

SPECTROSCOPIC STUDY OF 3, 4-DIETHYL PYRIDINE

Vipin Kumar¹ and Mohit Kumar²

¹Deptt. of Physics, SKD University, Hanumangarh (INDIA)

²Research Scholar at Deptt. of Physics, SKD University, Hanumangarh (INDIA)

Corresponding Author: *Vipin_bit71@rediffmail.com

ABSTRACT

The aim of present study is to obtain and investigate infrared and laser Raman spectrum in their respective regions for 3,4-diethyl pyridine. During the interpretation of spectra C_s point group symmetry has been assumed. The assignment of the vibrations are made in accordance with that of identical molecules as well as group frequency approach.

INTRODUCTION: The infrared and laser Raman spectroscopic study of N-heterocyclic molecules like, pyridine, pyrimidine, aniline, uracil have been made by many workers. Pyridine constitute an important class of compounds because of their biological important in the structure of nucleic acid and pronounced physiological effect (Martin 1951). Thiopyridone and its derivatives have found an increasing application in pharmaceutical and chemical field.

Pyridine molecule has planar structure in ground state and a quasi-planar in excited state (Bersani et al 2010 and Bellamy 1975). The spectroscopic studies of pyridine have been discussed by John and co-workers (2012). A significant study has been made by some workers (Deep et al 2013, Dellish et al 1974, Govindarajan et al 2012 and Hernandez et al 2016). Tough the vibrational spectra of biological important derivatives of pyridines have been examined (Carmona et al 1993 and Govindarajan et al 2012 & 2014) but due to the high complexity and low symmetry the detailed interpretation of the spectra is very difficult. The nature and position of the substituents in the pyridine ring affects the absorption bands very much. Almost all absorption bands in the 3300 cm^{-1} region have

been identified and a number of frequencies in the 200–6000 cm^{-1} region corresponding to fundamental vibrations have been observed (Bersani et al 2010, Bellamy 1975, Colthup 1964, Dellish and Rao 1963). The presence of hydrogen bonding in certain heterocyclic derivatives can be detected by infrared and Raman spectroscopy by many workers (Abdulaziz et al 2007, Demtroder 2003, Kumar et al 2021 and Leon et al 2018) and reported the appropriate study regarding pyridines and its derivatives.

The objective of this study is to identify the vibrational (infrared and Raman) frequencies corresponding to substituent as well as ring fundamentals whether they are stretching or associated bending vibrations. All the interpretation has been made by assuming the C_s point group symmetry.

EXPERIMENTAL: The spectroscopic grade compound 3,4-diethyl pyridine (hereafter referred as 3,4-DMP) were obtained readymade and used as such without further purification. The purity has been confirmed by elementary analysis and melting point determination. The infrared spectrum of both compounds was recorded on Perkin Elmer infrared spectrophotometer in the range 200–4000 cm^{-1} . The laser Raman spectrum had been recorded using 4880 nm line of Ar^+ for excitation in the region 100–4000 cm^{-1} on carry model-82 grating spectrophotometer and using 4 W Argon laser. The spectral width was 2.0 cm^{-1} and the scanning 30 cm^{-1} .

RESULT AND DISCUSSION: The molecular structure of the Compounds (3,4-DEP) is shown Figure 1 with classical numbering of atom. The infrared and laser Raman spectra are presented in Figure 2 and 3 respectively for 3,4-DEP. Due to the similarity in the infrared spectra of benzene and pyridine the observed frequencies and their intensities with probable assignments of title molecules are given in Table 1 comparing to pyridine obtained frequencies of ethyl groups of the said molecules and their comparison with similar molecules is given in Table 2. The aromatic nature of the title compounds indicates tri substitution. Considering C_2H_5 group as a single mass point the molecule 3,4-DEP belongs to C_{2v} symmetry. The molecules have planar and non planar vibrations. Apart from these vibrations the fundamental frequencies due to C_2H_5 group also appear.

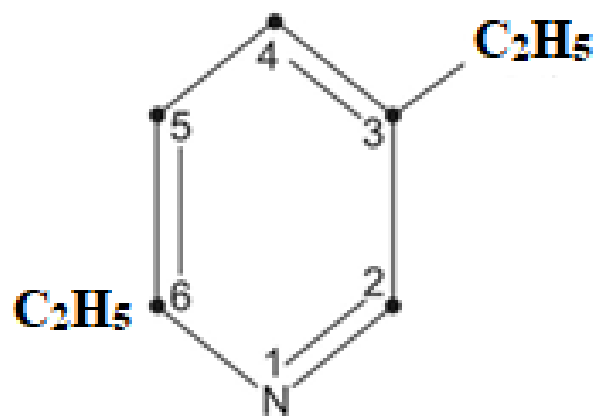


Figure 1: Molecular structure 3,6-Dimethyl Pyridine

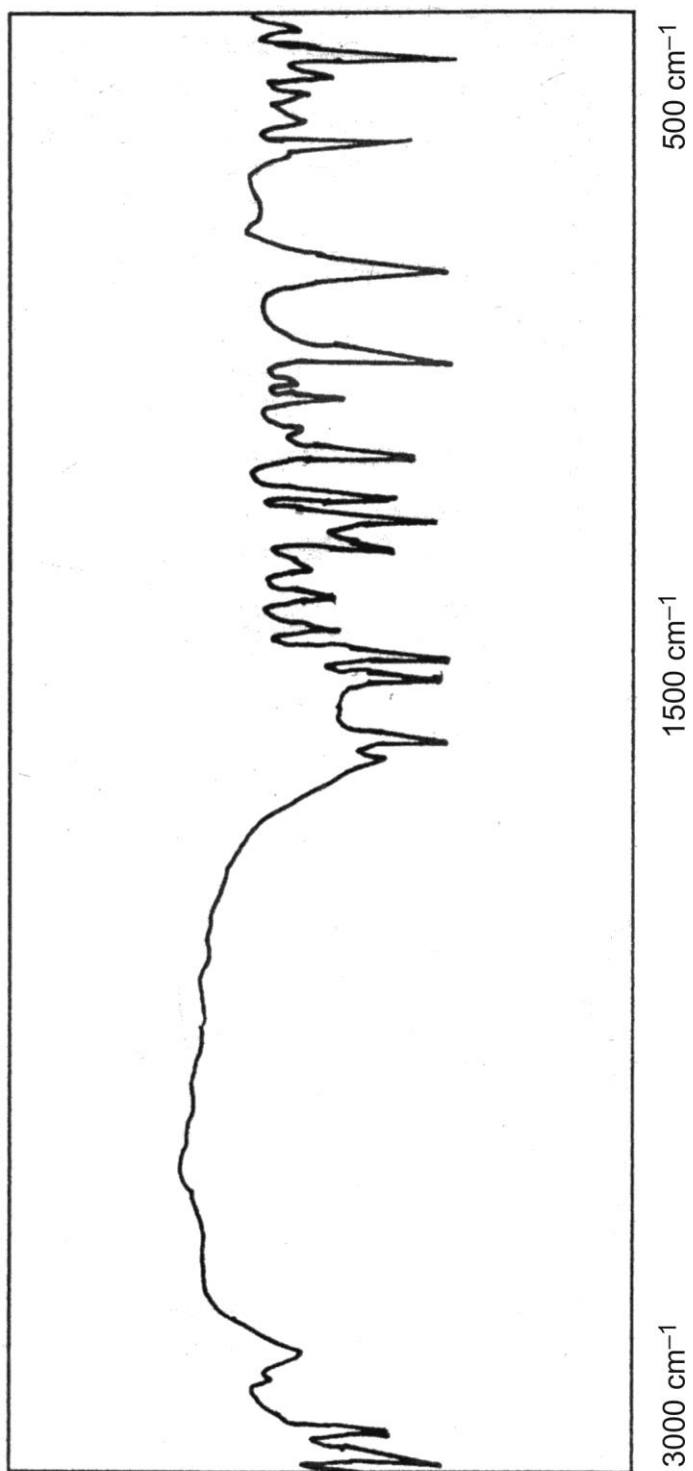


Figure 2: INFRARED SPECTRUM OF 3, 4 DEP

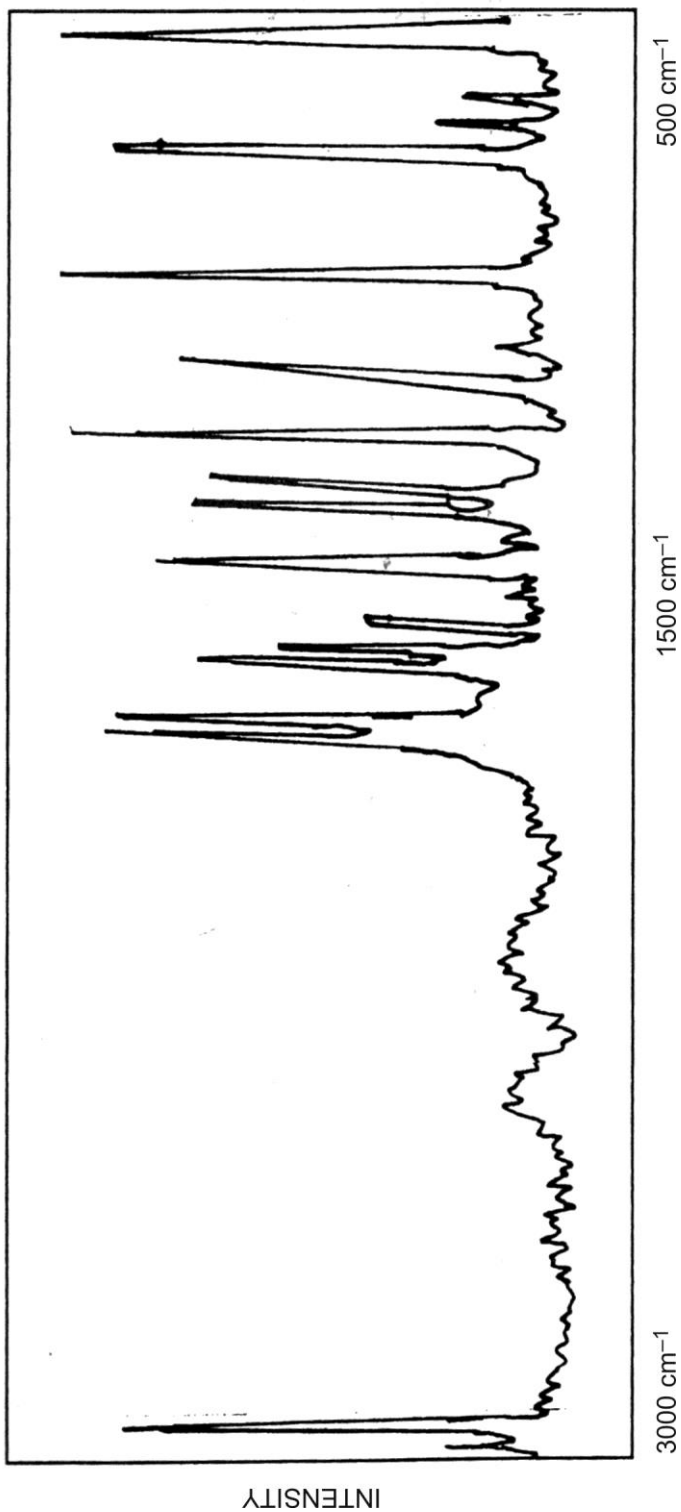


Fig. 3 RAMAN SPECTRUM OF 3, 4 DEP

TABLE 1
Assignments of Vibrational Frequencies of
3, 4-DEP (All Values in cm⁻¹)

Vibration no	Assignment	IR	Raman	Pyridine (Innes 1967)
1.	Ring breathing, v(C—C)	1010 m	—	9942
2.	v(C—H)	—		3045
	v(C—C ₂ H ₅)	1130 s	1140 m	
3.	(C—H) i.p.b.	1321 m	1326 w	1218
4.	(C—C) o.p.b.	850 vs	865 vs	700
5.	(C—H) o.p.b.	—	—	942
6a.	(C—C) i.p.b.	770 vs	—	652
6b.	(C—C) i.p.b.	495 w	496 m	605
7a.	v(C—C)	1600 s	1605 s	1583
7b.	v(C—C)	1585 vs	1570 s	1192
8a.	(C—H) i.p.b.	1232 s	1236 vw	1218
8b.	(C—H) i.p.b.	1164 vs	1170 m	—
9a.	(C—C ₂ H ₅) o.p.b.	—	—	886
10b.	(C—C ₂ H ₅)o.p.b.	275	280 vs	886
11.	(C—H) o.p.b.	715 vs	720 vs	—
12.	(C—H) i.p.b.	1032 w	1037	1030
14.	v(C—C)	1272 w	1260 s	1375
15.	(C—H)i.p.b.	—	—	1148
	(C—C ₂ H ₅) i.p.b.	351 w	—	
16a.	(C—C) o.p.b.	435 w	440 vw	374
16b.	(C—C) o.p.b.	390 w	395 vw	405
17a.	(C—H) o.p.b.	945 w	—	981
17b.	(C—H) o.p.b.	930 w	935 w	—
18b.	(C—H) i.p.b.	—	—	1085

19a.	v(C—C)	1485 vs	1450 m	1482
------	--------	---------	--------	------

Vibration no	Assignment	IR	Raman	Pyridine (Innes 1967)
19b.	v(C—C)	1430 vs	1435 m	1439
20a.	v(C—H)	—	3050 m	3036
20b.	v(C—H)	3038 vs	3028 m	3085

Where vs = very strong

S = strong

m = medium

w = weak

vw = very weak

sh = shoulder

v = stretching

i.p.b. = in-plane bending

o.p.b. = out of plane bending

TABLE 2

**Methyl Group Frequencies in the IR & Raman spectra of 3,4-DEP
& Correlation with Similar Molecules [in cm⁻¹]**

Assignments	3, 4-DEP		Thymine	N methyl anisole
	IR	Raman		
Asymmetrical Stretching	—	—	—	3012
	2985 vs	2990 m	2991	—
	2970 vs	2965 w	—	—
	—	—	—	2954
	2930 vs	2920 vs	—	—
	—	—	—	—
Symmetrical Stretching	—	—	—	—
	—	—	—	—

	—	—	—	2846
	2740	—	—	—
Asymmetrical Stretching	1465 vs	1445 m	1641	1469
	—	—	—	1458
	—	—	1374	—
Symmetrical Stretching	1381 shm	1387 W		—
Rocking	—	—	1091	—
Vibration	1046 shs	—	1044	—
Torsion Vibration	205 m	210 m	215 v	212 vs

vs = very strong, s = strong, m = medium

Sh = Shoulder w = weak vw = very weak

BANDS ORIGINATING FROM RING VIBRATIONS:

In the following study using the numbering recommended by some workers (Murrell 1971 and Suzuki 1967), an attempt has been made to identify the vibrations from infrared and Raman spectra of the title compounds whose schematic picture resembles closely to normal vibrations of benzene and pyridine numbered.

TANGENTIAL SKELETAL VIBRATIONS:

The Skeletal stretching vibrations are prominent and characteristic of benzene derivatives. Bellamy (1975) and others (Mortimer 2017) observed the vibrations 8 and 19 in the region 1400–1610 cm^{-1} for pyridine (Rao 1963, Ruiz et al 2019 and Sverdlov et al 1974). The double degenerate mode 8 (1596 cm^{-1}) in benzene consists of lateral dilation and contraction of the ring made by stretching and compressing of bonds. It is separated in to 8a and 8b after the degeneracy removed. The frequency of skeletal vibration 8a is insensitive towards the substituents. In the present study mode 8a has been found at 1605 and 1610 cm^{-1} in infrared and Raman spectra of 3,4-DEP and at 1600 and 1605 cm^{-1} (Varsanyi 1973). This mode is found to be more sensitive towards the substituents. This

mode is detected in infrared and Raman at 1585–1580 cm^{-1} for 3,4-DEP. The modes 8a and 8b in the present molecules have been assigned to C—C stretching and supported by various workers (Bersani et al 2010, Handschumacher et al 1960, Yadav et al 1997 and Yadav et al 1998).

The ring deformation mode 19 involves both stretching and bending of C—C bond and is analogous to e_{1u} (1485 cm^{-1}) mode of benzene. Under reduced symmetry it can be divided into 19a and 19b and be detected in the region 1450 to 1525 cm^{-1} and 1365 to 1438 cm^{-1} in infrared and Raman respectively and found to be sensitive in small extent (Chand et al 2021, Kumar et al 2021, Gupta et al 1986 and Dyer 1965). In the present study, mode 19a has been found at 1458–1450 cm^{-1} for 3,4-DEP. The mode 19b has been found at 1430-1435 cm^{-1} for 3,4-DEP. Rao (1963) corresponding to b_{1u} (1310 cm^{-1}) mode of benzene assigned it at 1310 cm^{-1} in pyridine and attributed to coupled C-C and C-N stretching vibrations. Some workers (Bersani et al 2010, Chand et al 2021, Dyer 1965, Gupta et al 1986 and Kumar et al 2021) assigned these frequencies very well.

The band regarding b_{1u} (1310 cm^{-1}) mode 14 of benzene occurs in the region 1260-1290 cm^{-1} (Anderson et al 2014, Singh et al 1996, Yadav 1999 and Zoski et al 2007) and assigned to carbon stretching mode. This mode is identified at 1272 and 1268 cm^{-1} for 3,4-DEP in their infrared and Raman spectra attributed to C—C stretching. These vibrations are in well accordance with the assignments of some workers (Braz et al 2021, Goel et al 1982, James et al 2006 and Matago et al 1970).

RADIAL AND O.P.B. SKELETAL VIBRATION:

The carbon stretching (ring breathing mode-1) and Carbon planar vibration-12 are similar to a_{1g} (995 cm^{-1}) and b_{1u} (1010 cm^{-1}) modes of benzene. The energies of these modes are very close to each other. These modes belong to the same symmetry a^1 as given by Bellamy (1975) and Bersani et al (2010). So, the interaction between these modes modifies their energies. The ring stretching vibration reduces to a large amount depending upon the mass nature and number of substituents. The bending vibration remain close to 1010 cm^{-1} (Bernstein et al 1957, Ibanez et al 2016 and Sahu et al 2011).

The vibration 1 is totally symmetric and seems to be polarized and intense in Raman spectra. In the title molecules, the mode 1 is obtained at 847 cm^{-1} . At 1010 cm^{-1} in their

infrared and laser Raman spectra. Bellamy (1975) and Rao (1963) assigned this mode at 994 cm^{-1} in substitute pyridine. Innes showed vibration 1 for pyridine at 992 cm^{-1} while the vibration 12 Carbon bending have been obtained at 1032 and 1037 cm^{-1} for 3, 4 DEP in the infrared and Raman spectra. All these assignments are in accordance with the work reported by some workers (Bernstein et al 1957, Braz et al 2021, Goel et al 1982, Ibanez et al 2016, James et al 2006, Matago et al 1970 and Sahu et al 2011).

The carbon in-plane bending vibration 6, e_{2g} (608 cm^{-1}) appear separately under reduced symmetry as 6a and 6b. Spectroscopic studies given by Varsanyi (1973) for substituted benzenes reveal that both the components are very much sensitive to the mass, nature and the number of substituents. Out of the two the lower component reduces to a large amount as compared to the upper one. Some workers (Dellish et al 1974, Garoz et al 2019, Guirgis et al 2015 and Jeergal et al 1991) assigned the mode 6 and 16 are strongly influenced by substitutions in the methyl group and also dependent on changes in electronic structure show sensitiveness to the orientation of substituent group on considering the above it is observed that the mode 6a and 6b have assigned in infrared and laser Raman spectra of 3,4-DEP at 770 cm^{-1} .

C—H Vibrations:

In the title molecules there are only three hydrogen atoms left attached to the ring at various position. The three C-H bonds involve three C-H stretching in plane and out of plane bending vibrations. Bellamy (1975) and others (Bernstein et al 1957, Braz et al 2021, Garoz et al 2019, Goel et al 1982, Guirgis et al 2015, Ibanez et al 2016, James et al 2006 and Sahu et al 2011) shown that multiple absorption bands in the vibrational spectra of pyridine in the region $3020\text{--}3070\text{ cm}^{-1}$ are due to C-H stretching vibrations 20a, 20b and 2. The bands observed at 2998 cm^{-1} , 3012 cm^{-1} and 3028 cm^{-1} and 3028 cm^{-1} due to 20b and at 3065 cm^{-1} and 3055 cm^{-1} due to 20a with only one at 3025 cm^{-1} due to mode 2 have been assigned to C-H stretching mode in the present work. The results are in agreement with Green (1971) and others (Braz et al 2021, Dellish et al 1974, Garoz et al 2019, Guirgis et al 2015, James et al 2006, Jeergal et al 1991 and Matago et al 1970).

Spectra of benzene shows the appearance of C-H in-plane-bending vibration modes 3,9,15 and 18. In this present work these modes yield three planar bending vibrations 3,

9a, 9b for 3,4-DEP involving C-H in plane bending. The frequencies observed at $1321/1326\text{ cm}^{-1}$, $1232/1236\text{ cm}^{-1}$ and $1164/1170\text{ cm}^{-1}$ for 3,4-DEP in their respective spectra have been assigned to C-H in-plane bending vibrations. These assignments shows the good agreement with the work of many workers (Bernstein et al 1957, Goel et al 1982, Guirgis et al 2015, Ibanez et al 2016, Matago et al 1970 and Sahu et al 2011). The band occurring at $770, 495, 496\text{ cm}^{-1}$ for 3,4-DEP was found for this assignment. The bands at 580 cm^{-1} was reported by Ahmad et al (1990), Bersani et al (2010) and Kumar^b et al (2021) in substituted pyridine. Medhi et al (1990) observed the pair of this mode at 710 cm^{-1} . These assignments also find support from literature value (Braz et al 2021, Goel et al 1982, Guirgis et al 2015, Ibanez et al 2016, Matago et al 1970 and Sahu et al 2011) substituted pyridine and others. The Carbon out of plane bending modes 4, and 16 originate from b_{2g} (703 cm^{-1}) and e_{2u} (404 cm^{-1}) bands of benzene. The vibration 4 is constant while 16 splits up into non totally symmetric parts 16a and 16b. The mode 4 is found in the region $653\text{ to }738\text{ cm}^{-1}$ (Dellish et al 1974, Garoz et al 2019 and Sahu et al 2011) and 735 cm^{-1} and $850/ 865\text{ cm}^{-1}$ in infrared and Raman spectra of both the molecules. The mode 16a and 16b behave like the vibration 6. The mode 16a is sensitive towards orientation of substituent group and depends on charge in electronic structure. It is also affected strongly by ethyl group whereas the component 16b is located in small frequency range around 405 cm^{-1} .

In view of the above the mode 16a and 16b arise at $435/445\text{ cm}^{-1}$ and 390 cm^{-1} for 3,4-DEP in infrared and Raman spectra. The work is in close agreement with the work of Green et al (1971), Medhi et al (1990) and others (Braz et al 2021, Dellish et al 1974, Garoz et al 2019 and Jeergal et al 1991). The C-H out of plane deformations result from 5, 17 and 11 Vibrational modes of benzene (Bersani et al 2010, Bellamy 1975, Lozic et al 2019 and Varsanyi 1973). These values have been well listed in table-2.

C—X-Vibration:

Peter et al (2019) and Bernstein (1957) assigned a band at 1210 cm^{-1} to $-\text{C}-\text{C}_2\text{H}_5$ stretching mode while Sathyanarayana (1996) and Rao (1963) assigned this mode at $1212, 1175$ and 1210 cm^{-1} in substituted xylenes.

In the present study the bands at $1130/1140\text{ cm}^{-1}$ have been identified at C—C₂H₅ valence oscillation in 3,4-DEP. The C—C₂H₅ out of plane bending mode usually lie near 300 cm^{-1} (Bernstein et al 1957, Braz et al 2021, Dellish et al 1974 and Ibanez et al 2016). In the present case it has been identified at $275/280\text{ cm}^{-1}$ in infrared and Raman spectra of the title molecule respectively. These values are well supported by literature value (Atkins et al 2009, Hubert 2014, Leila et al 2016).

C—C₂H₅ In-plane bending vibrations have been identified for title molecules in their spectra and listed in table 4.7 and supported well by literature (Atkins et al 2009, Bernstein et al 1957, Braz et al 2021, Dellish et al 1974, Garoz et al 2019, Hubert 2014, Ibanez et al 2016, James et al 2006, Leila et al 2016 and Sahu et al 2011).

CH₃—GROUP VIBRATIONS:

The C₂H₅ group gives rise to two types of vibrations.

- (i) The internal vibrations which appear even if the group is an isolated one.
- (ii) The external vibration in which C₂H₅ group does not internally deform but moves as a whole.

First kind of vibration consists of C₂H₅ stretching and deformation modes. The magnitude of frequencies of these modes remains unchanged. The second type of vibrations are twisting or torsional vibrations (For one C₂H₅ group two rocking and one torsional vibration appear).

There will be three C—H stretching vibrations. Two will be symmetric while one will be asymmetric. The two asymmetric vibrations have nearly same magnitude and appear with varying intensity in the region $3000\text{--}2900\text{ cm}^{-1}$ (Bersani et al 2010 and Colthup et al 1964). One of such mode, involves the outward motion of two hydrogen atom and inward motion of third hydrogen atom. In the symmetric stretching vibrations of all the three hydrogen atoms move away from the carbon atom lying in the region $2900\text{--}2850\text{ cm}^{-1}$ (Varsanyi 1973) and appear prominently in the infrared spectrum of ethyl substituted benzenes. Atkins et al (2009) and Bellamy (1975) analyzed the spectra of large hydrocarbon containing the ethyl group and revealed that in all such molecules two bands appearing around 2962 and 2872 cm^{-1} represent the asymmetric and symmetric stretching vibrations of ethyl group. In the present study the asymmetric stretching vibrations for the

molecule 3,4-DEP molecules have been assigned in table 2 in their infrared and Raman spectra. These values are in accordance with the literature (Atkins et al 2009, Braz et al 2021, Dellish et al 1974, James et al 2006, Leila et al 2016 and Sahu et al 2011).

Each ethyl group has three C—H deformation, modes also, one of these is again symmetric while the other two are asymmetric. The symmetric deformation is also called umbrella vibration in which all the three hydrogen atoms move towards each other Simultaneously and the electronegativity of the atom to which the C₂H₅ group is attached. This mode lies in the region 1450–1250 cm⁻¹ (James et al 2006 and Leila et al 2016). The two asymmetric deformation mode have nearly the same magnitude. One of these correspond to each other while other is moving away from both. This mode is found less sensitive to the electronegativity of the attached atoms and lie in the region 1475–1400 cm⁻¹.

In the present study bands obtained at 1465, 1445 cm⁻¹ in 3,4-DEP in their infrared and Raman spectra have been assigned to asymmetric deformation mode. The symmetric deformation mode has been identified and assigned at 1381/1387 cm⁻¹ for 3,4-DEP in their respective spectral regions in IR/Raman spectra. These modes seem to be correlated with C—C-Stretching vibrations. These results are in agreement with the literature (Bernstein et al 1957, Braz et al 2021, Dellish et al 1974, Garoz et al 2019, Hubert 2014, Ibanez et al 2016, James et al 2006, Leila et al 2016 and Sahu et al 2011).

For one ethyl group attached to the ring two rocking modes are expected. The magnitude changes due to interaction with skull stretching modes. Wilmshurst and Bernstein et al (1957) and Leila et al (2016) assigned this mode at 1040/1048 cm⁻¹ in heterocyclic compounds. Some workers (Bernstein et al 1957, Braz et al 2021, Dellish et al 1974 and Garoz et al 2019) assigned this mode at 1041 and 1091 cm⁻¹ in substituted toluene & others. Thus, three infrared bands at 1046 cm⁻¹ of 3,4-DEP have been assigned to C₂H₅ rocking vibrations. Some workers (Braz et al 2021, Hubert 2014 and Ibanez et al 2016) have assigned the C₂H₅ torsional mode between 177-240 cm⁻¹ while others (Bersani et al 2010 and Sahu et al 2011) have assigned this mode around 280 cm⁻¹. In the title molecule 3,5-DEP the torsional variations have been assigned at 205/210 cm⁻¹. These all values find good support from the literature (Atkins et al 2009, Bernstein et al 1957, Braz et al

2021, Dellish et al 1974, Garoz et al 2019, Hubert 2014, Ibanez et al 2016, James et al 2006, Leila et al 2016 and Sahu et al 2011).

REFERENCES

- 1) Abdulaziz A.A.S., Jaan L. (2007). "Ab initio and DFT calculations for the structure and vibrational spectra of cyclopentene and its isotopomers" J. Mol. Struct. **830**, 46–57.
- 2) Ahmad S. and Verma P.K.(1990). "Laser Raman, infrared and far infrared spectra of 3,4,5-trimethoxybenzaldehyde" Indian Journal of Physics, **64B(1)**, 50.
- 3) Andersen N.H., Nielsen C.J., Klæboe P., Guirgis G.A., Overby J.S., Askarian S.M. (2014). "Infrared and Raman spectra, DFT-calculations and spectral assignments of 1,3,5- trisila cyclo hexane", J. Mol. Struct, **1076**, 419.
- 4) Atkins P.W., de Paula J. (2009). "Elements of Physical Chemistry" (5th ed.). Oxford: Oxford U.P. 459.
- 5) Bellamy L.J. (1975)."The Infrared Spectra of Complex molecules", Chapman and Hall, London.
- 6) Bernstein and Wilmshurt (1957), Can J. Chem. 35, 1183.
- 7) Bersani D. and Lottici P.P. (2010). "Applications of Raman spectroscopy to gemology", Anal Bioanal Chem., **397(7)**,2631.
- 8) Braz A., Silva C.S., Peixoto A.C., Pimentel M.F., Pereira G., Braga P.C.C.S., Martini A.L. and Alcantara T.L.F. (2021). "Preliminary study on the identification of synthetic cathinones in street seized samples by Raman spectroscopy and chemometrics", J of Raman Spectroscopy, **2**,6074.
- 9) Carmona, Molina and Escobar. (1993). "Studies on aminopyridines in aqueous solution by laser Raman spectroscopy", Spectrochim Acta, **49(A)**,1.
- 10) Chand S., Kumar S. and Kumar V.(2021)."IR spectra of substituted bromo-hydroxy pyridine", Wutan Hutan Jisuan Jishu Journal, **XVII (II)**.357.
- 11) Colthup N.B., Daly L.H. and Wiberlay S.E.(1975). "Introduction of Infrared and Raman Spectroscopy", Academic Press, New York.
- 12) Deep G., Kumar V. and Jetley U.K. (2013). "Infrared absorption spectra of 5-bromo-2,3-dihydroxy pyridine", J. of Ind. Res., **1(4)** 84-88. (ISSN: 2321-4155)

- 13) Dellish, Fateley and Bentley (1974). "Characteristic Raman frequencies of organic compounds", John Wiley and Sons, New York.
- 14) Demtroder W.(2003). "Laser Spectroscopy", 3rd Ed. Springer.
- 15) Dyer J.R. (1965). "Application of Absorption Spectroscopy of Organic Compounds", Printice Hall Inc., Englewood Chiffs, USA.
- 16) Garoz R.J., Perales R., Juan V., Heras A., Colina A.(2019). "Spectro-electrochemical Sensing: Current Trends and Challenges". *Electro-analysis*. **31** (7): 1254. ISSN 1040-0397.
- 17) Goel RK and Agarwal ML (1982), *Acta Physica Polonica* **61A**, 1017.
- 18) Govindarajan M., Periyandy S., Carthigayen K. (2012). "FT-IR and FT-Raman spectra, thermo dynamical behavior, HOMO and LUMO, UV, NLO properties, computed frequency estimation analysis and electronic structure calculations on α -bromotoluene", *Spectrochim Acta*, **97**, 411.
- 19) Govindarasu K. and Kavitha E. (2014). "Synthesis, structural, spectral (FTIR, FT-Raman, UV, NMR), NBO and first order hyper polarizability analysis of N-phenyl benzene sulfonamide by density functional theory". *Spectrochim Acta A*, **133**, 417.
- 20) Green J.H.S., Harrison D.J. and Kynaston W. (1971). "Vibrational spectra of benzene derivatives—XV: The dimethylphenols, 2,6-, 2,5- and 3,4-dichloro-phenol", *Spectrochim Acta*, **27**, 2199.
- 21) Guirgis G.A., Dukes H.W., Wyatt J.K., Nielsen C.J., Horn A., Aleksa V. and Klaeboe P. (2015). "Vibrational spectra, quantum chemical calculations and spectral assignments of 1,1-difluoro-1-silacyclohexane", *Spectrochim. Acta A* **136**, 51.
- 22) Gupta S.P., Gupta C., Sharma S. and Goel R.K. (1986), *Indian J Pure & Appl Phys*, **24**, 111.
- 23) Handschumacher RE and Welch AD(1960), "The Nucleic Acids". (Academic press, New York).
- 24) Hernandez C.N., Garcia M.B.G., Santos D.H., Heras M.A., Colina A., Fanjul B. and Pablo (2016). "Aqueous UV–VIS spectroelectrochemical study of the voltammetric reduction of graphene oxide on screen-printed carbon electrodes". *Electrochemistry Communications*. **64**: 65.
- 25) Hubert M.P.(2014). "Microspectroscopy in the Mid-Infrared". *Encyclopedia of Analytical Chemistry*, 1.

- 26) Ibanez D., Garoz R., Jesus, Heras, Aranzazu, Colina and Alvaro (2016). "Simultaneous UV–Visible Absorption and Raman Spectroelectrochemistry". *Analytical Chemistry*. **88** (16): 8210. ISSN 0003-2700.
- 27) James, Amal R.A., Reghunathan, R.V, Jayakumar, S., and Habert J.I. (2006). "Structural conformation and vibrational spectroscopic studies of 2,6-bis (p-N,N-dimethyl benzylidene) cyclo hexanone using density functional theory" *J. Ram. Spect.* **37**, 1381-1392.
- 28) Jeergal P.R., Katti N.R., Khannavar M.K.A., Rao R. and Shashidhar M.A.(1991). *Indian J Pure Appl Phys*, **29(II)**, 752.
- 29) John X.R. and Gobinath E.(2012). "Experimental and theoretical spectroscopic studies, HOMO–LUMO, NBO and NLMO analysis of 3,5-dibromo-2,6-dimethoxy pyridine", *Spectrochimica Acta Part A*, **97**,215.
- 30) Kumar V., Kumar A. and Kumar M. (2021). "Laser Raman and Infrared spectra of amino hydroxy Pyrimidine", *Wutan Huatan Jisuan Jishu Journal*, **XVII (I)**,710.
- 31) Leila D., Hassan V. and Esmail V. (2016). "Synthesis, characterization and DFT studies of diethyl 4-hydroxy-6-nitro-4H-chromene-2,3-dicarboxylate", *Journal of Molecular Structure*, **1105**, 118-127.
- 32) Leon L. and Mozo J.D. (2018). "Designing spectroelectrochemical cells: A review". *TrAC Trends in Analytical Chemistry*. **102**: 147–169.
- 33) Lozic and Dejan.(2019). "Introduction to Raman Microscopy/Spectroscopy." *Application of Molecular Methods and Raman Microscopy/Spectroscopy in Agricultural Sciences and Food Technology*, edited by Dejan Lazic et al., Ubiquity Press, pp. 143–50.
- 34) Martin G.T.(1951), "Biological Antagonism, "(Blakiston, New York).
- 35) Mataga N. and Kubata T.(1970). "Molecular Interactions and Electronic Spectra" (Marcel Dekker Inc., New York).
- 36) Medhi K.C. and Medhi R.N. (1990). "The electronic spectra and excited state dipole moment of 2-fluoropyridine", *Spectrochim. Acta*, **46(8)**,1169.
- 37) Mortimer R.J. (2017). "Spectroelectrochemistry Applications", *Encyclopedia of Spectroscopy and Spectrometry*, Elsevier, pp. 160–171, ISBN 978-0-12-803224-4, retrieved 2020-06-15
- 38) Murrell J.N. (1971). "The Theory of the Electronic Spectra of Organic Molecules", Chapman and Hall, London.

- 39) Peter A., Paula J.D., Keeler J. and Atkins (2019). "Physical Chemistry 11e: Volume 3: Molecular Thermodynamics and Kinetics". Oxford University Press. p. 89. ISBN 978-0-19-882336-0.
- 40) Rao C.N.R. (1963). "Chemical Applications of Infrared Spectroscopy", Academic Press, New York.
- 41) Ruiz G., Jesus, Rondon P., Victor J., Aranzazu H., Colina and Alvaro (2019). "Spectro-electrochemical Sensing: Current Trends and Challenges". *Electroanalysis*. **31** (7): 1254–1278.
- 42) Sahu R.C., Patel R.K. and Ray B.C.(2011). "Removal of hydrogen sulfide using red mud at ambient conditions". *Fuel Processing Technology*. **92**,(8).
- 43) Sathyanarayana D.N. (1996). "Vibrational Spectroscopy", New Age International (P) Ltd., New Delhi.
- 44) Singh V., Kumar V., Yadav M.K., Seema and Yadav B.S.(1996). "Vibrational spectra of 2,4-hydroxy-6-methyl pyrimidine", *Oriental Journal of Chemistry*, **12**(3),267.
- 45) Suzuki H. (1967). "Electronic Absorption Spectra and Geometry of Organic Molecules", (Academic Press, New York).
- 46) Sverdlov, Kovner and Krainor (1974). "Vibrational spectra of polyatomic molecule", J. Willey and Sons London.
- 47) Varsanyi G.(1973). "Assignment for Vibrational spectra of seven hundred benzene derivatives", Vol 1-2 Academic Kiaclo, Budapest.
- 48) Yadav B.S., Singh V., Kumar V., Seema and Singh J. (1997). "Thermodynamic functions of some biological molecules", *J of Institutions of Chemists (India)*,**69**(1),5.
- 49) Yadav B.S., Kumar V. and Yadav M.K. (1998). "Vibrational spectra, thermodynamic parameters and fungicidal activity of 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazone", *Indian Journal of Pure and Applied Physics*, **36**,557.
- 50) Yadav B.S., Kumar V., Singh V. and Semwal B.S. (1999). "Thermodynamic parameters of antifungal 3,4,5-trimethoxy benzaldehyde thiosemicarbazone", *Indian Journal of Pure and Applied Physics*, **37**,34.
- 51) Zoski and Cynthia G. (2007). "Handbook of Electrochemistry"(1st ed.). Amsterdam: Elsevier. ISBN 978-0-08-046930-0