Thermodynamic Functions Molecular Polarizability of 2,6-dichloro-4-fluoro Phenol

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ABSTRACT

The Laser-Raman and FT-IR spectra of 2,6-dichloro-4-fluoro phenol (2,6,4-DCFP) have been recorded. The thermodynamic functions, namely, the enthalpy, the heat capacity, the free energy and entropy of 2,6,4-DCFP have been calculated at a pressure of 1 atmosphere in the temperature range 200-1500 K under rigid rotor harmonic oscillator. The one-dimensional semi-empirical delta-function model of chemical binding has been used to evaluate the average molecular polarizability of 2,6,4-DCFP.

Keywords

Laser-Raman; FT-IR spectra; Thermodynamic function; Molecular polarizability.

Academic Discipline And Sub-Disciplines

Science (Physics)

SUBJECT CLASSIFICATION

Physics (Molecular Spectroscopy)

TYPE (METHOD/APPROACH)

Quasi-Experimental;

1. INTRODUCTION

Phenol has been the subject of numerous studies, since it is a good model for the investigation of hydrogen bonding and proton transfer in enzymes and other systems containing aryl alcohols [1]. Phenol and its derivatives have been widely used as starting material in a vast amount of pharmaceutical, agriculture and many other industrial processes. The understanding of their molecular properties as well as nature of reaction mechanism they undergo has great importance. Hence, the investigation on structures, and the vibrations of phenol and substituted phenols are still being carried out, increasingly. The inclusion of a substituent group in phenol leads to the variation of change distribution in molecule, and consequently, this greatly affects the structural, electronic and vibrational parameters [2, 3].

Due to the great biochemical importance the vibrational spectral studies of 2,6,4-DCFP have been carried out in present investigation. Knowledge of the thermodynamic functions is of great importance to study the chemical kinetics and chemical equilibrium of the system. The direct experimental measurement of these quantities is usually tedious and may not be reliable. The fundamental vibrational frequencies have been utilized to calculate the various thermodynamic function, namely the enthalpy function $[H_0-E^0_0]$,the heat capacity $[Cp_0]$,the free energy function $[-(F_0-E^0_0)]$ and entropy function (S_0) in the temperature range 200-1500K at 1 atmospheric pressure.

Molecular polarizability are important for the evaluation of several kinetic aspects of positive ion chemistry. Semi-empirical approaches are of considerable interest for studying the molecular structure and properties of organic compounds [4]. Molecular polarizability is considered to be one of the important properties of hydrocarbons in view of the structural application [5]. The survey of literature indicates that no work have been reported on, thermodynamic functions and molecular polarizability of title compound.

2. EXPERIMENTAL SECTION

The spec-pure compound 2,6,4-DCFP was obtained from M/s Aldrich Chemie, West Germany and used as such. The purity of the compound was confirmed by elemental analysis and melting point determination. The FTIR absorption spectrum of the compound was recorded at room temperature in the region 400-4000 cm^{-1}, at a resolution of 4 cm^{-1} with scanning speed 2 mm per second using Perkin Elmer spectrophotometer model FT/IR-4100 type A, equipped with TGS detector using KBr pellet and Nujol Mull. Laser-Raman spectrum was recorded on spex Rama Lab spectrophotometer using 52 MW argon-krypton laser of wavelength 488 nm.
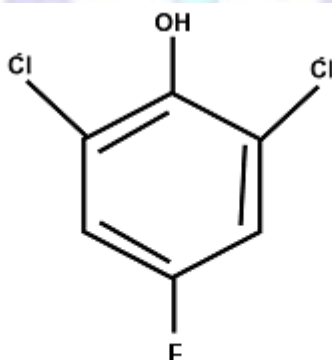
2. RESULT AND DISCUSSION

Fig. 1 : Molecular Structure of 2 , 6 - dichloro - 4 - fluoro phenol

The molecular structure of 2,6,4-DCFP is shown in Fig 1. Laser-Raman spectrum of 2,6,4-DCFP is shown in Fig 2 while FT-IR absorption spectra using KBr pellets technique and using Nujol mull is shown in Fig 3 and Fig 4 respectively. The corrected wave numbers together with their probable assignments are presented in Table 1. The structure parameters and statistically computed thermodynamic functions viz the enthalpy, the free energy, the heat capacity and entropy are presented in Table 2 and Table 3 respectively. The variation of enthalpy function and heat capacity function with absolute temperature is shown in Fig 5, while the variation of the free energy and entropy with absolute temperature is shown in Fig 6. The calculated values of molecular polarizabilities of 2,6,4-DCFP have been presented in Table 4.

3.1 Vibrational Spectra

According to the theoretical calculations, title molecule belong to C_s point group symmetry, and its 26 fundamentals are distributed amongst the symmetry species as

$$T=19 A^I +7 A^{II}$$

A^I are in plane and A^{II} are out of plane vibrations The vibrational assignments have been made essentially on the basis of magnitude and relative intensities of the Laser-Raman, FT-IR bands and available for similar molecules.
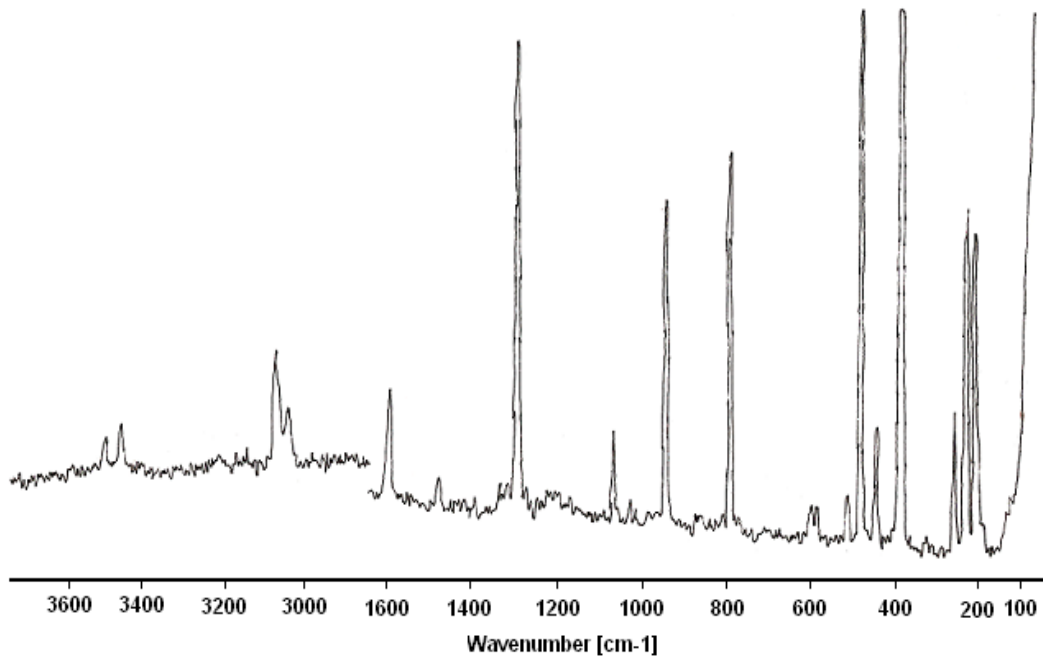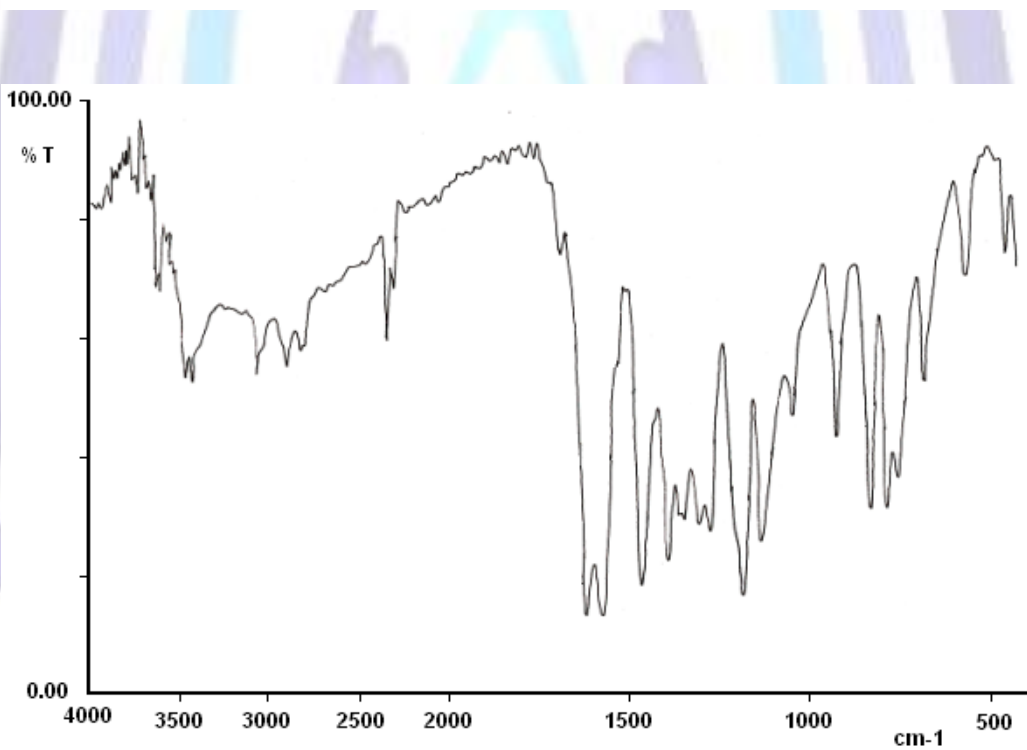
Fig 2. FT-Raman spectrum of 2,6,4-DCFP

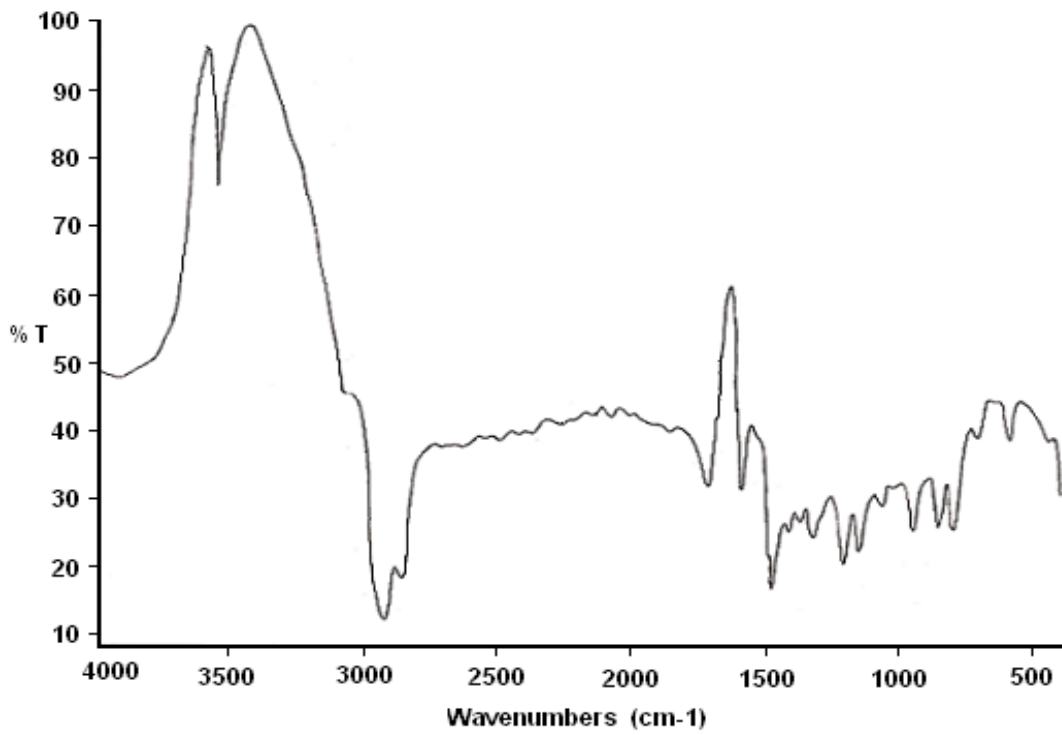Fig 3. FT-IR spectrum of 2,6,4-DCFP in KBr pellets

Fig 4. FT-IR spectrum of 2,6,4-DCFP in Nujol Mull

Table 1. Assignments of fundamental frequencies of 2,6,4-DCFP (in cm^{-1})

No.	Symmetry Species C_s	Raman	I R Bands		Assignment
			K Br Pellet	Nujol Mull	
1	A$^{\prime\prime}$	205 (s)	-	-	ring torsion
2	A$^{\prime\prime}$	223 (s)	-	-	γ (C-Cl)
3	A$^{\prime}$	385 (s)	-	-	β (C-Cl)
4	A$^{\prime\prime}$	442 (w)	-	443 (s)	γ (O-H)
5	A$^{\prime\prime}$	479 (vs)	478 (w)	-	γ ring, γ (C-F)
6	A$^{\prime\prime}$	510 (vw)	-	-	γ ring
7	A$^{\prime}$	582 (vw)	588 (w)	589 (s)	β (C-OH)
8	A$^{\prime}$	595 (vw)	-	-	β (C-F)
9	A$^{\prime}$	-	703 (w)	713 (s)	υ (C-Cl)
10	A$^{\prime}$	786 (vs)	778 (s)	796 (vs)	υ (C-Cl)
11	A$^{\prime\prime}$	-	807 (s)	-	γ (C-H)
12	A$^{\prime\prime}$	-	851 (s)	853 (vs)	γ (C-H)
13	A$^{\prime}$	940 (s)	945 (s)	947 (vs)	β (C-C)
14	A$^{\prime}$	1028 (vw)	-	-	β (C-C)
15	A$^{\prime}$	1064 (w)	1065 (s)	1065 (w)	β (C-H)
16	A$^{\prime}$	-	1155 (s)	1150 (s)	β (O-H)
17	A$^{\prime}$	-	1205 (vs)	1205 (vs)	υ (C-OH)
18	A$^{\prime}$	1289 (vs)	1297 (s)	-	υ (C-F)
19	A$^{\prime}$	-	1328 (s)	1324 (s)	υ (C-C)
20	A$^{\prime}$	-	1368 (s)	1373 (s)	υ (C-C)
21	A$^{\prime}$	-	1412 (vs)	-	υ (C-C)
22	A$^{\prime}$	1477 (vw)	1485 (vs)	1477 (vs)	υ (C-C)
23	A$^{\prime}$	1592 (w)	1592 (vs)	1590 (s)	υ (C-C)
24	A$^{\prime}$	3062 (vw)	-	-	υ (C-H)
25	A$^{\prime}$	3092 (w)	3089 (w)	-	υ (C-H)
26	A$^{\prime}$	3435 (w)	3458 (w)	-	υ (O-H)

Where s=strong; vs= very strong; w=weak; vw=very weak

υ = stretching; β = in-plane bending; γ = out-of-plane bending,

3.2 Thermodynamic Functions Analysis

The total energy (E) of a system of molecules is given as

$$E = \varepsilon_{trans} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{elec} \text{---------------- (1)}$$

And total partition function (Q) can be expressed as the product of the individual partition function.

Hence,

$$Q = Q_{trans} \times Q_{rot} \times Q_{vib} \times Q_{elec} \text{---------------- (2)}$$

Where the subscripts trans, rot, vib and elect stands for translation, rotational, vibrational and electronic respectively. Also

$$Q = \Sigma g_i \exp (-\varepsilon_i / kT) \text{---------------- (3)}$$

Where g_i is the statistical weight of the i-th energy level [21], k is the Boltzmann constant and T is the absolute temperature. Contribution of each partition function may be evaluated separately and then added to the corresponding thermodynamic functions to obtain the total values. The electronic contribution is small and hence ignored. This is because ε_{elec} is large in comparison to kT at ordinary temperature. The various equations used in computation of various partition functions and their contribution to different thermodynamic functions are given by Heizberg [22]. The entropy function represents the total energy stored in a system and the entropy is regarded as a measure of randomness in a system.

Thermodynamic functions viz enthalpy, heat capacity, frequency and entropy of the said compound have been computed using the standard expression [20] by z-axis perpendicular to the molecular plane and y-axis to pass through the para position. For determining the rotational contribution the following structural parameters are given in Table (2) were used [22-24].

Table 2. Structural parameters

Bond length (A^0)		Bond angles (^{0})			
C_1-O	= 1.37	OC_1C_2	= 120	C_5C_6Cl2	= 117
C_1-C_2	= 1.40	OC_1C_6	= 119	$C1C_6Cl2$	= 122
C_2-Cl1	= 1.74	$C_6C_1C_2$	= 121		
C_6-Cl2	= 1.73	C_1C_2Cl1	= 122		
O-H	= 0.96	C_3C_2Cl1	= 117		
C_2-C_3	= 1.38	$C_1C_2C_3$	= 121		
C_3-C_4	= 1.39	$C_2C_3C_4$	= 118		
C_4-C_5	= 1.37	$C_3C_4C_5$	= 120		
C4-F	= 1.36	$C_4C_5C_6$	= 119		
C_5-C_6	= 1.38	C_3C_4F	= 119		
C_6-C_1	= 1.40	C_5C_4F	= 121		
C_3-H	= 1.08	$C_5C_6C_1$	= 121		
C_5-H	= 1.08				

Where C_1 to C_6 are carbon atoms of phenol ring. O is the atom of phenol. Cl1 and Cl2 are chlorine atoms.

The thermodynamic functions have been calculated with the help of computer program at different temperatures 200-1500 K using fundamental frequencies and assuming the rigid rotor-harmonic oscillator approximation. The symmetry number for overall rotation is three. The principal moments of inertia are found to be, 0.8189, 1.0799 and 1.8988 x 10^{-37} gm cm^2 respectively.

The various thermodynamic functions computed for 2,6,4-DCFP have been given in Table (3).

Table 3. Thermodynamic functions of 2,6,4-DCFP (in Cal./Mol-K)

| Temperarture (K)	$(H^0-E^0_0)/T$	C_p^o	$-(F^0-E^0_0)/T$	S^0
200	8.87	11.91	102.88	111.75
300	10.85	17.9	106.83	117.68
400	13.39	24.04	110.29	123.68
500	16.09	29.57	113.57	129.66
600	18.74	34.36	116.73	135.47
700	21.28	38.49	119.82	141.1
800	23.66	42.08	122.81	146.47
900	25.88	45.24	125.73	151.61
1000	27.96	48.02	128.57	156.53
1100	29.90	50.49	131.32	161.22
1200	31.71	52.68	134	165.71
1300	33.40	54.62	136.61	170.01
1400	35.00	56.34	139.14	174.14
1500	36.45	57.86	141.61	178.06
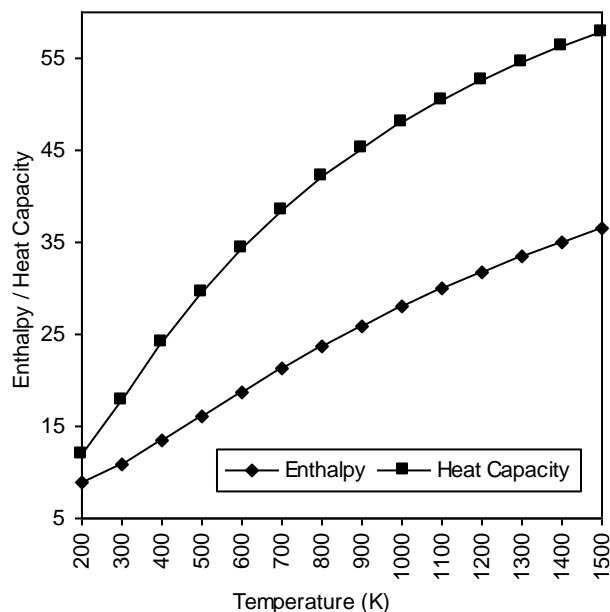
Figure 5: Temperature vs. enthalpy and heat capacity for 2,6,4-DCFP
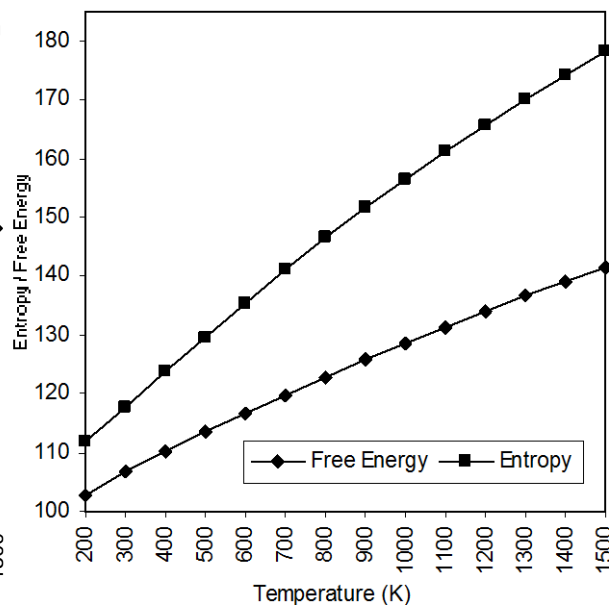

Figure 6: Temperature vs. entropy and free energy for 2,6,4-DCFP

It is found that the thermodynamic functions rise more rapidly in the low temperature range and less rapidly in the high temperature range. The variation of these thermodynamic functions with temperature is in good agreement with the trend reported in literature [24-26].

3.3 Molecular Polarizability

Molecular polarizability is composed of bond parallel and perpendicular components. The bond parallel component is obtained from the contribution of two sources, namely the bond region and non- bond region electron. The contribution by the bond region electrons is calculated by δ- function wave functions, represented by the two nuclei in the bond. This is the expectation value of the electronic position squared along the bond axis and is used to compute the bond parallel components of the polarizability αII_b from the expression;

$$\alpha II_b = (4nA_{ij}/a_0) \ (<X^2>)^2 \qquad \text{--------------------(4)}$$

where n is the bond order and A_{ij} is the root mean square δ- function strength of the nuclei i and j involved in the bond ij . The expectation value $<X^2>$ is evaluated from the relation;

$$<X^2> = (R_{ij}^2/4) \ + 1/(2 \ C_{Rij}^2) \qquad \text{--------------------(5)}$$

where R_{ij} is the internuclear distance and $C_{Rij}=(n_i \ n_j \ N_i \ N_j)^{1/4} \ (A_iA_j)^{1/2}$. Here n_i, N_i and n_j , N_j represent the principal quantum number and the number of electrons contributing to the bonding in atoms i and j respectively. where A_i and A_j are delta-function strengths for atoms i and j respectively.

For a heteronuclear bond, a polarity correction is introduced using Pauling's scale [27] of electronegatively to determine the percent covalent character; accordingly, the expression with polarity correction is given as;

$$\alpha II_p = \sigma \ \alpha II_b \ \text{ where } \ \sigma = \exp [\ -1/4 \ (X_i - X_j)^2 \ ] \qquad \text{--------------------(6)}$$

Where X_i and X_j are electronegativities of the atoms i and j respectively on the Pauling's scale.

The contribution of the non-bond region electrons to the bond parallel component of the polarizabilities is calculated from the fraction of remaining electrons not involved in the bonding and the electronic polarizabilities of the atom concerned. This is analytically expressed as

$$\Sigma \ \alpha II_n = \Sigma \ f_i \ \alpha_i \qquad \text{--------------------(7)}$$

where f_i is the fraction of electrons in the ith atom not involved in the bonding and α_i the atomic polarizability of the atom i, obtainable from the δ- function strength A_i.

The sum of the bond perpendicular components of the bond polarizability is obtained by an empirical approach made by Lippincott and Stutman [28], which is given by the expression :

$$\Sigma \ 2\alpha_\perp = (3N\text{-}2n_b) \ \Sigma \ X_i^2 \ \alpha_i \ / \ \Sigma \ X_i^2 \qquad \text{--------------------(8)}$$

Where N is the number of atoms in the molecule and n_b the number of bonds in the molecule. The term $(3N\text{-}2n_b)$ gives the number of residual atomic polarizability degrees of freedom, denoted by n_{df}. This is obtained by the knowledge of the

symmetry of the geometry of the molecular system. Now the analytical expression for the mean polarizabilities for a polyatomic molecule with polarity correction is given by:

$$\alpha_M = 1/3 \left[\Sigma\sigma_i \alpha \, II_{bi} + \Sigma f_i \alpha_i + n_{df} \left(\Sigma x_i^2 \alpha_i \right) / \Sigma x_i^2 \right]$$

The bond parallel component of molecular polarizability of 2,6,4-DCFP is calculated by using equation (6) and the bond lengths in the molecule presented in Table 2. The contribution of the nonbond region electrons to the bond parallel component of polarizability of said molecule and bond perpendicular component are calculated by using equation (7) and (8). Molecular polarizability of the title compound is presented in Table 4. The result have been compared with the experimental values wherever available and discussed. It has been observed that the model is good for computation of such data and definite trend exists in the variation of α_M for the molecule of particular series [29,30].

Table 4. Molecular Polarizability of 2,6,4-DCFP

Molecule	n_{df}	$\Sigma 2\alpha_\perp$	$\Sigma\alpha_{||b}$	$\Sigma\alpha_{||n}$	α_M
2,6,4-DCFP	19	165.712	242.997	31.941	146.88
Bond and Molecular Polarizability arein 10^{-25} cm^3.					

4. CONCLUSION

A satisfactory vibrational band assignment of 2,6,4-DCFP was made with FT-IR in KBr pellet, Nujol Mull solution and Laser-Raman spectra. The observed vibrational frequencies are used to compute the thermodynamic functions in temperature range 200-1500 K at an increment of 100 K. The calculated values of thermodynamical function indicate that the stability of the molecule decreases as the temperature increases. The result of present study show that the delta-function model can be used for the calculations of average molecular polarizabilities for a wide variety of inorganic and organic molecules and complex metal carbonyls, etc.

5. ACKNOWLEDGEMENT

6. REFERENCES

[1] Wiktor Zierkiewicz, Danuta Michalske J. Phys. Chem. 104, 11685 – 11692 (2000).

[2] D. N. Singh, I. D. Singh and R. A. Yadav, Indian J. of Phys. 76B(3), 307-318 (2002).

[3] S. P. Gupta and S. Ahmed and A Gupta, Acta Physica Polonica, 68A, 637-645 (1985).

[4] Bottcher C J F, Theory of electric polarization (Elsevier, Amsterdam), 1952.

[5] Denbigh K G, Trans Faraday Soc, 36, 936 (1940).

[6] R. M. Silverstein, G.C. Bassler and T. C. Morrill "Spectrometric Identification of Organic Compounds" New York: John Wiley (2004).

[7] S Gunasekaran and P. Abitha, Indian J. of Pure and Appl. Phys. 43, 329-334 (2005).

[8] T.Karthick and V Balchandran, Spectrochemica Acta, 92, 137- 147 (2012).

[9] V. Krishna Kumar and Balachandran, Indian J. of Pure and Appl. Phys. 42, 313-318 (2004).

[10] B Sing and R.P. Singh, Indian J. of Phys. 75 B(4), 373-375 (2001).

[11] D. N. Satyanarayana, Vibrational Spectroscopy – Theory and Applications, Second ed., New Age International (P) Limited Publishers, New Delhi (2004).

[12] A.Janki, V. Balachandan, Indian J Pure & Applied Physics,51,601-614(2013).

[13] V. Balachchandan and M. Arivazhagan, Indian J. of Pure and Appl. Phys. 50,, 91-97 (2012).

[14] N. Sundarganesan, S. Hakiamani, H Saleem and S. Mohan, Indian J. of pure and Appl. Phys. 42, 582-590 (2004).

[15] G. Socrates, Infrared and Raman Characteristic group frequencies – Tables & charts, third ed. J Wiley & Sons, Chichester (2001).

[16] B. S. Yadav, Vir Singh & M. K. Yadav, "Indian J. Pure & Appl Phys" 35, 305-309 (1997).

[17] V. K. Rastogi, Vaibhav Jain, M. Alcolea Palafox, Spectrochimica Acta. 57 (A), 209-216 (2001).

[18] V Krishna Kumar and R. John Xavier, Spectrochimica Acta. 61 (A), 253-260 (2005).

[19] V. Krishna Kumar and Balachandran, Indian J. of Pure and Appl. Phys. 39, 623-627 (2001).

[20] V Krishna Kumar and R. John Xavier, Indian J. of Pure and Appl. Phys. 41, 597-601 (2003).

[21] W J Moore, physical chemistry (Englewood cliffs; Prentice Hall) (1962).

[22] L. H. Herzberg "Molecular Apectra and Molecular Structure" (New Yark: D Von Nostrand) (1966).

[23] K.S.Pitzer and W D Gwinn J.A. Chem. Phys., 10, 428 (1942).

[24] Interatomic distances special publication, No.11, The Chem. Soc., London (1958).

[25] B.S.Yadav, Vipin Kumar and M.K. Yadav, Indian J. Phys. 72(B), 249-256 (1998).

[26] B. S. Yadav, Nitin Kumar, M.K. Yadav, Indian J. Phys., 80(1), 61-65 (2006).

[27] Pauling L, The nature of chemical bond (Cornel University Press, New York) (1960).

[28] Lippincott E R and Stutman J M, J. Phys. Chem, 68, 2926 (1964).

[29] Y C Sharma P.hd Thesis "Spectroscopic investigation of some compounds and new complexs, C C S Univ. Meerut (1996).

[30] Molecular Polarizabilities of some organic solvents, Indian J. of Pure & App Phy., 42, 407-410 (2004).