ABSTRACT

This chapter deals with the vibrational and electronic spectra of 2,6-dichloro-4-fluoro phenol and 2,6-dibromo-4-methyl phenol. The laser Raman, FT-IR absorption spectra of these molecules have been recorded and analysed. The bands obtained are discussed assuming the molecule under \( C_{2v} \) point group symmetry. The ultraviolet absorption spectra of molecules have been recorded in various solvents and at different pH. The effect of solvents and pH variation on electronic transitions has also been discussed. The thermodynamic parameters have been calculated using vibrational frequencies at different temperatures with the help of computer programming.
The n-π* transitions are considered as out of plane transitions while π-π* transitions are inplane transitions. M. S. Navati et al.\textsuperscript{15} have made a systematic study of the electronic absorption bands of difluoro phenol. On substitution the π-π* and n-π* system of pnenol normally show bathochromic and hypsochromic shift respectively and vibrational frequencies also get modified. In view of the above discussion, the present chapter reports the vibrational spectra and ultraviolet absorption spectra of 2,6,4-DCFP and 2,6,4-DBMP. The thermodynamic functions viz enthalpy, heat capacity, free energy and entropy functions of this molecule have also been computed statistically on the basis of their assigned frequencies taking into account a single top by using computer programming.

**EXPERIMENTAL PROCEDURE**

The spec-pure compounds 2,6,4-DBMP and 2,6,4-DCFP were obtained from M/s Aldrich Sigma Chemical, USA and used as such. The purity of the compounds was confirmed by elemental analysis and melting point determination. The FTIR absorption spectra of the compounds were 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 pellets and Nujol mull techniques. The laser-Raman spectra were recorded on Specs Rama Lab spectrophotometer using 52 MW argon-krypton laser of wavelength 488 nm in the region 4000 - 50 cm\(^{-1}\). The ultraviolet spectra of these compounds were recorded in solvents (ethanol, methanol and chloroform) on UV-VIS double beam spectro-photometer, Model M-1601 in the region of 200 - 400 nm in liquid state, The solvents used for preparing the solution of the compounds were of spectroscopic grade. The pH value of solution was measured with Systronic pH digital meter (model M-LI-120).
This system was standardized at pH $4 \pm 0.01$, $7 \pm 0.01$, $9 \pm 0.01$ at room temperature with the help of standard buffers. The concentration of the solution in all cases was kept constant ($8 \times 10^{-3}$ gm/litre). The ratio of pure solvent and acid or alkali was maintained at 9.1 by volume.

RESULT AND DISCUSSION

The molecular structure of both compounds 2,6,4-DBMP and 2,6,4-DCF are shown in Fig 3.1. The FT-IR absorption spectra of 2,6,4-DBMP and 2,6,4-DCF using KBr pellets and Nujol mull technique are shown in Fig 3.2 & 3.3 and Fig. 3.4 & 3.5 respectively. The laser-Raman spectrum of 2,6,4-DBMP and 2,6,4-DCF Fig 3.6 and 3.7 respectively.

![Molecular Structure of 2,6-dichloro-4-fluoro phenol and 2,6-dibromo-4-methyl phenol.](image)

The $C_{2v}$ point group symmetry has been assumed for these molecules. The corrected wave numbers together with their probable assignments are presented in Table 3.1. The near ultra-violet absorption spectra of these two molecules in solvents (chloroform, ethanol and methanol) are shown in Fig 3.8 and 3.9 respectively, while the absorption spectra of these molecules in ethanol solvent at different pH is shown in Fig 3.10 and 3.11 respectively. The electronic bands are
Fig 3.2: FT-IR absorption spectrum of 2,6,4-DBMP in KBr pellets
Fig. 3.3: FT-IR absorption spectrum of 2,6,4-DCFP in KBr pellets
Fig 3.4: FT-IR absorption spectrum of 2,6,4-DBMP in Nujol mull
Fig 3.5: FT-IR spectrum of 2,6,4-DCFP in Nujol mull
given in Table 3.2. The effect of solvents on the electronic transitions of ultra-violet absorption spectra of these molecules are given in Table 3.3. The effect of pH variation in solvent ethanol on the electronic transitions of these compounds are given in Table 3.4.

The statistically computed thermodynamic functions viz the enthalpy, the free energy, the heat capacity and entropy of 2,6,4-DBMP and 4,2,6-DBMP are presented in Table 3.5 and Table 3.6 respectively. The variation of enthalpy function and heat capacity function with absolute temperature of 2,6,4-DBMP and 2,6,4-DCFP are shown in Fig 3.12 and 3.13, while the variation of the free energy and entropy with absolute temperature are shown in Fig 3.14 and 3.15 respectively.

**VIBRATIONAL SPECTRA**

The compounds 2,6,4-DBMP and 2,6,4-DCFP are tetra substituted benzene compounds. Assuming –OH and –CH₃ groups as single mass point, the molecules under investigation belong to Cᵥ point group symmetry. The vibrational assignments have been made essentially on the basis of magnitude and relative intensities of the vibrational spectra are available for similar molecules. All the spectra are well interpreted and cited here under:

**RING VIBRATIONS**

**CH VIBRATIONS**

The molecules 2,6,4–DBMP and 2,6,4-DCFP are tetra substituted benzene and thus there are two hydrogen atoms left around the ring which should give rise to two C-H valance oscillations. The C-H stretching vibrations appear in the region 3100-3000 cm⁻¹. These vibrations are highly characteristic of aromatic ring itself
and afford a ready identification for the structure. The C-H stretching frequencies in benzene derivatives arise from non degenerate modes $a_{1g}$ (3073 cm$^{-1}$) and $b_{1u}$ (3060 cm$^{-1}$) and two degenerate modes $e_{2g}$ (3046 cm$^{-1}$) and $e_{1u}$ (3080 cm$^{-1}$). In this region, the bands are not much affected due to the nature and the position of the substituents. S. M. Pandey et al. have assigned this stretching mode at 3140, 3100 cm$^{-1}$ in tri-chloro phenol. R. K. Goel et al. have assigned C-H stretching vibration at 3128, 3058 cm$^{-1}$ in 2,6-dibromo Phenol. In the present study, the infrared bands observed at 3092 / 3089 cm$^{-1}$ (KBr pellet / Nujol mull) and Raman band at value 3062 cm$^{-1}$ in 2,6,4-DCFP and the infrared band at 3038 cm$^{-1}$ (KBr pellets) with counterpart Raman band at 3038 cm$^{-1}$, Raman band at 3056 cm$^{-1}$ in 2,6,4-DBMP have been assigned to C-H stretching mode. These assignments are in good agreement with the literature values.

According to Varsnayi et al., there are two degenerate $e_{2g}$ (1178 cm$^{-1}$) and $e_{1u}$ (1033 cm$^{-1}$) and two non degenerate $b_{2u}$ (1150 cm$^{-1}$) and $a_{2g}$ (1326 cm$^{-1}$) modes of vibration in benzene with C-H in plane vibrations in benzene with C-H in plane bending vibrations. In tetra substituted benzene, these modes should give rise to two C-H in plane bending vibrations. In present study, the infrared bands observed at 1322 / 1317 cm$^{-1}$ (KBr pellets / Nujol mull) and Raman band at 1062 cm$^{-1}$ in 2,6,4-DBMP and infrared band at 1328 / 1324 cm$^{-1}$ (KBr pellets / Nujol mull), 1065 cm$^{-1}$ (KBr pellets and Nujol mull) with counter Raman band at 1064 cm$^{-1}$ in 2,6,4-DCFP have assigned to C-H in plane banding vibrations. These assignments are in agreement with literature values.

Colthup et al. also displays corresponding to C-H nonplaner bending mode of aromatic ring in the reign 1000-700 cm$^{-1}$. While Bellamy displays the region 1000-650 cm$^{-1}$ for the same vibration mode. During C-H nonplaner bending
vibrations of substituent aromatics, the substituent tend to stay nearly motionless and these vibrations tend to stay substituent insensitive. So it is most useful to designate aromatic hydrogen into sets of adjacent hydrogens. Although all these vibrations are group frequencies in the sense that they found with in a relativity small frequency range, they are not all useful group frequencies because many are weak or absent in the spectrum. The C-H out of plane bending vibrations are called umbrella vibrations. The most useful of the modes are (a) where all the hydrogen move in plane and thus give rise to a large dipole moment change and a strong infrared band. (b) Another useful mode in meta and 1,2,4-trisubstituted benzenes, which involves the isolated hydrogen way (out of plane bending), usually seen in the infrared near 870 cm\(^{-1}\). The (c) mode in monosubstitued benzene usually absorbs weakly near 900 cm\(^{-1}\) in the infrared. In 1,2,3,4 tetra substitution these vibrations lie in the region 850-795 cm\(^{-1}\). In view of this in present study, the infrared bands observed at 739 / 738 cm\(^{-1}\) (KBr pellets / Nujol mull), 883 cm\(^{-1}\) (KBr pellets) with counter part Raman band at 896 cm\(^{-1}\) in 2,6,4-DBMP and infrared band at 851 / 853 cm\(^{-1}\) (KBr pellets / Nujol mull) in 2,6,4-DCFP have been assigned to C-H out of plane vibrations. These assignments are in accordance with literature values\(^{24,28,29}\).

**C-C VIBRATIONS**

According to Colthup et al\(^{25}\), the C-C stretching vibrations lies in the region 1600-1400 cm\(^{-1}\). However Silverstein et al.\(^{30}\) displays frequencies for C-C stretching modes of an aromatic ring in the region 1650-1400 cm\(^{-1}\). The vibrations near 1600 cm\(^{-1}\) mainly involve "quadrant stretching" of the aromatic ring C-C bonds but there is a little interaction with C-H in plain bending vibrations. However the vibrations near 1500 cm\(^{-1}\) involve "semicircle stretching" of the C-C bonds, which mixes strongly with the C-H in plain modes and absorbs in the infrared spectra at 1486
and 1037 cm\(^{-1}\). Moreover, the alternating ring stretching vibrations of benzene occur at 1311 cm\(^{-1}\) considerably lower than expected because the electronic structure can change and approach the Kekule benzene structure from where the electrons have partially slipped away from the stretched bonds into contracted bonds.

According to Varsnay et al.\(^{18}\), the C-C stretching modes are the components of the two doubly degenerate vibrations of benzene \(e_{2g} (1595 \text{ cm}^{-1})\) and \(e_{1u} (1485 \text{ cm}^{-1})\) and two non degenerate modes \(b_{2u} (1310 \text{ cm}^{-1})\) and \(a_{1g} (995 \text{ cm}^{-1})\). All these vibrations practically remain unaffected by substitution. As suggested by Bellamy\(^{26}\) under reduce symmetry, the \(e_{2g}\) mode (1595 cm\(^{-1}\)) of benzene splits up to its components in the region 1610-1560 cm\(^{-1}\), which generally appears with weak intensity in the infrared. In present study the infrared band observed at 1592 cm\(^{-1}\) (KBr pellets and Nujol mull both) with counterpart Raman band at 1592 cm\(^{-1}\) in 2,6,4-DCFP and Raman band at 1607 cm\(^{-1}\) in 2,6,4-DBMP have assigned C-C stretching mode which have been coorelated to the components of \(e_{2g} (1595 \text{ cm}^{-1})\) mode of benzene. The Raman band observed at 1414 cm\(^{-1}\) in 2,6,4-DBMP and infrared band at 1412 cm\(^{-1}\) (KBr pellets), in 2,6,4-DCF have assigned to C-C stretching mode corresponds to \(e_{1u} (1485 \text{ cm}^{-1})\) mode of benzene. The infrared bands at 1378 cm\(^{-1}\) (Nujol mull) with counter Raman band at 1379 cm\(^{-1}\) in 2,6,4-DBMP and infrared band at 1368 / 1373 cm\(^{-1}\) (KBr pellets / Nujol mull) in 2,6,4-DCF have been assigned to C-C stretching corresponds to the component of \(b_{2u} (1310 \text{ cm}^{-1})\) of benzene. These are also in good agreement with the assignment made by many workers\(^{23,28,29}\). The magnitude of the ring vibrations depends upon the masses and the nature of the substituents and is considerably reduced in substituted benzenes.
The inplane carbon banding vibrations are derived from non degenerate $b_{1u}$ (1010 cm$^{-1}$) and degenerate $e_{1u}$ (606 cm$^{-1}$) mode of benzene. R. K. Goel et al. have assigned C-C inplane bending mode at 667 cm$^{-1}$ in 2-amino-4-chloro phenol. In present study the Raman band observed at 1028 cm$^{-1}$ in 2,6,4-DCFP have assigned to C-C in plane bending vibrations which corresponds to non degenerate mode $b_{1u}$ (1010 cm$^{-1}$) of benzene has been assigned to in plane C-C bending mode. The infrared band observed at 705 cm$^{-1}$ (KBr pellets) in 4,2,6-DBMP have been assigned to in plane C-C bending mode which corresponds to the degenerate $e_{2u}$ (606 cm$^{-1}$) mode of benzene. As pointed out earlier by Bellamy that the carbon out of plane carbon bending vibrations are derived from the non degenerate $b_{2g}$ (707 cm$^{-1}$) and degenerate $e_{2u}$ (404 cm$^{-1}$) modes of benzene. In view of this in present study Raman band at 510 cm$^{-1}$ in 2,6,4-DCFP have assigned to C-C out of plane ring bending vibrations which corresponds to the $b_{2g}$ (707 cm$^{-1}$) mode of benzene. The infrared bands observed 420, 444 cm$^{-1}$ (KBr pellets) in 2,6,4-DBMP and infrared band at 443 cm$^{-1}$ (Nujol mull) with counter Raman band at 442 cm$^{-1}$ have assigned to C-C out of plane bending vibration which corresponds to the $e_{2u}$ (404 cm$^{-1}$) modes of benzene. These assignments are in accordance with.

RING BREATHING MODE AND TRIGONAL BENDING VIBRATIONS

Under reduced symmetry $C_{2v}$, the C-C ring breathing $a_{1u}$ (995 cm$^{-1}$) and closely lying C-C-C trigonal bending $b_{1u}$ (1010 cm$^{-1}$) vibrations of benzene give rise to the combined modes. As a result of which an appreciable interaction is possible. When the symmetry of benzene ring lowered due to the substitution, the breathing vibration occurs at greatly reduced frequency. This could be understood by the interaction of ring breathing mode with trigonal bending mode $b_{1u}$. R. K. Goel et al. assigned this mode at 972 cm$^{-1}$ in 2-amino-4-chloro phenol. In present study,
the Raman band at 980 cm\(^{-1}\) in 2,6,4-DBMP and 945 / 947 cm\(^{-1}\) (KBr pellets / Nujol mull) with counter Raman band at 940 cm\(^{-1}\) in 2,6,4-DCFMP have assigned to breathing and trigonal bending mode. These results are in close agreement with various workers\(^{23,29,32}\).

**CX Vibrations**

Vir Singh et al.\(^{34}\) have assigned C-CH\(_3\) stretching modes at 1180 cm\(^{-1}\) in 24-dihydroxy-6-methyl pyrimidine. R. Ramasamy et al.\(^{33}\) have assigned this mode at 1225 cm\(^{-1}\) in 5,6-dihydroxy-5-methyl uracil. In present study Raman band at 1133 cm\(^{-1}\) in 2,6,4-DBMP has assigned to C-CH\(_3\) stretching mode. This result is in accordance with literature values\(^{35-37}\). Kalsi\(^{38}\) pointed out the C-OH stretching vibrations occurs near 1300 cm\(^{-1}\) have accordingly assigned to the higher frequency to the C-OH stretching mode. Vir Singh et al.\(^{34}\) have the C-OH stretching mode at 1245 cm\(^{-1}\) in 2,4-dimethyl-6-hydroxy pyrimidine. G. Ramana Rai et al.\(^{39}\) have assigned this mode at 1243, 1249 cm\(^{-1}\) in hydrogen methyl derivatives of phenol. In present study the infrared band at 1272 / 1275 cm\(^{-1}\) (KBr pellet / Nujol mull) with counter Raman band at 1276 cm\(^{-1}\) in 2,6,4-DBMP and the infrared band at 1205 cm\(^{-1}\) (KBr pellets and Nujol mull both) in 2,6,4-DCFMP have assigned to C-OH stretching modes. B. S. Yadav et al.\(^{19}\) have assigned in plane C-OH bending vibrations in 560 cm\(^{-1}\) in 4-hydroxy-2-mercapto-6-propyl pyrimidine. In present study the infrared band observed at 470 cm\(^{-1}\) (KBr pellets) with counter part Raman band at 473 cm\(^{-1}\) in 2,6,4-DBMP and the infrared band at 478 cm\(^{-1}\) (KBr pellets) with counter Raman band at 479 cm\(^{-1}\) in 2,6,4-DCFMP have assigned to in plane bending vibrations. In present study Raman band at 205 cm\(^{-1}\) in 2,6,4-DCFMP has assigned to the out of plane C-OH bending vibrations. These assignments are in accordance with literature values\(^{37,40,41,42}\).
Colthup et al.\textsuperscript{25} have suggested that in benzene derivatives containing F atoms on the ring, C-F stretching frequencies appear in the region 1300-1000 cm\(^{-1}\). According to Silverstein et al.\textsuperscript{30}, in mono fluoronated benzene ring narrow strong absorption band near 1230 cm\(^{-1}\) is assigned as C-F stretching mode. N. Syam Sundar et al.\textsuperscript{43} have assigned C-F stretching mode at 1292 cm\(^{-1}\) in substituted toluenes. J. Marshel\textsuperscript{44} have assigned this mode at 1252 cm\(^{-1}\) in fluoro-quinoline complex. In present study the strong band at 1297 cm\(^{-1}\) (KBr pellets) with counterpart Raman band at 1289 cm\(^{-1}\) has been assigned to C-F stretching mode. This assignment is in accordance with literature values\textsuperscript{45,46}.

Varasayni et al.\textsuperscript{18} displays the frequencies of C-X in plane bending vibrations lower than 500 cm\(^{-1}\) for aromatic ring. N. P. Singh et al.\textsuperscript{45} has assigned C-F in plane bending vibration at 480 cm\(^{-1}\) in the spectrum of 5-amino-2-fluoro benzotrifluoride. In present study the Raman band observed at 1595 cm\(^{-1}\) has been assigned to C-F in plane bending vibration in 2,6,4-DCFP. This vibration is in good agreement with literature value\textsuperscript{46,47,48}.

The C-Cl stretching gives strong bands in the 760-505 cm\(^{-1}\) region\textsuperscript{25,43}. R.K. Goel et al.\textsuperscript{9} have assigned C-Cl stretching mode at 665 cm\(^{-1}\) in 4-chloro phenol. S. Mohan et al.\textsuperscript{49} have assigned at 714 cm\(^{-1}\) in para chloro benzoic acid. V. K. Rastogi et al.\textsuperscript{50} have assigned C-Cl stretching mode at 668, 832 cm\(^{-1}\) in 2,4-dichloro benzonitrile. In view of this assignment, a strong infrared band at 807/797 cm\(^{-1}\) (KBr pellets / Nujol mull) and 778 cm\(^{-1}\) (KBr pellets) with counter Raman band at 786 cm\(^{-1}\) in 2,6,4-DCFP have been assigned to C-Cl stretching mode which is further found supported by the previous literature\textsuperscript{46,47,52,53}. R. K. Yadav et al.\textsuperscript{46} have assigned C-Cl in plane bending mode at 403 cm\(^{-1}\) in 5-amino-2-chloro benzotrifluoride. Vir Singh et al.\textsuperscript{54} have assigned C-Cl in plane
bending mode at 330, 290, 250 cm\(^{-1}\) in trichloro pyrimidine. In view of this assignment a Raman bands observed at 385, 328 cm\(^{-1}\) have been assigned to C-Cl in plane bending mode in 2,6,4-DCFP which is in good agreement with literature values\(^{47,48}\). In present study, the Raman band observed at 223 cm\(^{-1}\) has assigned to C-Cl out of plane bending mode which is in accordance with literature values\(^{53,54}\).

C-Br stretching frequencies usually appear in the region 650-485 cm\(^{-1}\)\(^{27,30}\). S.K. Sharma et al.\(^{13}\) have assigned this mode at 583, 673 cm\(^{-1}\) in 2,4 and 2,6-dibromo phenol. V. Balchandran et al.\(^{24}\) have assigned this mode at 544 cm\(^{-1}\) in 5-bromo-cytocine. R.N. Medhi et al.\(^{55}\) have assigned this mode at 612 cm\(^{-1}\) in 2-fluro-5 bromo pyridine. In present study the infrared bands observed at 518 cm\(^{-1}\) (KBr pellets), 562 / 561 cm\(^{-1}\) (KBr pellets / Nujol mull) with counter part Raman band at 555 cm\(^{-1}\) in 2,6,4-DBMP have assigned to C-Br stretching mode. These results are in good agreement with literature values\(^{47,56,57}\). S. Mohan et al.\(^{49}\) have assigned in plane C-Br bending mode at 315 cm\(^{-1}\) in 5-bromo-2-nitro pyridine. In present study the Raman band at 348, 264 cm\(^{-1}\) have assigned to in plane C-Br bending mode in 2,6,4-DBMP. In present study the Raman band observed at 133 cm\(^{-1}\) has assigned to C-Br out of plane bending mode. These assignments are in accordance with literature values\(^{46,47,57}\).

**OVERTONES OF ARYL RING VIBRATIONS**

According to Jagmohan\(^{27}\) usually intense overtones of aryl ring vibrations occur in the region 2000-1650 cm\(^{-1}\). These bands are somewhat weaker than fundamentals and are most clearly seen in the spectra of moderately thick samples. In the present study, the infrared bands observed in the region 2048-1660 cm\(^{-1}\) (KBr pellets), 1720 cm\(^{-1}\) (Nujol mull) in 2,6,4-DBMP and 1704-1852
cm$^{-1}$ (KBr pellets), 1714 cm$^{-1}$ (Nujol mull) in 2,6,4-DCFP. These assignments are further in agreement with the standard literature.$^{25,27,30}$

**GROUP VIBRATIONS**

- **CH$_3$ VIBRATIONS**

There are three C-H bonds in a methyl group so there will be three C-H stretching vibrations, out of which one is symmetric stretching vibration and two are asymmetric stretching vibrations.$^{25}$ The two asymmetric vibrations have nearly the same magnitude and usually appear with varying intensity in the region 3000-2900 cm$^{-1}$. One of these modes can be approximately described as involving the outward motion of the two hydrogens and onward motion of third hydrogen. In symmetric stretching vibrations all three hydrogen atoms move away from carbon atoms simultaneously and lie in the region 2940-2865 cm$^{-1}$. $^{25,30}$

V. Singh et al.$^{34}$ have assigned asymmetric and symmetric stretching mode at 2820, 2480, 2800 cm$^{-1}$ respectively in 2,4-dihydroxy-6-methyl pyrimidine. L D. Singh et al.$^{36}$ have assigned asymmetric and symmetric modes at 2945 and 2853 cm$^{-1}$ respectively in methoxy-benzaldehyde. In present study, the infrared band at 2923 / 2925 cm$^{-1}$ (KBr pellets / Nujol mull) with the counter part Raman band at 2920 cm$^{-1}$ has assigned to asymmetric C-H stretching due to methyl group in 2,6,4-DBMP. The infrared band at 2856 cm$^{-1}$ (KBr pellets / Nujol mull both) has assigned to C-H symmetric stretching due to methyl group. These assignments are in good agreement with literature values.$^{58,59}$

According to Silverstein$^{30}$, the symmetrical C-H bending vibrations occur near 1380 cm$^{-1}$ while, the asymmetrical bending vibration near 1465 cm$^{-1}$. R. P. Singh et al.$^{35}$ have assigned asymmetric CH$_3$ deformation at 1462, 1445, 1452 cm$^{-1}$ and
symmetric CH₃ deformation at 1382, 1370 cm⁻¹ in 2,4 and 3,4-dimethyl phenols. In present study the infrared band at 1558 / 1552 cm⁻¹ (KBr pellets / Nujol mull) and Raman band at 1588 cm⁻¹ in 2,6,4-DBMP have assigned asymmetric CH₃ deformation bands. The infrared band at 1395 cm⁻¹ (KBr pellets) in 2,6,4-DBMP has assigned to symmetric CH₃ deformation modes. These assignments are in accordance with literature values⁵⁸,⁵⁹.

According to Coulthup et al.²⁵, there should be two rocking mode for methyl group one is directed towards the XZ plane and second towards the YZ plane. Vir Singh et al.¹⁹ have assigned this mode at 1100, 1020 cm⁻¹ in 4-hydroxy-2-mercapto-6-propyl pyrimidine. In present study, the infrared band at 1040 cm⁻¹ (KBr pellets), in 2,6,4-DBMP have assigned to rocking modes. This assignment is in close agreement with literature values⁵⁸.

Owen and Hester⁶⁰ assigned the CH₃ torsional mode in the lower region at 300 cm⁻¹ in substituted methyl phenol and in aromatic methyl substituted benzenes while Tylli et al.⁶¹ have assigned this mode around 280 cm⁻¹. In the present study the Raman bands at 210 cm⁻¹ 2,6,4-DBMP has assigned to CH₃ torsion mode. This assignments is in good agreement with literature values⁵⁷,⁵⁸,⁵⁹.

-OH GROUP VIBRATIONS

Coulthup et al.²⁵ suggested the OH valance oscillations in the region 3500-3700 cm⁻¹ for the molecules containing -OH groups. Varsanyi et al.¹⁸ pointed out these vibrations around 3600 cm⁻¹. Evans¹ have suggested this mode at 3628 cm⁻¹ in phenol. In associated species it is reported in 3145-3430 cm⁻¹. S. Gunasekar et al.⁶² have assigned O-H stretching mode at 3461 cm⁻¹ in chloroxylene. In present study, the infrared band at 3420 cm⁻¹ (KBr pellets) with counter Raman band at
3140 cm\(^{-1}\) in 2.6.4-DBMP and infrared at 3458 cm\(^{-1}\) (KBr pellets) with counter Raman band at 3449 cm\(^{-1}\) in 2.6.4-DCFP have assigned to O-H stretching modes. These results are in agreement with literature values\(^{52,54,58,59}\).

The frequency due to in plane vibration in phenols, in general lies in the range 1150-1250 cm\(^{-1}\)\(^{26,30}\). In almost all 1,2,3,5-tetra substituted benzene derivatives, with one O-H and two hydrogen substituents, this vibration was found in a narrow region\(^{27}\). Vir Singh et al\(^{34}\) have assigned this mode at 1205 cm\(^{-1}\) in dimethyl hydroxy pyrimidine. B. Singh et al.\(^{24}\) have assigned this mode at 1178 cm\(^{-1}\) in 2,4 and 3,4-dimethyl phenol. In present study the infrared band at 1163 / 1158 cm\(^{-1}\) (KBr pellets / Nujol mull) Raman band at 1154 cm\(^{-1}\) in 2,6.4-DBMP and infrared band at 1155 / 1150 cm\(^{-1}\) (KBr pellets / Nujol mull) in 2,6.4-DCFP have assigned to in plane O-H bending vibrations. These are in accordance with literature values\(^{58,59}\).

S P. Gupta et al.\(^{23}\) have assigned O-H out of plane deformation at 626 cm\(^{-1}\) in 2,6-di-iodo-4-nitro phenol while R. John Xavier et al.\(^{22}\) have assigned this mode at 584, 528 cm\(^{-1}\) in 4,6-dihydroxy-2-mercapto pyrimidine. In present study the infrared band at 588 / 589 cm\(^{-1}\) (KBr pellets / Nujol mull) with counter part Raman band at 582 cm\(^{-1}\) in 2,6.4-DCFP have assigned to O-H out of plane deformation.

**ELECTRONIC SPECTRA**

According to Silverstein et al.\(^{30}\) the spectra of phenol is comparable with that of benzene. Benzene itself displays three absorption bands: 184 nm (\(\varepsilon_{\text{max}} = 60000\)), 204 nm (\(\varepsilon_{\text{max}} = 7900\)) and 256 nm (\(\varepsilon_{\text{max}} = 200\)). These bands originate from \(\pi\rightarrow\pi^*\) transitions. The intense band near 180 nm results from an allowed transitions, whereas the weaker band near 200 and 260 nm results from
Fig 3.8: Near ultraviolet absorption spectra of 2,6,4-DBMP in

- Ethanol
- Methanol
- Chloroform
Near ultraviolet absorption spectra of 2,6,4-DBMP at different pH in Ethanol
Near ultraviolet absorption spectra of 2,6,4-DCFP at different pH in Ethanol
forbidden transitions in the highly symmetrical benzene molecule. Different notation have been used to designate the absorption bands of benzene, these are summarised in the Table 3.2. We shall discuss these bands using Braude's E and B notation. B band generally found in between 230-280 nm. The spectra of phenols can usually be readily identified from their ultra violet spectra. We have already referred to the effect of interaction of the aromatic \( \pi \)-system with substituent lone pairs of electrons, and in comparing the long wavelength values for benzene, phenol. We find that they occur at 256, 270nm respectively.

In present study bands observed at 284, 287, 286 nm in 2,6,4-DBMP in chloroform, ethanol and methanol solvents and bands at 284, 288, 287 nm in 2,6,4-DCFP in chloroform, ethanol, methanol solvents respectively are originated from \( \pi^{-}\pi^* \) transition and designated as B-band. The intense shoulder bands observed at 210, 206 nm in 2,6,4-DBMP in ethanol and methanol and the bands observed at 207, 211 nm in 2,6,4-DCFP in ethanol and methanol respectively are also originated from \( \pi^{-}\pi^* \) transition and designated as \( E_2 \)-bands. The R-bands originated from \( n^{-}\pi^* \) transitions are observed due to the attachment of group containing lone pair of electrons. In present study, bands observed at 230, 225, 222 nm in chloroform, ethanol and methanol in 2,6,4-DBMP and band at 241 nm in chloroform in 2,6,4-DCFP are originated from \( n^{-}\pi^* \) transitions.

**EFFECT OF SUBSTITUTION ON ELECTRONIC TRANSITIONS**

An auxochromic group like (OH, NH\(_2\), Cl, Br, F etc.) substituted to chromophore, the \( E_2 \)-band and B-band shift towards longer wavelength frequently with intensification of the B-band and loss of its fine structure, because of \( n^{-}\pi^* \) conjugation. Generally the B-band of phenol observed at 270 nm. Conversion of phenol to the corresponding anion results in a bathochromic shift to the \( E_2 \)-bands.
and B-bands. Auxochrome on aromatic ring forms the E₂-band in near ultraviolet region, although in many cases it does not appear at wavelength much greater than 210 nm. In auxochrome substitution, the hetroatom with lone pair of electrons shares these electrons with the π electron system of the ring facilitating the π-π⁺ transition and thus causing a red shift of E₂-band. The occurrence of E₂-band above 210 nm is due to the shift of π-π⁺ transition towards the longer wavelength, which is originated due to the combined mesomeric, inductive, hyperconjugation and steric effects exerted by auxochrome and alkyl substitution on the aromatic ring. According to Kalsi, when benzene is substituted by simple alkyl group the absorptions are shifted slightly to longer wavelength and fine structure remains intact. The small bathochromic shift in π-π⁺ transition system of ring is ascribed to the hyper conjugation due to CH₃ group, in which the σ electron of alkyl C-H bond participate in resonance with ring in 2,6,4-DBMP. The para isomer generally absorbs at the longest wavelength whereas the ortho isomers generally absorbs at the shortest wavelength. This effect is due to the steric interaction between ortho substituents, which effectively reduces hyper conjugation. In 2,6,4-DCF P molecule, the chlorine atom is at ortho position does not affect the wavelength of B-band but F atom at para position gives red shift in B-band. The additive effect of auxochromatic and chromophoric groups are responsible for n-π⁺ conjugation. The auxochrome groups present on aromatic ring are responsible for n-π⁺ transition due to the presence of non-bonding electrons available on auxochrome group. In molecule 2,6,4-DBMP, -Br group is largely responsible for n-π⁺ transition while in 2,6,4-DCF P, -Cl, -F groups are responsible for n-π⁺ transition.
EFFECT OF SOLVENT

The electronic spectra of a molecule when recorded in a solvent generally shifts the bands in comparison to those obtained in the vapour phase. This is called the solvent shift effect and is due to the weak physical interactions between solute and solvents. The interaction may be generally classified into specific and non-specific solvent on the electronic states of solute. Specific solvent effects are due to the dispersive inductive and electrostatic forces that may occur between solute and the surrounding solvent molecules. Solvent polarity effects the electronic transitions and this depends on whether the solute becomes more or less polar, after excitation polar solvent which can form hydrogen bonding tends to interact electrostatically with various chromophores. This changes the charge distribution in the molecule which results in increase delocalization. For \( \pi-\pi^* \) transitions both the ground and excited states are stabilized and the absorption moves towards longer wavelength. For \( n-\pi^* \) transition, the ground state is more stabilized then the excited state and consequently absorption moves towards shorter wavelength. Dyer has also reported a red shift for \( \pi-\pi^* \) transition and a blue shift for \( n-\pi^* \) transition with the increasing polarity of the solvent.

During the present observations, it is found clearly from Table 3.3, the \( n-\pi^* \) transitions (R-band) observed at 230 nm in chloroform and 225 nm in ethanol in 2,6,4-DBMP are blue shifted with increasing the polarity of the solvents while in 2,5,4-DCFP, R-band observed only in chloroform. On going from nonpolar to polar solvents the polarity of the solute also plays an important role in the electronic transition. The shift of absorption spectra of slightly polar solute are predominantly due to the dipole-dipole interaction between the solute and solvent in the ground and excited states respectively and the orientation strain in the
excited state. The orientation strain will result a blue shift if the solute dipole increases and red shift if the solute dipole decreases on excitation. These shift are related to vapour phase spectrum with a polar solute in a non polar solvent dipole induce dipole interaction take place and there will no orientation strain. Therefore, a blue shift may appear while going from vapour state to non polar solvents. As the solute is non polar, therefore no orientation strain will occur and there may be slight packing strain due to the interaction among themselves to form a cage around the solute molecule resulting a blue shift. Both the molecule clearly shows a blue shift in n-\(\pi^*\) transition. It was observed by some workers\(^{67-70}\).

In present study \(\pi-\pi^*\) transitions (B-band) show red shift on going from chloroform to methanol in 2,6,4-DBMP, the B-band in ethanol has not been observed in this molecule. In 2,6,4-DCFP, B-bands also show red shift on going from chloroform to ethanol to methanol are given in Table 3.3. These assignments are in good agreement with literature values\(^{70-74}\). In present study \(\pi-\pi^*\) (E2-band) in 2,6,4-DCFP show red shift on going from ethanol to methanol, which agrees with literature value\(^{70-73}\). In molecule 2,6,4-DBMP, the E2-band show blue shift on going ethanol to methanol. This trend is also observed by many workers\(^{75,76}\).

**EFFECT OF pH VARIATION ON ELECTRONIC TRANSITIONS**

Coe et al.\(^{74}\) have suggested that with increasing pH, red shift occur in \(\pi-\pi^*\) and \(n-\pi^*\) transitions in phenol. B.S. Yadav et al.\(^{72}\) have suggested that with increasing pH red shift occurs in \(\pi-\pi^*\) and \(n-\pi^*\) transitions 2,4-dibromo-6-nitro aniline. The interpretation of spectral measurements, to a considerable extent, mainly depend on the choice of sites of localization of protons, the question of possible effect of \(\Delta \) variation on electronic transitions of the present molecule, an usual behaviour is found i.e. red shift is observed in \(\pi-\pi^*\), \(n-\pi^*\) transitions. The substituents such as
O-H have an electrons withdrawing inductive effect but they exert an electron donating mesomeric effect from ortho position. However, it is the position of hydroxyl group which affects the spectral shift dominantly due to its more active and electron donating nature. Moreover on increasing the pH of the solvent the hydrogen atom of hydroxyl group has been removed in the form of a proton, leaving behind the bonding pair of electrons. In the present study the red shift is observed in n-π* and π-π* transitions on increasing the pH in both molecules given in Table 3.4. These results are in accordance with literature value⁷⁰,⁷².

**THERMODYNAMIC PARAMETERS**

On the basis of molecular data obtained from the spectra, as was first suggested by Tolman and Badger⁷⁷, Urey⁷⁸ it is possible to predict with great precision the value of thermodynamic parameters such as enthalpy, heat capacity, free energy and entropy of the particular gases. This possibility is of great practical importance. Particularly since the direct experimental measurement of these quantities is usually difficult. The values calculated from the spectroscopic data are more accurate than those determined by direct thermal measurement.

Thermodynamic function, namely the enthalpy function [H₀-E₀⁰], the heat capacity Cᵥ, the free energy function [F₀-E₀⁰] and entropy function (S⁰) of 2,6,4-DBMP and 2,6,4-DCFP have been computed using the standard expressions⁷⁹-⁸¹ taking z-axis perpendicular to the molecular plane and y-axis to pass through the para position.

For determining rotational contribution, the following structure parameters were used⁷⁹,⁸⁰.
STRUCTURAL PARAMETERS OF 2,6,4-DBMP

**Bond Lengths (Å)**

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Where C<sub>1</sub> to C<sub>6</sub> are carbon atoms of phenol ring while C<sub>7</sub> is the carbon atom of methyl group and Br<sub>1</sub> and Br<sub>2</sub> are bromine atoms.

STRUCTURAL PARAMETERS OF 2,6,4-DCFP

**Bond Lengths (Å)**

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Fig 3.12: Variation of enthalpy function and heat capacity with absolute temperature of 2,6,4-DBMP
Fig 3.14: Variation of free energy and entropy function with absolute temperature of 2,6,4-DBMP
Fig 3.15: Variation of free energy and entropy function with absolute temperature of 2,6,4-DCFP
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Where C₁ to C₆ 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 30 fundamental frequencies. Assuming CH₃, OH as a single mass atom and assuming the rigid rotor-harmonic oscillator approximation. The symmetry number for overall rotation is three. The principal moments of inertia of 2,6,4-DCFp are found to be 81.89, 107.98, and \(189.88 \times 10^{-39}\) gm cm² respectively. The principal moments of inertia of 2₆,4-DBMP are found to be 115.87, 233.85 and \(349.72 \times 10^{-39}\) gm cm² respectively.

It is found that the variation of thermodynamic functions enthalpy function, the heat capacity with absolute temperature have been shown in Fig 3.12 and 3.13 in 2₆,4-DBMP and 2,6,4-DCFp respectively. These figures show that at very high temperature the influence of anharmonicity will make itself felt and will no longer give an accurate representation. The variation of free energy function and entropy function is shown in Fig 3.14 and 3.15 respectively, which show that in case of free energy function at temperature as high as 1000 K, the effect is quite small.
While in case of entropy, at very high temperature the vibrational contribution is very small, compared to other contribution thus, a statistical calculation of the entropy is much less dependent upon vibrational data than the other thermodynamic functions. The trend of variation of thermodynamic parameters is similar to those reported for similar molecules in literature$^{19,20,54,82-84}$. 
<table>
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<th>FREQUENCY (cm⁻¹)</th>
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Lattice Vibration

γ (C-Br)

γ (C-OH)

γ (CH₃)

γ (C-Cl)

β (C-Br)

β (C-Cl)

β (C-Br)

γ (C-C)
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|-----|-----|-----|-----|-----|
| γ (C-C) | β (C-OH) | γ (C-C) | ν (C-Br) | ν (C-Br) |
| γ (O-H) | β (C-F) | β(C-C) | γ (C-H) | ν (C-Cl) |
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<td>νₛ (C−H) of methyl group</td>
<td>νₐ (C−H) of methyl group</td>
<td>νₛ (C−H)</td>
</tr>
<tr>
<td>----------</td>
<td>----------</td>
<td>----------</td>
<td>-----------</td>
<td>--------------------------</td>
<td>--------------------------</td>
<td>-----------</td>
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<td>1385 (w)</td>
<td>1588 (w)</td>
<td>2856 (s)</td>
<td>2923 (s)</td>
<td>3038 (s)</td>
<td>3056 (s)</td>
<td>3420 (w)</td>
</tr>
<tr>
<td>1411 (w)</td>
<td>1588 (w)</td>
<td>1592 (s)</td>
<td>1704 (w)</td>
<td>1714 (w)</td>
<td>3059 (w)</td>
<td>3458 (w)</td>
</tr>
<tr>
<td>1412 (w)</td>
<td>1592 (s)</td>
<td>1592 (s)</td>
<td>1704−1852</td>
<td>(v)</td>
<td>3089 (w)</td>
<td>3092 (w)</td>
</tr>
<tr>
<td></td>
<td>1592 (w)</td>
<td>1592 (w)</td>
<td>1720 (w)</td>
<td>(v)</td>
<td>3082 (w)</td>
<td>3092 (w)</td>
</tr>
<tr>
<td>1552 (s)</td>
<td></td>
<td>1592 (w)</td>
<td>1704−1852</td>
<td>(v)</td>
<td>3089 (w)</td>
<td>3458 (w)</td>
</tr>
<tr>
<td>1592 (s)</td>
<td></td>
<td>1592 (s)</td>
<td>1704−1852</td>
<td>(v)</td>
<td>3089 (w)</td>
<td>3458 (w)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1592 (s)</td>
<td>1704−1852</td>
<td>(v)</td>
<td>3089 (w)</td>
<td>3458 (w)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(v)</td>
<td>3089 (w)</td>
<td>3458 (w)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(v)</td>
<td>3089 (w)</td>
<td>3458 (w)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(v)</td>
<td>3089 (w)</td>
<td>3458 (w)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(v)</td>
<td>3089 (w)</td>
<td>3458 (w)</td>
</tr>
</tbody>
</table>
Where,

\[ \begin{align*}
  s &= \text{strong;} \\
  v = \text{stretching;} \\
  vs &= \text{very strong;} \\
  \beta &= \text{in-plane bending;} \\
  w &= \text{weak;} \\
  \gamma &= \text{out-of-plane bending;} \\
  vW &= \text{very weak;} \\
  s &= \text{symmetric;} \\
  as &= \text{asymmetric;} \\
  \gamma_t &= \text{twisting;} \\
  \gamma_r &= \text{rocking}
\end{align*} \]
### TABLE 3.2. ELECTRONIC ABSORPTION BANDS OF BENZENE MOLECULE

<table>
<thead>
<tr>
<th>184 nm</th>
<th>204 nm</th>
<th>256 nm</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>E₁-band</td>
<td>E₂-band</td>
<td>B-band</td>
<td>63</td>
</tr>
<tr>
<td>------</td>
<td>------</td>
<td>------</td>
<td>64</td>
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</tbody>
</table>

### TABLE 3.3. EFFECT OF SOLVENTS ON ELECTRONIC TRANSITION OF 2,6,4-DBMP AND 2,6,4-DCFP

(All values are in mm)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>R.I.</th>
<th>DC</th>
<th>2,6,4-DBMP</th>
<th>2,6,4-DCFP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>π - π⁺</td>
<td>n - π⁺</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(B-band)</td>
<td>(R-band)</td>
</tr>
<tr>
<td>Chloroform</td>
<td>1.458</td>
<td>4.5</td>
<td>284</td>
<td>230</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.3773</td>
<td>25</td>
<td>287</td>
<td>225</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.3662</td>
<td>32.5</td>
<td>286</td>
<td>222</td>
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R.I. = Refractive index, DC = Dielectric constant
<table>
<thead>
<tr>
<th>Solvent</th>
<th>2,6,4-DBMP</th>
<th>2,6,4-DCFP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH value</td>
<td>$\pi - \pi'$</td>
</tr>
<tr>
<td>Ethanol</td>
<td>6.60</td>
<td>286</td>
</tr>
<tr>
<td>Ethanol + HCl</td>
<td>3.34</td>
<td>287</td>
</tr>
<tr>
<td>Ethanol + NaOH</td>
<td>9.41</td>
<td>293</td>
</tr>
</tbody>
</table>

R.I. = Refractive index, DC = Dielectric constant
<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>((H^0 - E^0) / T)</th>
<th>(C_p^0)</th>
<th>(- (F^0 - E^0) / T)</th>
<th>(S^0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>16.70</td>
<td>26.59</td>
<td>111.53</td>
<td>128.23</td>
</tr>
<tr>
<td>300</td>
<td>21.47</td>
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<td>30.03</td>
<td>49.72</td>
<td>132.24</td>
<td>162.27</td>
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<td>138.05</td>
<td>171.84</td>
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<td>79.50</td>
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</tr>
<tr>
<td>Temperature (K)</td>
<td>$(H^0 - E^0)/T$</td>
<td>$C^0_p$</td>
<td>$-(F^0 - E^0)/T$</td>
<td>$S^0$</td>
</tr>
<tr>
<td>----------------</td>
<td>-----------------</td>
<td>---------</td>
<td>-----------------</td>
<td>-------</td>
</tr>
<tr>
<td>200</td>
<td>8.87</td>
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<td>57.86</td>
<td>141.61</td>
<td>178.06</td>
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REFERENCES


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78. H.C. Urey, J Amer Chem Soc, 45 (923) 1445.


