*	0.00800	C10 - C11	π*	118.59	0.01	0.081	

Table 9. Second-order perturbation theory analysis of fock matrix in NBO basis of Diphenyl Ketone using DFT/B3LYP /6-311++G(d,n )basis set

<sup>a</sup> E (2) means energy of hyper conjugative interaction (stabilization energy).

<sup>b</sup> Energy difference between donor and acceptor i and j NBO orbitals.

 $^{c}F(i, j)$  is the Fork matrix element between i and j NBO orbitals.

# Table 10. The charge distribution calculated by the Mulliken atomic charges method for Diphenyl Ketone DFT/6-311++(d,p) basis set

Dasis set								
Atoms	B3LYP/6-311+G(d,p)							
C1	-0.094848							
C2	-0.165242							
C3	-0.037782							
C4	0.064479							
C5	-0.094767							
C6	-0.138847							
C7	0.133699							
C8	0.064479							
C9	-0.037782							
C10	-0.165242							
C11	-0.094848							
C12	-0.138847							
H13	-0.094767							
H14	0.173397							
H15	0.131973							
H16	0.127852							
H17	0.130662							
H18	0.083890							
H19	0.083890							
H20	0.130662							
H21	0.127852							
H22	0.131973							
H23	0.173397							
O24	-0.495232							

The first and second terms represent the contributions to the potential due to nuclei and electrons, respectively. V(r) is the resultant at each point r, which is the net electrostatic effect produced at the point r by both the electrons and nuclei of the molecule. The GAUSSVIEW 5.0.8 visualisation program has been utilised to construct the MESP surface. The total electron density and MESP surfaces of the molecule under investigation are constructed by using B3LYP/6-311++G(d,p) method. These pictures illustrate an electrostatic potential model of the compound, computed at the 0.002 a.u. isodensity surface. The total electron density surface of DPK is depicted in Fig. 10 (Supplementary section). The MESP mapped surface of the compound and electrostatic potential contour map for positive and negative potentials is shown in Fig.11 (Supplementary section). The colour scheme of MESP in the negative electrostatic potentials are shown in red, the intensity of which is proportional to the absolute value of the potential energy, and positive electrostatic potentials are shown in blue while Green indicates surface areas where the potentials are close to zero. The Fig. 12 (Supplementary section) shows the molecular electrostatic potential surface of DPK. The colour code values are projected onto the 0.002 a.u. isodensity surface to produce a three-dimensional electrostatic potential model. As can be seen from the figure and the calculated results, this molecule has several possible sites for electrophilic attack (red) over oxygen atom. For possible nucleophilic reactions, the maximum positive region (blue) is found on the hydrogen atoms of the benzene ring. The green counter parts of the molecule where electrostatic potentials are close to zero (C-C and C-O bonds).

# Temperature dependence of Thermodynamic properties



# Fig 10. The total electron density surface of Diphenyl ketone

The temperature dependence of the thermodynamic properties heat capacity at constant pressure (Cp), entropy (S) and enthalpy change ( $\Delta$ H0 $\rightarrow$ T) for DPK were also determined by B3LYP/6–311+G(d,p) method and listed in Table 11.

The Figures 13-15 depicts the correlation of entropy (S), heat capacity at constant pressure (Cp) and enthalpy change  $(\Delta H0 \rightarrow T)$  with temperature along with the correlation equations. From Table 11, one can find that the entropies, heat capacities, and enthalpy changes are increasing with temperature ranging from 100 to 1000 K due to the fact that the molecular vibrational intensities increase with temperature [24]. These observed relations of the thermodynamic functions vs. temperatures were fitted by quadratic formulas, and the corresponding fitting regression factors (R<sup>2</sup>) are all not less than 0.9995. The corresponding fitting equations for DPK are 
$$\begin{split} S &= 257.977 + 0.5 \text{ T} - 1.408 \text{ x } 10^{-4} \text{ T}^2 \\ Cp &= 79.816 + 0.333 \text{ T} - 2.478 \text{ x } 10^{-4} \text{ T}^2 \\ \Delta H &= -46.658 + 0.274 \text{ T} + 1.293 \text{ x } 10^{-4} \text{ T}^2 \end{split}$$



Fig 11.The contour map of electrostatic potential surface of Diphenyl ketone



Fig 12. The molecular electrostatic potential surface of Diphenyl ketone Table 11. Thermodynamic properties of Diphenyl

Ketone determined at different temperatures with B3LYP/6–311++G(d,p) level

T (K)	S (J/mol.K)	Cp (J/mol.K)	$\Delta H0 \rightarrow T (kJ/mol)$							
100.00	275.97	58.87	4.19							
200.00	330.74	107.40	12.37							
298.15	384.56	167.23	25.79							
300.00	385.60	168.40	26.11							
400.00	442.49	228.95	46.02							
500.00	499.33	280.77	71.60							
600.00	499.33	280.77	71.60							
700.00	554.37	322.69	101.85							
800.00	656.17	383.77	172.91							
900.00	702.72	406.41	212.45							
1000.00	746.55	425.35	254.07							

#### Vibrational spectra

The molecule under consideration would belong to C1 point group symmetry. The harmonic vibrational frequencies calculated for DPK at B3LYP level using the triple split valence basis set along with the diffuse and polarization functions, 6-311+G(d,p) respectively. The maximum number of potentially active observable fundamentals of a non-linear compound that contains N atoms is equal to (3N-6). Accurate vibrational frequency assignment for aromatic and other conjugated system is necessary for characterization of compound. All the calculated mode of vibrations is numbered

from the largest to smallest within each fundamental wavenumber. The observed FT-IR and FT-Raman bands for various modes of vibrations are assigned and presented in Table 12. Comparison of the vibrational modes calculated at B3LYP with experimental values (Table 12) reveals that over estimation of the calculated vibraional modes due to neglect of anharmonicity in the real system. Inclusion of electron correlation in the 6-31+G (d,p) to a certain extent makes the wavenumber values smaller in comparison with the 6-311++G(d,p) wavenumber data. The observed FT-IR and FTRaman spectra of DPK are shown in Figs. 16 and 17, respectively. It is convenient to discuss the vibrational spectra of DPK in terms of characteristic spectral regions as described below:



Fig 13. The effect of temperature on entropy (S) of Diphenyl ketone



Fig 14. The effect of temperature on heat capacity (C<sub>p</sub>) of Diphenyl ketone



Fig 15. The effect of temperature on enthalpy change  $(\Delta H0 \rightarrow T)$  of Diphenyl ketone.



Fig 16. Comparison of observed and calculated IR spectra of Diphenyl ketone

(a) observed in solid phase (b) calculated with B3LYP\6-311+G(d,p) (c) calculated with B3LYP\6-311++G(d,p)



Fig 17. Comparison of observed and calculated Raman spectra of Diphenyl ketone (a) observed in solid phase (b) calculated with B3LYP \ 6 -311+G(d,p) (c) calculated with B3LYP\6-311++G(d,p)

# Table 12. The observed FT IR, FT-Raman and calculated (unscaled and scaled) frequencies (cm<sup>-1</sup>), IR intensity (km mol<sup>-1</sup>), Raman activity (A<sup>0</sup> amu-1) and force constant (m dyne A<sup>0</sup>) and probable assignments (Characterized by TED) of Diphenyl Ketone using B3LYP/6-311+G(d,p) and B3LYP/6-311++G(d,p) calculations

Symmetry species	y Observed frequencies (cm <sup>-1</sup> )		Calculated frequencies (cm <sup>-</sup> <sup>1</sup> )(Unscaled)		Scaling frequency (cm <sup>-1</sup> )		Force constant (mDyne/A)		IR intensity (KM/Mole)		Raman activity (A <sup>4</sup> /amu)		Assignment (% TED)
$C_1$	FT-IR	FT-	B3LYP/	B3LYP/	B3LYP/	B3LYP/	B3LYP/	B3LYP/6	B3LYP/	B3LYP/	B3LYP/	B3LYP/	
		RAMA	6-311+	6-311 +	6-311	6-11++	6-311+	-11++G	6-311+	6-311 +	6-31+	6-311+	
		N	G(d,p)	+G(d,p)	+G(d,p)	G (d,p)	G (d,p)	(d,p)	G (d,p)	+G(d,p)	G(d,p)	+G(d,p)	
A'	3150w	-	4810	4720	4142	3152	10.052	8.9572	34.4492	29.1020	51.4689	63.8942	vCH(98)
A'	3128w	-	4730	4657	4115	3127	9.4071	7.9904	91.4206	54.4516	112.400	317.400	υCH(97)
A'	3101W	-	4579	4469	4100	3103	9.3941	8.2166	69.3341	70.8244	91.8614	150.130	vCH(88), vCC(10)
A A'	30908	- 3072s	4355	4222	4091	3098	9.0184	6.6759	01.4301	2 4603	87.0880	100 587	$\nu CH(87), \nu CC(11)$
A'	3064vs	-	3900	3791	4062	3065	7.452)	6 5985	3 3087	4 6828	51 0702	61 0710	$\nu$ CH(85), $\nu$ CC(8)
A'	200110	3031w	3765	3652	4031	3033	7.2184	6.5022	12.6096	12.8585	97.2062	117.774	νCH(84), νCC(6)
A'	3012vw	-	3455	3345	4018	3014	20.850	16.761	40.3830	27.4836	96.9603	140.589	υCH(83), υCC(7)
A'	3001vw	-	3335	3315	4009	3005	20.013	15.296	1038.22	728.989	11.1084	12.0205	vCH(82), vCC(8)
A'		1823w	3232	3201	3823	1826	2.4964	2.5478	277.74	400.755	55.1328	72.821	vCH(81), vCC(10)
A'	1809vw	-	3121	2999	3805	1807	7.2776	4.3733	173.891	122.226	146.688	76.425	υCC(80),υCH(12)
A	1700vw	-	3089	2870	3708	1703	13.452	11.117	13.9598	1.8244	5.3600	5.9784	vCC(79), vCH(11)
A'	168578	- 1671ws	3029	2855	3689	1673	3.2972	4.5510	25.7765	31.0339	25.2976	27 635	vCC(78), vCH(9)
A'	-	1664vs	2950	2842	3660	1666	4.0008	3 8751	41 7697	6.8890	3 2794	2.1319	$\nu CC(76) \nu CH(14)$
A'	-	1651vs	2793	2742	3651	1653	3.2983	1.9633	143.211	125.504	30.7818	27.7756	vCC(75).vCH(15)
Α'	-	1640vw	2653	2544	3640	1643	3.4802	8.0207	384.315	9.7534	39.9099	2.5137	υCC(74),υCH(16)
A'	-	1633w	2536	2313	3536	1635	2.7202	5.4908	46.741	290.340	9.4974	140.366	vCC(73),vCH(10)
Α'	-	1624vw	2434	2214	3576	1626	4.7285	2.4526	79.773	32.6167	43.6925	8.5424	υCC(72),υCH(18)
A'	1611ms	-	2311	2100	3510	1613	2.2849	3.7188	98.3102	52.4394	15.4910	22.9486	υCC(71),υCH(16)
A'		1602vw	2278	2064	3499	1604	2.9335	1.5582	2.1129	33.8240	0.8881	2.8489	vCC(70),bCH(17)
A'	1475	1520w	2201	1999	3450	1524	2.3498	1.9457	32.3403	27.0784	6.8650	7.6373	vCC(69),bCH(18)
Α Δ'	14/31118	- 1412s	2136	1972	3428	1478	2 3978	1.0554	36.4015	38.9157	3.4303	1 4208	$\nu CC(68), \nu CH(19)$
A'	1352ms	-	2089	1881	3351	1355	1 4310	1.8330	5 5271	32,8545	2.7850	3 0296	$\nu CO(66) bCH(18)$
A'	-	1299w	2023	1832	3290	1297	2.1246	1.2839	36.2891	14.1331	9.6887	1.0408	bCH(65),vCC(21)
A'	-	1254w	1966	1755	3251	1256	0.9841	0.7650	0.6080	1.0290	0.3153	0.1706	bCH(64), vCC(22)
A'	-	1223w	1934	1670	3229	1225	1.2751	1.9805	8.9294	9.1837	10.9773	20.6688	bCH(63),vCC(12)
Α'	-	1210w	1910	1623	3210	1213	1.3957	0.7185	19.8925	14.3108	8.3671	0.1496	bCH(62),vCC(18)
A'	-	1180vw	1867	1601	3189	1184	0.8417	0.6717	30.5459	23.5194	0.6174	0.6773	bCH(61),vCC(23)
A'	-	1164vw	1832	1565	3160	1165	2.1917	1.9514	17.8447	13.6639	0.4078	0.5720	bCH(60),vCC(20)
A'	-	11/1VW 1152w	1812	1400	2150	11/5	2.1083	1.8/39	26.0512	8.0804	2.2053	1.6320	bCH(59), bCO(24)
A'	-	1152w	1730	1371	2139	1122	1 9269	1 9104	10 5929	4 9374	18 8803	20.9881	bCH(57) R <sub>1</sub> sym(24)
A'	-	1123 w	1689	1337	2110	11122	1.1983	1.2136	16.0067	4.7622	1.0073	1.2335	bCH(56),R <sub>1</sub> symd(26)
A'	-	1088w	1629	1309	2089	1089	1.1804	0.9684	7.0684	20.3089	2.9791	1.8906	R <sub>1</sub> asym(47),bCH(25)
A'	-	1026s	1605	1290	2029	1025	1.3025	1.1582	11.4700	1.6671	1.1820	1.4933	R <sub>1</sub> symd(51),ωCH(22)
Α'	-	989s	1586	1266	1900	987	0.5072	0.3997	200.301	150.540	1.7199	0.5374	R <sub>1</sub> trigd(54),ωCH(28)
A'	-	954s	1552	1232	1952	956	0.8064	0.6287	16.9937	38.7213	5.3193	19.0146	R <sub>2</sub> asym(44),ωCH(29)
A'	- 974	926s	1521	1201	1924	928	0.8124	0.6568	19.4920	34.2921	10.8988	3.3225	$R_2$ symd(51), $\omega$ CH(26)
A A'	8/4VW	- 851c	1430	1189	1872	873	0.3399	0.5155	135.88	0.2342	4.9549	1.5725	$R_2 \ln ga(47), \omega CH(27)$
A'	-	8238	1410	1101	1829	825	0.2482	0.3885	44 4156	4 6969	0.4052	1 5534	$R_2$ asym(44) $\omega$ CH(25)
A'	-	801s	1389	1078	1805	804	0.4085	0.2595	37.9667	50.3506	2.2894	4.0659	$R_{3}$ symd(49), $\omega$ CH(22)
Α'	-	786s	1334	1045	1782	788	0.4690	0.1302	24.7558	385.067	1.5754	11.9521	R <sub>3</sub> trigd(47), wCH(18)
A'	-	772s	1309	1012	1770	774	0.5452	0.3722	5.0019	2.3595	1.4269	1.6556	ωCH(68),tR1asym(10)
A"	-	764w	1289	999	1760	765	0.6230	0.0860	10.9623	25.8499	2.8685	0.9397	$\omega$ CH(63),tR <sub>1</sub> symd(21)
A"	-	732w	1250	978	1739	734	0.0702	0.5172	20.1637	6.4530	0.4209	3.3123	$\omega$ CH(60),tR <sub>1</sub> trigd(27)
Α" Δ"	/12VW	- 604112	1208	945	1/19	/10	0.2606	0.2251	1.5035	1.0309	0.8944	0.0703	$\omega CH(01), tR_2asym(34)$
A"	-	681w	1170	901	1682	683	0.1300	0.1656	1.0991	2 44162	0.4967	1 7243	$\omega CH(58)tR_{strigd}(37)$
A"	-	6798	1100	878	1670	677	0.0837	0.0732	0.9114	1.5780	0.7975	0.8168	$\omega CH(54)tR_3asym(24)$
A"	-	651s	1078	845	1659	654	0.0511	0.0515	8.5254	7.0904	0.4494	0.5338	$\omega$ CH(50)tR <sub>3</sub> symd(41)
A"	-	648vw	1044	823	1643	649	0.0269	0.0265	6.1292	6.8361	0.4963	0.5088	ωCH(55)tR <sub>3</sub> trigd(39)
A"	-	624vw	1012	809	1627	625	4.0608	2.7173	2.7410	1.6812	2.3909	27.635	ωCH(58),ωCO(32)
A"	-	599vw	1000	789	1591	598	4.8396	3.8751	41.7697	6.8890	3.2794	2.1319	$tR_1asym(52),\omega CH(12)$
A"	-	574vw	990	777	1572	575	3.2983	1.9633	143.211	125.504	30.7818	27.7756	$tR_1symd(50),\omega CH(15)$
A"	-	558vw	978	756	1550	559	3.4802	8.0207	384.315	9.7534	39.9099	2.5137	$tR_1trigd(57), \omega CH(7)$
Δ"	-	530vw	930	709	1548	533	4 7285	2 4526	40.741	290.340	9.49/4	8 5424	$tR_{asymd}(51) \oplus CH(0)$
A"	-	512vw	901	689	1510	515	4.0608	2.7173	2,7410	1.6812	2.3909	27.635	$tR_2 trigd(47)$
A"	-	435vw	878	654	1434	437	2.1246	1.2839	36.2891	14.1331	9.6887	1.0408	tR <sub>3</sub> asym(44)
A"		412vw	856	623	1419	413	0.9841	0.7650	0.6080	1.0290	0.3153	0.1706	tR <sub>3</sub> symd(48)
A"	-	369vw	812	601	1362	367	1.2751	1.9805	8.9294	9.1837	10.9773	20.6688	tR <sub>3</sub> trigd(49)
A"	-	301vw	799	578	1354	304	1.3957	0.7185	19.8925	14.3108	8.3671	0.1496	ωCO(40)
A"	-	175ms	754	555	1270	177	0.8417	0.6717	30.5459	23.5194	0.6174	0.6773	Butterfully(39)

## **C-H vibrations**

The aromatic structure shows the presence of C-H stretching vibration in the region 3100-3000 cm-1, which is the characteristic region for the prepared recognition of C-H stretching vibration [25]. Therefore in our present work, the FT-IR band observed at 3150 ,3128 ,3101 ,3096 ,3064 ,3012 ,3001 cm-1 and the FT-Raman bands at 3072, 3031, 1823 cmlare assigned to C-H stretching vibrations. The scaled vibrations by B3LYP/6-31G+(d,p) and B3LYP/6-311++G (d,p)level shows very good agreement with recorded spectrum as well as the literature data. The C-H in-plane and out-ofplane bending vibrations generally lie in the region 1300-1000 cm-1and 1000-675 cm-1, respectively. In accordance with above literature data in our present study, the band observed in FT-Raman spectrum at 1299 ,1254 ,1223, 1210 ,1180 ,1164 ,1171,1152 cm-1. They show good agreement with the theoretically computed B3LYP/6-31G++(d,p) method. The bands observed at 712 cm-1in the FT-IR and Raman spectrum at 694,681,679,651,648,624 cm-1 is assigned to C-H out-ofplane bending vibration for DPK. The theoretically computed wavenumber for this mode are coincides with B3LYP/6-31G+(d,p) and B3LYP/6-311++G(d,p).

#### C-C vibrations

The ring C-C stretching vibrations, usually occurs in the region 1400–1625 cm-1 [26]. In accordance with above literature data in our present study, the bands for C-C stretching vibrations are observed at 1725,1700,1685,1611, 1475,1352 cm-1and 1671,1664,1651,1640,1633 ,1624 ,1602, 1520,1412 cm-1in FT-IR and FT-Raman spectra, respectively. All the bands lie in the expected range when compared to the literature values. These observed frequencies show that, the substitutions in the ring to some extend affect the ring mode of vibrations. The comparison of the theoretically computed values were very good agreement by B3LYP/6-31G+(d,p) and B3LYP/6-311++G(d,p) method. The in-plane and out-of-plane bending vibrations of C-C group are also listed out in the Table 12.

## C-O vibrations

The C-O stretching vibrations in DPK produce a strong band near 1360–1260 cm-1are sensitive to the nature of the substituents bonded to the carbonyl carbon. Consequently, this provides valuable information in determining the nature of the hydroxyl compound. The characteristic response of DPK in infrared is associated with the stretching vibration of the C-O system. Since the vibrational characteristics of this system would not be expected to differ greatly from the C-C system, it is not surprising to find that response to C-O vibrations involving oxygen atoms results in greater dipole moment charge that those involving carbon atoms. Both these bands involve some interaction between C-O stretching and in-plane C-O bending. The most important contribution due to the C-O stretching mode was at 1352 cm-1in FT-IR spectrum [26]. **Conclusion** 

A new nonlinear semi-organic material DPK was synthesized. DPK crystals were grown from solution using mixed solvent of ethanol and water (1:1) and the synthesized compound was confirmed by single crystal XRD. Various functional groups present in the grown crystal confirmed from the FTIR and FT-Raman spectrum. Kinetic and thermodynamic parameters were calculated and the results could be used in thermal decomposition optimization. The dielectric constant and dielectric loss studies of DPK establish the normal behavior. Mechanical strength of the material was calculated using Vickers microhardness and it was found that

the material belongs to soft materials category. Yield strength and stiffness constant for DPK have been reported. The UV-Vis spectrum showed good transparency in the UV and Vis region. The SHG relative efficiency of DPK crystal was found to be 1.4 times higher than that of KDP. In this present investigation molecular structure, vibrational frequencies, HOMO, LUMO, and polarizability analysis of DPK have been studied using DFT (B3LYP/6-311+G(d,p)) calculation. On the basis of the agreement between the calculated and observed results, assignments of fundamental vibrational modes of DPK were examined and some assignments are proposed. This study demonstrates that scaled DFT/B3LYP calculations are powerful approach for understanding the vibrational spectra of medium sized semi-organic compound. NBO analysis has been performed on DPK molecule in order to elucidate intermolecular hydrogen bonding, intermolecular charge transfer (ICT), rehybridization, delocalization of electron density and cooperative effect due to  $L(O) \rightarrow \pi^*(C-C)$ . The total atomic charges of DPK obtained by Mulliken population analysis are also discussed. Temperature dependence of the thermodynamic properties heat capacity at constant pressure (Cp), entropy (S) and enthalpy change ( $\Delta H0 \rightarrow T$ ) for DPK were also determined by B3LYP/6-311+G(d,p) method. The theoretically constructed FT-IR and FT-Raman spectrum shows good correlation with experimentally observed FT-IR and FT-Raman spectrum.

#### References

[1] Chemla D.S. and Zyss J. (1987), 'Vol.1–2, Academic Press, Orlando, New York.

[2] Levine.B.F,

Bethea.C.G, Thurmond.C.D, Lynch.R.T, Bernstein.J.L. (1979), J. Appl. Phys. 50, 2523.

[3] Kerkoc.P, Zgonic.M, Sutter.K, Bosshard.Ch, Gunter.P (1989), Appl. Phys. Lett. 54, 2062.

[4] Agata Biatonska, Zbigniew Ciunik, Acta Crystallogr. E61 (2005) o4222–o4224.

[5] Gaussian 09 Program, Gaussian Inc., Wallingford CT., 2009.

[6] T. Sundius, MOLVIB; A program for harmonic force field calculations, QCPE

Program no.604, J. Mol. Struct. 218 (1990) 321.

[7] T. Sundius, Vib. Spectrosc. 29 (2002) 89.

[8] P.L. Polavara, J. Phys. Chem. 94 (1990) 8106.

[9] G. Keresztury, S. Holly, J. Varga, G. Besenyei, A.V. Wang, J.R. Durig, Spectrochim. Acta 49A (2007) 1993.

[10] G. Keresztury, in: J.M. Chalmers, P.R. Griffiths (Eds.), Raman spectroscopy Theory, Handbook of vibrational spectroscopy, Vol. 1, John Wiley and sons Ltd., 2002, p.71.

[11] G. Fogarasi, X. Zhou, P.W. Jaylor and P. Pulay, J. Am. Chem. Soc., 114, 1992,819.

[12] P. Pulay, G. Fogarasi, G. Pongar J.E. Boggs and A. Vargha, J.Am. Chem. Soc., 105, no 1983, 7073.

[13] J. Karpagam, N. Sundaraganesan, S. Sebastain, S. Manoharan, M. Kurt, J. Raman Spectrosc. 41 (2010) 53–62.

[14] D.A. Kleinman, Phys. Rev. 126 (1962) 1977–1979.

[15] K. Sambathkumar, S. Jeyavijayan, M. Arivazhagan Spectrochim. Acta A 147 (2015) 124-138.

[16]R.G..Parr,L.V.szentpaly,S.J.Liu.Am.Chem.soc.1999,121,1 922.

[17]P.K.Chattraj,B.Maiti,U.J.Sarkar.J.Phys.ChemA,2003,107, 4973.

[18]R.G.Parr,R.A.Donnelly,M.Levy,W.E.Palke.J.Am.Chem.s oc.1978,68,3807.

[19] R.G.Parr, R.G. Pearson, J.Am. Chem. soc. 1983, 105, 7512-7516.

[20] R.G..Parr, P.K.Chattraj, J.Am.Chem.soc, 1991, 113, 1854.

[21] R.Parthasarathi, J.Padmanabhan, B.Maiti, P.K.Chattraj, J.Ph

ys.ChemA 2008, 107,10346,P.Thanikaivelan, V.Subramanian, J.RaghavRao, B.V.Nair, Chem.

Phys.Let2000,323,59.R.Parthasathi;J.Padmanabhan, .Elango, V.Subramanian, K.Chattraj,Chem.Phys.Lett. 2004,394,225.

[22] R.Parthasarathi, J.Padmanabhan, V.Subramanian,

B.Maiti, P.K.Chattraj, Curr. Sci.2004, 86,535.

[23] R.Parthasarathi, J.Padmanabhan, V.Subramanian, U.Sarkar, B.Maiti, P.K.Chattraj, Internet. Electron J.Mol.Des.2003,798.

[24] Kuppusamy Sambathkumar Spectrochim. Acta A 147 (2015) 51-66.

[25] M. Arivazhagan, K. Sambathkumar and S. Jeyavijayan, Indian J. Pure Appl. Phys., 48 (2010) 716-722.

[26] K.Sambathkumar, "Density functional theory studies of Vibrational spectra, Homo-Lumo, Nbo and Nlo analysis of some cyclic and Heterocyclic Compounds", Ph.D. Thesis, Bharathidasan University, Tiruchirappalli, August 2014.

[27] S. Ramalingam, P. Anbusrinivasan, S. Periandy, Spectrochim. Acta Part A 78 (2011) 826–834.