Fourier transform infrared and Fourier transform Raman spectra and normal coordinate analysis of ethyleneimine

S Gunasekaran[1] & D Uthra[2]

[1]Spectrophysics Research Laboratory, Pachaiyappa's College, Chennai 600 030
[2]Department of Physics, D G Vaishnav College, Chennai 600 106
E-mail : uthra_13@yahoo.com

Ethyleneimine (C_2H_5N) also known as dimethyleneimine, azirane, aziridine is a toxic chemical that finds variety of uses in industries. It is volatile, highly reactive, corrosive and is considered as a potential carcinogen, but widely used in the paper, lacquer and photography industries. This molecule has eighteen fundamental modes of vibration under C_S point group distributed as $\Gamma_{vib} = 10A' + 8A''$. In the present paper, normal coordinate analysis has been carried out for the molecule ethyleneimine with an orthonormal set of symmetry coordinates by using Wilson's F-G matrix method. A satisfactory vibrational band assignment has been made in terms of normal modes of vibration using Fourier transform infrared and Fourier transform Raman spectroscopy. A reasonable set of potential constants was evaluated and found to be in good agreement with literature. The potential energy distribution has been evaluated which confirms the frequency assignment done, thus, providing a strong support to the present work.

Keywords: Ethyleneimine, Fourier transform Infrared and Raman spectra, Normal coordinate analysis, Potential energy distribution

1 Introduction

Ethyleneimine is a toxic chemical that finds a wide usage in petroleum refining, photographic, textile, paper and cosmetic industries. It is used in polyester resins, as a coating for polyolefin films and as a flocculant in waste water and potable water treatment. Its toxicity on animals and human beings has been studied as it causes burns, acute toxic pneumonitis and respiratory irritation and is regulated as a potential occupational carcinogen[1] and a secondary hepatotoxin. Due to exposure, signs of irritation of eyes and nose, delayed onset of pulmonary oedema and renal tubular damage with proteinuria, hematuria, and elevated blood urea nitrogen were noticed. In some exposed animals, a decrease in the white blood cell count and a depression of all blood elements have also been observed. Carpenter *et al*[2,3]. have carried out studies on the toxic concentration and exposure period upon guinea pigs and rats. The toxic effect on few other animal species have been reported by Izmerov *et al*[4,5]. Gresham and West [6] have discussed the injury and repair of the tracheobronchial cartilage due to accidental exposure to ethyleneimine[6] in human beings. With a wide spread usage in industries and a high toxicity , the title molecule compels a systematic study and hence, the current work is a detailed vibrational analysis on the same. The molecular formula of ethyleneimine is C_2H_5N with a molecular mass of 43.07 g/mol. This three member heterocyclic ring combines with sulphurous acid to form taurine which occurs in human bile[7]. The present investigation is an attempt to provide A satisfactory vibrational analysis of ethyleneimine has been carried out through FTIR and FT Raman spectroscopy. To check whether the chosen set of vibrational frequencies contributes maximum to the potential energy associated with the normal coordinates of the molecule, the potential energy distribution have been evaluated.

2 Experimental Details

The pure sample of ethyleneimine was procured from Sigma-Aldrich Company, USA and used for spectral recording as such without any further purification. The FTIR spectrum of the compound is recorded in the region 4000-400cm^{-1} with ABB BOMEM series spectrophotometer with a resolution of 4cm^{-1} by KBr pellet technique at CEEAL Analytical Lab, Chennai, India. The FT Raman spectrum is recorded in the region 4000-50cm^{-1} using Brucker IFS 66V FTIR spectrophotometer with FRA 106 Raman module equipped with Nd:YAG laser
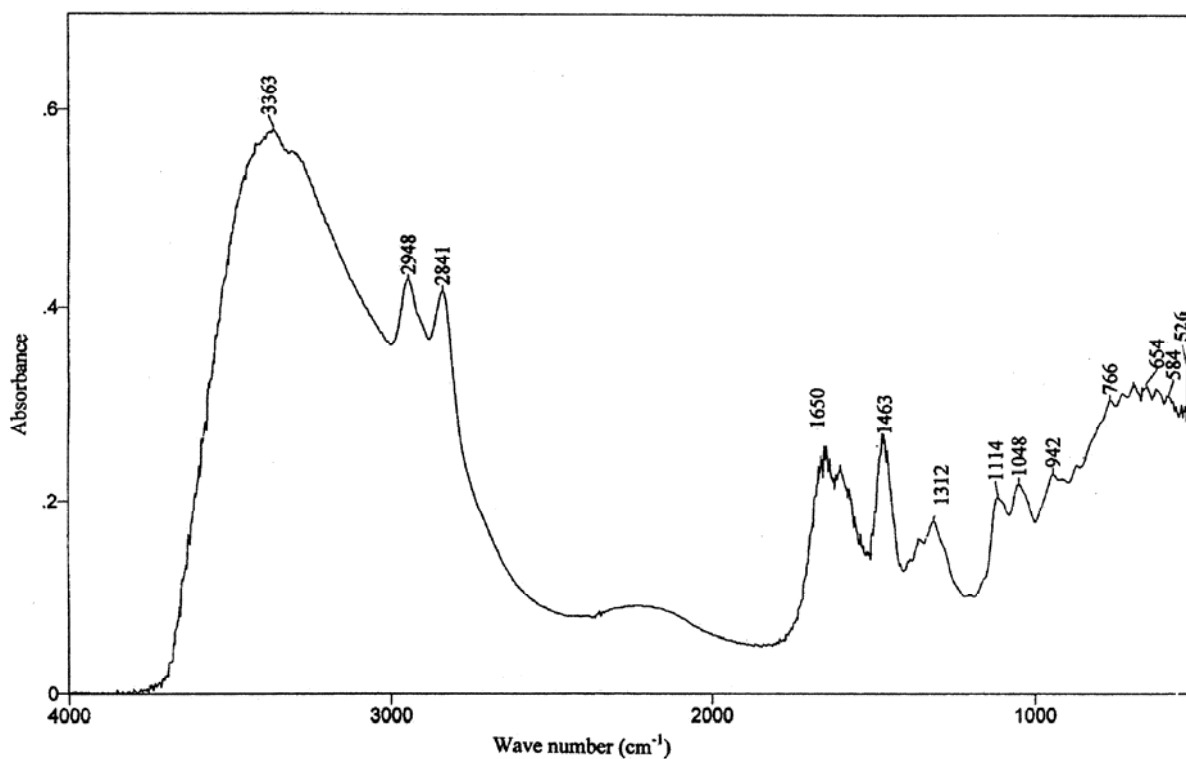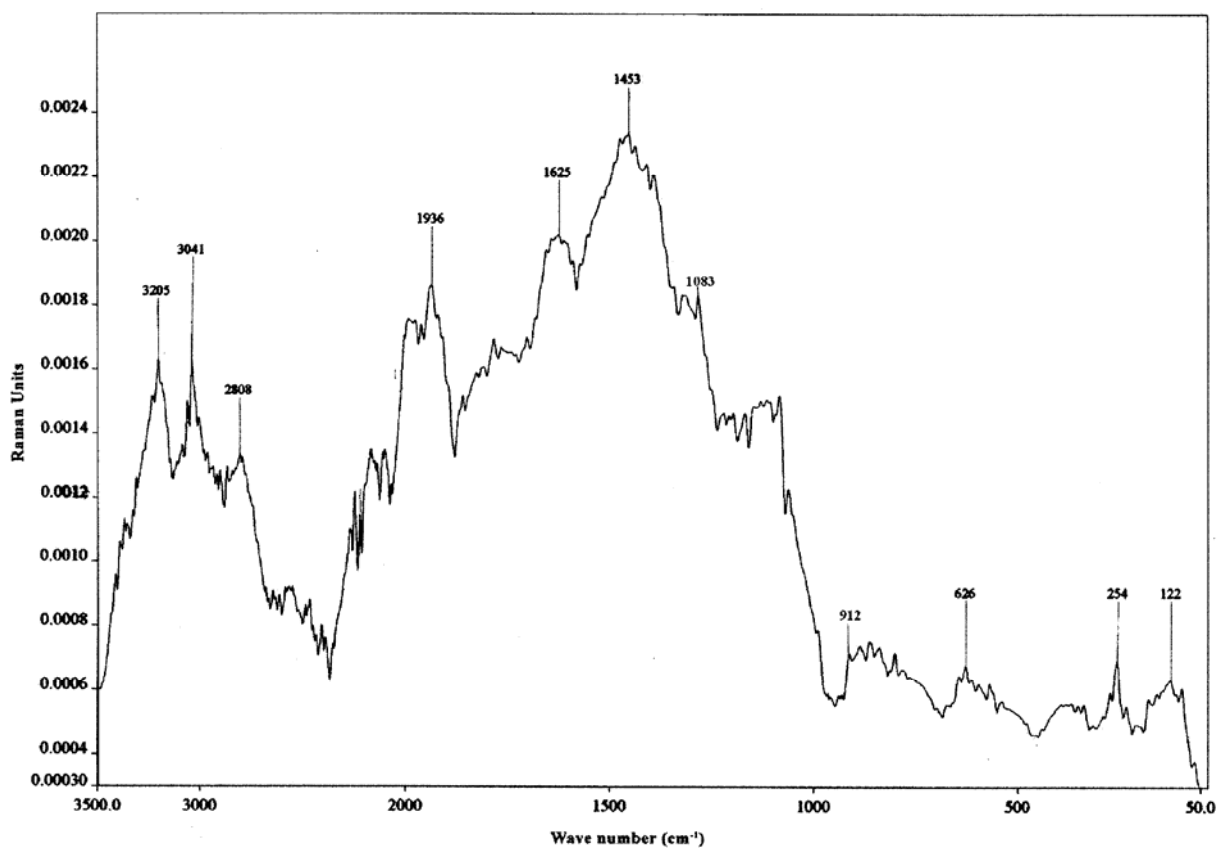
Fig. 1—FTIR spectrum of ethyleneimine

Fig. 2—FT Raman spectrum of ethyleneimine

source operating at 1.06μm line with 200mW power at the Sophisticated Analytical Instrument Facility, IIT, Chennai, India. The frequencies for all sharp bands are accurate to ±1cm⁻¹. Both the spectra have been recorded at room temperature. The FTIR and FT Raman spectra are presented in the Figs 1 and 2 , respectively.

3 Normal Coordinate Analysis

The structure and the orientation of the principal axes of the ethyleneimine molecule are shown in Fig. 3. Ethyleneimine has eighteen fundamental modes of vibration under C_s point group distributed as $\Gamma_{vib} = 10A'$ $+ 8A''$, all are active in both Raman and IR. In the present study, only 14 significant vibrational modes have been considered which are distributed as $\Gamma_{vib} =$ $8A'+6A''$. For the normal coordinate analysis, the molecular parameters have been taken from the Sutton's Table[8] and are presented in Table 1.
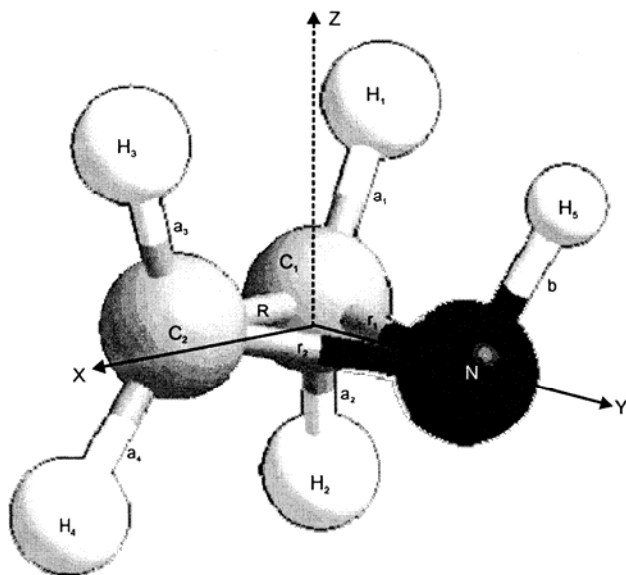

Fig. 3—Structure and the orientation of the principal axes of ethyleneimine molecule

Table 1—Molecular parameters of ethyleneimine

Bond Length (A°)			Bond angle (°)		
Nature	Symbol	Value	Nature	Symbol	Value
N-H₅	b	1.000	C_1-N-C_2	ξ	59.6
C_1-C_2	R	1.480	N-C_1-C_2	τ_1	60.2
N-C_1	r_1	1.488	N-C_2-C_1	τ_2	60.2
N-C_2	r_2	1.488	H_1-C_1 H_2	α_1	116.7
C_1-H_1	a_1	1.083	H_3-C_2-H_4	α_2	116.7
C_1-H_2	a_2	1.083	H_5-N-C_1	γ	112.0
C_2-H_3	a_3	1.083			
C_2-H_4	a_4	1.083			

3.1 Symmetry Coordinates

A set of symmetry coordinates for the ethyleneimine molecule was constructed using the internal coordinates with the aid of projection operators. The symmetry coordinates considered in the present work are given below:

A' species

$$S_1 = \Delta b$$
$$S_2 = \Delta R$$
$$S_3 = 1/\sqrt{2}\ [\Delta r_1 + \Delta r_2]$$
$$S_4 = \Delta \gamma$$
$$S_5 = \Delta \xi$$
$$S_6 = 1/\sqrt{2}\ [\Delta \tau_1 + \Delta \tau_2]$$
$$S_7 = 1/\sqrt{2}\ [\Delta \alpha_1 + \Delta \alpha_2]$$
$$S_8 = 1/2\ [\Delta a_1 + \Delta a_2 + \Delta a_3 + \Delta a_4]$$

A'' species

$$S_9 = 1/\sqrt{2}\ [\Delta r_1 - \Delta r_2]$$
$$S_{10} = 1/\sqrt{2}\ [\Delta \tau_1 - \Delta \tau_2]$$
$$S_{11} = 1/\sqrt{2}\ [\Delta \alpha_1 - \Delta \alpha_2]$$
$$S_{12} = 1/2\ [\Delta a_1 - \Delta a_2 + \Delta a_3 - \Delta a_4]$$
$$S_{13} = 1/2\ [\Delta a_1 + \Delta a_2 - \Delta a_3 - \Delta a_4]$$
$$S_{14} = 1/2\ [\ \Delta a_1 - \Delta a_2 - \Delta a_3 + \Delta a_4]$$

where Δs represent the changes in corresponding bond lengths and bond angles.

3.2 Vibrational band analysis

The vibrational band assignment of ethyleneimine has been made based on the position, shape and relative intensity of the recorded spectra and in correlation with the vibrational bands of structurally related molecules. The vibrational band assignment of ethyleneimine derived from the FTIR and FT Raman spectra recorded is presented in Table 2.

C-H stretching—In most hydrocarbons, the CH_2 asymmetric stretch occurs near 2930 cm⁻¹ and the symmetric stretch near 2850cm⁻¹. In cyclic rings, there is a steady increase in CH_2 asymmetric stretching frequency[9] from the normal 6 membered ring near 2930cm⁻¹ to the strained 3-membered ring near 3080cm⁻¹. In general, bands due to alkene C-H stretching occur above 3000cm⁻¹. In the present study, the strong band occurring at 2948cm⁻¹ in the FTIR spectrum is assigned to asymmetric stretching (v_{12}) of CH_2 group. Moreover, the very strong bands at 2947cm⁻¹, 3041cm⁻¹(v_{13}) and 3205cm⁻¹ (v_{14}) in the FT Raman spectrum of the present work are due to the

Table 2—Vibrational band assignments, force constants and potential energy distribution of ethyleneimine

Fundamental frequencies	Frequency (cm^{-1})		Band assignment	Force constant ($\times 10^2$ N/m)	PED %
	FTIR	FT Raman			
A' species					
v_1	3363 (vs)	3300 (s)	NH stretching	6.0609	97
v_2	1048 (m)	1083 (s)	CC stretching	4.5132	98
v_3	942 (m)	912 (w)	CN symmetric stretching	4.9103	98
v_4	1650 (m)	1625 (vs)	CNH deformation	0.5461	85
v_5	584 (m)	563 (w)	CNC deformation	0.4194	60
v_6	526 (m)	538 (w)	NCC symmetric bending	0.4493	31
v_7	1312 (w)	1375 (vs)	CH_2 symmetric bending	0.5351	89
v_8	2841 (s)	2808 (s)	CH_2 symmetric stretching	4.6962	98
A'' species					
v_9	1114 (m)	1163 (vs)	CN asymmetric stretching	5.6011	83
v_{10}	654 (w)	626 (m)	NCC asymmetric bending	0.9426	34
v_{11}	1463 (m)	1453 (vs)	CH_2 asymmetric bending	0.5421	78
v_{12}	2948 (s)	2947 (s)	CH_2 asymmetric stretching	5.0416	98
v_{13}	—	3041 (vs)	CH_2 asymmetric stretching	4.7489	89
v_{14}	—	3205 (vs)	CH_2 asymmetric stretching	5.0413	93

vs – very strong; s – strong; m– medium; w – weak

same vibration. In ethers, alcohols and amines, the absorption of the symmetric stretch of the CH_2 group usually has the same intensity as the asymmetric. In secondary and tertiary amines (but not in amides), the symmetrical CH_2 stretching frequency of the CH_2 group next to the nitrogen atom, in addition to being intensified, becomes lower in frequency[9], appearing near 2800cm^{-1}. In these lines, the strong band present at 2841cm^{-1} in the FTIR vibration (v_8) can be assigned to the symmetric stretching of the CH_2 group of ethyleneimine, which is confirmed by the presence of a band at 2808cm^{-1} in the FT Raman spectrum.

C-N stretching—The medium to weak absorption bands for the C-N linkages in amines appear in the 1200–1020cm^{-1} region. It is a difficult task to identify the C-N stretching in the side chain from other vibrations. In the present study, the symmetric stretching vibration (v_3) is found at 942cm^{-1} peak in the FTIR spectrum and at 912cm^{-1} in the FT Raman spectrum. The band appearing at 1114cm^{-1} in the FTIR spectrum is assigned to C-N asymmetric stretching mode of vibration (v_9). This mode of vibration is traced at 1163cm^{-1} in the FT Raman spectrum.

N-H stretching—Heteroaromatics containing NH group show NH stretching absorption in the region of 3500–3220cm^{-1}. The NH bond, like OH, can participate in hydrogen bonding, although the lower electro negativity of nitrogen weakens the effect. The position of absorption within this general region depends upon the degree of hydrogen bonding, and hence, upon the physical state of the sample or polarity of the solvent[10]. NH stretching vibration may be used to distinguish imines from amines, by converting the sample into its hydrohalide and examine their corresponding spectra. The nature and position of the NH stretching bands clearly show the difference between the imines and amines[11]. The molecule under study possesses only one NH group and hence, only one NH stretching vibration is expected which should be present in the 3400-3300cm^{-1} region. Hence, the band observed at 3363cm^{-1} in the FTIR spectrum is assigned to NH stretching vibration ($_1$) of the molecule. In case of Raman spectrum, the peak due this vibration can be located at 3300cm^{-1}.

C-C stretching—Of the skeletal vibrations, the C-C stretching absorptions occur in the region 1260-700 cm^{-1} and are normally weak and of little use in assignments[11]. Gunasekaran *et al*. have reported 1061cm^{-1} and 1032cm^{-1} bands due to C-C stretching of isoniazid[12] and allopurinol[13] molecules, respectively. Based on this, in the present study, the band at 1048cm^{-1} in FTIR spectrum is assigned to C-C stretching ($_2$) of the molecule under study. The strong band at 1083cm^{-1} in the FT Raman spectrum could be attributed to C-C stretching vibration.

Deformation vibrations—The deformation of CH_2 in most hydrocarbons occurs near 1465cm^{-1}. The asymmetric bending of CH_2 group in epoxide[11] has been reported at 1500cm^{-1}. The asymmetrical deformation of

methylene group gives rise to absorption bands close to $1465cm^{-1}$ and the symmetric deformations have been reported[15] in the region $1385-1370cm^{-1}$.The peak present at $1463cm^{-1}$ in the FTIR spectrum is hence, assigned to the CH_2 asymmetric bending vibration ($_{11}$), while the counterpart of this peak in FT Raman spectrum can be seen at $1453cm^{-1}$. The symmetric deformation ($_7$) of the CH_2 group of the title molecule is present at $1312cm^{-1}$ in FTIR spectrum and $1375cm^{-1}$ in FT Raman spectrum. In the present paper , the band observed at $1650cm^{-1}$ in the FTIR spectrum and at $1625cm^{-1}$ in the FT Raman spectrum is due to CNH deformation ($_4$).While, those present at 654 and $526cm^{-1}$ are assigned to NCC asymmetric ($_{10}$) and symmetric ($_6$) bending vibrations of the ethyleneimine molecule. The corresponding frequencies in the FT Raman spectrum can be traced at $626cm^{-1}$ and $538cm^{-1}$, respectively, which are in line with the reported values[14]. The CNC deformation ($_5$) gives rise to a medium intensity peak at $584cm^{-1}$ in the FTIR spectrum and a weak peak at $563 cm^{-1}$ in the Raman spectrum.

3.3 Method of kinetic constants and potential energy distribution

The vibrational frequencies are related to masses of the atoms, the bond angles and bond lengths, and most particularly the force constants of the individual bonds and inter bond angles[15]. Based on this idea, Wilson's method of F and G matrices has been adopted for the molecular structural elucidation[16-18]. All of the required relations are combined in the master equation $|FG–\lambda E| \equiv 0$, in which F, G and E are matrices. F matrix brings the potential energies and G matrix brings the kinetic energies of vibration into the secular equation. E is a unit matrix and λ brings the frequency ν into the equation by the relation $\lambda = 4\pi^2 C^2 \nu^2$. Once the elements of the F and G matrices are known for the molecule, the determinant equation may be written out explicitly. With the knowledge of the transformation matrix L, related to G by $LL^T = G$, the secular equation can be solved, yielding the elements of the force constant matrix F. The method of kinetic constants relates the off–diagonal elements of the F matrix to its diagonal elements through the relation, $F_{ij} / F_{jj} = K_{ij} / K_{jj}$ ($i<j$; $i=j=1, 2, 3....$). In the present study, only the diagonal force constants ($i = j$) have been calculated by taking initial set of force constants from related molecules and subsequently refining them by using successive approximation technique. The frequency assignment is then verified by evaluating the potential energy distribution using

the relation $PED = F_{ij}L^2_{ij}/\lambda_j$. Here, PED is the contribution of the frequency ν_j to the potential energy and F_{ij} is the potential constant pertaining to that vibration and L_{ij} is the corresponding linear transformation matrix element.

4 Results and Discussion

Normal coordinate analysis of ethyleneimine has been successfully carried out by applying Wilson's F-G matrix method. The normal modes of vibration, calculated force constants and the corresponding PED values are presented in the Table 2. The evaluated force constant for NH stretching vibration is $6.0609x10^2$ N/m as expected and it contributes PED value of 97%. The force constants obtained for CH asymmetric stretching vibrations are found to be around $5x10^2$ N/m and they contribute PED value of more than 88%. While their symmetric counterpart contributes to a PED value of 98% with the force constant equal to $4.6962x10^2$ N/m, as reported in literature[14]. The asymmetric and symmetric CN stretching vibrations of ethyleneimine contribute to PED around 83% and 98% , respectively and have a force constant of $5.6011 x10^2$ N/m and $4.9103x10^2$ N/m, which coincides with cited values[19,20]. The stretching vibration of C-C contributes to 98% of PED with a calculated force constant of $4.132 x 10^2$ N/m. In addition to above stretching vibrations, the force constants for bending vibrations have also been evaluated and are found to be in good agreement with the reported values[16-18].

5 Conclusion

A complete assignment of vibrational frequencies has been made for the ethyleneimine molecule using FTIR and FT Raman spectra. A systematic set of symmetry coordinates has been constructed and the force constants have been evaluated. The calculated potential energy distribution of the fundamental vibrations confirms the frequency assignment of the molecule.

References

1 *Documentation for Immediately Dangerous To Life or Health Concentrations* of National Institute for Occupational Safety and Health, USA(2004).

2   Carpenter C P, Smyth H F Jr & Shaffer C B, *J Industr Hyg Toxicol*, *30 (1948)* 2.

3   Carpenter C P, Smyth H F Jr & Pozzani U C, *J Industr Hyg Toxicol 31 (1949)* 343.

4   Patty F A, *Industrial hygiene and toxicology* 2nd rev ed Vol II (Interscience, New York), 1963.

5   Izmerov N F, Sanotsky I V & Sidorov K K, *Toxicometric parameters of industrial toxic chemicals under single exposure,* Moscow, Russia: Centre of International Projects, GKNT (1982) 67.

6   Gresham G A and West I E, *J Clin Path,* 28 (1978) 564.

7   Finar I L, *Organic Chemistry,* Vol1, (Pearson Education Asia), 2003.

8   Sutton L E, *Table of Inter atomic Bond Distances and Bond Angles in Molecules and Ions*, (Chemical Society, London), 1956.

9   Colthup N B, Daly L H and Stephen E Wiberly, *Introduction to Infrared and Raman Spectroscopy*, (Academic Press, New York), 1964.

10 Silverstein R M, Clayton Bassler G & Morill T C, *Spectrometric identification of organic compounds*, 4ed, (John Wiley, New York), 1981.

11 Socrates G, *Infrared characteristic group frequencies*, (John Wiley, New York), 1980.

12 Gunasekaran S, Thilak Kumar, Ponnusamy S, Edward & Pushparaj S, *Indian J Phys*, 79(2) (2005) 171.

13 Gunasekaran S, Ponnambalam U & Muthu S, *Acta Ciencia Indica*, XXX (1) (2004) 1015.

14 Gunasekaran S & Abitha P, *Indian J Pure & Appl Phys*, 43 (2005) 329.

15 Cotton F A, *Chemical applications of group theory*, (John Wiley, New York) 1963.

16 Gunasekaran S, Seshadri S & Muthu S, *Indian J Pure & Appl Phys*, 44 (2006) 360.

17 Gunasekaran S & Ponnusamy S, *Indian J Pure & Appl Phys*, 43 (2005) 838.

18 Nallasamy P & Mohan S, *Indian J Pure & Appl Phys*, 43 (2005) 821.

19 Wilson E B, Decius J C & Cross P C*, Molecular Vibrations*, (Dover Publications Inc, New York).

20 Arivazhagan M & Mohan S, *Indian J Pure & Appl Phys*, 43 (2005) 329.