OPTOELECTRONİCS AND ADVANCED MATERİALS – RAPID COMMUNICATIONS Vol. 6, No. 1-2, January-February 2012, p. 205 - 210

Spectra and normal coordinate analysis of poly vinyl acetate

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Fourier transform infrared and Raman spectra ofpoly vinyl acetate and its deuterated derivative were recorded and observed frequencies were assigned to various mode of vibration in terms of fundamentals and combinations by assuming Cs point group symmetry. Anormal coordinate analysis was also carried out using simple valence force field. Acomplete vibrational analysis is presented here for these molecule and results are briefly discussed.

(Received December 2, 2011; accepted February 20, 2012)

Keywords: FTIR spectra, FT-Raman spectra, Poly Vinyl Acetate, PED Vibrations

1. Introduction

Poly Vinyl Acetate (PVAc) is an important polymer, exhibiting piezoelectric, pyroelectric and ferroelectric properties [1]. The typical advantages of PVAc are flexibility, formability and low density. X-ray diffraction studies identified four different polymorphs for PVAc [2]. It was revealed by IR and XRD studies that the PVAc homopolymer predominantly consists of form II crystalline structure. The most common form PVAc is normally obtained by crystallization from the melt at moderate or high super cooling. The structure of the chain is complicated by abnormal addition such as head-to-head monomer to a small extent in polymerization [3].

Polyvinyl acetate (PVA or PVAc) is a rubbery synthetic polymer. It is prepared by polymerization of vinyl acetate monomer, also referred to as VAM. Partial or complete hydrolysis of the polymer is used to prepare polyvinyl alcohol. Hydroylized alcohol product is typically in the 87% to 99% range (converted PVA). It was discovered in Germany by Dr. Fritz Klatte in 1912.

As an emulsion in water, PVA is sold as an adhesive for porous materials, particularly wood, paper, and cloth. It is the most commonly used wood glue, both as "white glue" and the yellow "carpenter's glue." PVA is widely used in bookbinding and book arts due to its flexibility, and because it is non-acidic, unlike many other polymers.

PVA is a common copolymer with more expensive acrylics, used extensively in paper, paint and industrial coatings, referred to as vinyl acrylics. It can also be used to protect cheese from fungi and humidity [citation needed]. It is slowly attacked by alkali, forming acetic acid as a hydrolysis product. Boron compounds like boric acid or borax will form tackifying precipitates by causing the polymer to cross-link. PVA is also commonly recommended for use in making leather handcrafted works and papier-mache.

PVAc is used in the manufacture of electronic devices - dielectrics to transductors. The most important industrial application of PVAc are long lasting architectural metal finishes [4]. These finishes are applied in a wide range of colours on exterior wall panels, roofing shingles or aluminium extrusions used on industrial, commercial and residential buildings. In computer back panels, PVAc is used as a primary insulator on computer hook-up wire. PVAc is also used in fluid handling systems that include solid and lined pipes and fittings, valves and pumps. PVAc filters and fluid handling systems are used by the chemical and food industry since PVAc meets high purity requirements.

Recently, concern about human health as well as the environment has been increasing. Poly(vinyl chloride) flooring which has been used in most Korean houses is currently being replaced by wood flooring materials, especially in new apartments [5]. Engineered flooring, one of the flooring materials, consists of plywood with a thin fancy veneer bonded onto the face of the plywood using urea-formaldehyde (UF) and melamine-formaldehyde (MF) resins as hot-press adhesives. In the case of engineered flooring, fancy veneer of 0.5 mm thickness consisting of wood such as birch, oak, beach, cherry, or maple is glued onto the plywood of 7.2 mm thickness and pressed at about 160°C. An ultra-violet (UV) curable coating is applied to this fancy veneer [6]. However, the toxicity of wood-based panels bonded with these formaldehyde-based resins could act as an obstacle to their acceptance by the public, due to the formaldehyde emission and the associated possible health hazard which conflicts with the prevailing environmental awareness and concern [7]. Poly(vinyl acetate) (PVAc)-based materials having higher bond strength and better film properties has grown considerably in the past two decades in the adhesive, paint, paper and the textile industries [8]. The PVAc adhesive is commonly known as resin emulsifier or simply as 'white glue'. It is manufactured by polymerizing vinyl acetate monomer and stabilizers with other polymers or co-polymers. Its application is very easy and it does not damage the tools during the cutting process. However, the mechanical resistance of PVAc adhesive decreases with increasing temperature and it loses its bonding capacity above 70°C [9,10]. When the PVAc was added to the MF resin and the blend used to bond plywood and fancy veneer in engineered flooring, the formaldehyde emission was dramatically reduced [5].

For the last two decades, PVAc has been the centre of attention of several publications. Samy et al [11] studied the crystalline forms of PVAc by infrared spectroscopy. They have carried out a normal coordinate analysis for these two forms using Urey-Bradley type force field and interpreted the spectra assuming C_s point group.

Boerio and Koenig [12] reported the Raman spectra of form PVAc and observed some unique bands that are not observed in the IR spectra. They discussed the band assignments by comparing the IR and Raman spectra of form PVAc.

Infrared and Raman spectra of PVAc have been studied extensively by Boerio and Koenig [13], Cessac and Curro [14], Lauchlan and Rabolt [15], Tashiro et al [16] and Armengaud et al [17].

Molecular vibrations of three crystal forms of PVAc have been investigated by Kobayashi et al [18] on the basis of group theoretical considerations and normal coordinate analysis. The infrared and Raman spectra of three crystal form of PVAc have been measured. The assignments of the bands are described using of potential energy distribution obtained from the calculation for a single molecular chain. The effect of the defects involved in the vibrational spectra are also discussed. The normal frequencies have been calculated using valence force field on the basis of C_s point group symmetry.

The Fourier transform infrared spectroscopic study of form PVAc was reported by Bachmann et al [19]. The spectra contained more bands than previously reported work but are not consistent with the available models for the crystal structure. They have also proposed possible models for the crystal structure of the three forms of PVAc.

The results obtained by differential scanning calorimetry (DSC), Fourier transform infrared (FT-IR) and high-resolution solid-state ^{13}C-NMR revealed strong enter-association hydrogen bonds between the hydroxyl groups of the phenolic and the carbonyl groups of the PVAc [20]. In the case of blends of phenolic resin with polymers such as poly(ethylene vinyl acetate) and aliphatic polyester, it was reported that hydrogen bond formation was critical in enhancing the miscibility of the various phenolic blends with modifiers containing ether, carbonyl, or hydroxyl functional groups [21, 22]. Considerable effort has been made to study the miscibility and phase behavior of different polymer blends [23]. Intermolecular interactions are usually considered to be the driving force for miscibility, and their important role in the miscibility of polymer blends has been clearly demonstrated [24].

Mohan et al [25] carried out a normal coordinate analysis for PVAc employing general quadratic valence force field and verified the vibrational assignments. Hsu et al [26] used the FTIR method to study the crystallization behaviour of PVAc from the melt in the presence of a weak electric field. Samy et al. [11] and samy obtained the variation in the crystallinity content of α, β and γ phase of PVAc as a function of temperature using infrared spectroscopy. More recently Kim et al. [27] examined the morphology, crystalline structure and thermal and mechanical and electrical properties of PVAc using FTIR spectra and x-ray diffraction techniques.

To understand the exact mechanism giving rise to electrical effects in PVAc, Barry et al [3] have carried out spectroscopic experiments to measure the microstructural changes at high temperature when the electric field is present.

The PVAc polymers are found to have wide applications but only limited studies have been reported so for [4-8]. Thus in this chapter a complete vibrational analysis is attempted. In the present study the FTIR and FT Raman spectra of the PVAc were recorded and normal coordinate analysis was carried out. Using their results various modes of vibrations and their probable assignment have been discussed.

2. Experimental details

The compound Poly Vinyl Acetate (PVAc) under study was obtained in spectroscopic grade from across organics BVBA/SPRL, Belgium and was used as such for recording the FT-IR and FT-Raman spectra. The FT-IR spectrum of this compound has been recorded in solid phase in the region between 4000 and 400 cm^{-1} using Bruker IFS 66 V spectrometer, with a scanning speed of 30 cm^{-1} min^{-1} of spectral width 2 cm^{-1}. The frequencies for all sharp bands are accurate to ±1 cm^{-1}. The FT-Raman spectrum was also recorded in the same instrument with FRA 106 Raman module equipped with Nd:YAG laser source operating at 1.064 μm line with 200 mW power and spectral resolution is 2 cm^{-1}. The geometrical structure of this molecule is shown in Fig. 1.

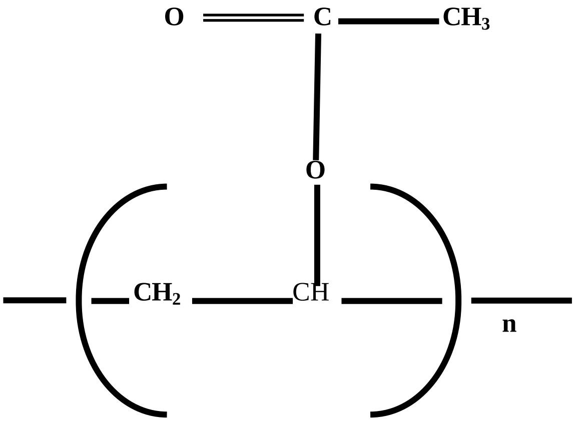

Fig. 1. Molecular structure of poly vinyl acetate.

Normal co-ordinate analysis (NCA)

To present a complete picture of the molecular forces holding the Polyvinyl Acetate (PVAc) on the whole, a normal coordinate analysis was carried out. The normal coordinate analysis also provided support to the assignment of the observed frequencies to the fundamental vibrational modes of the molecule under study. If the C–CH_3 group is considered as point mass and lies in the plane of the molecule, then Polyvinyl Acetae(PVAc) belongs to C_s point group. C_s

symmetry leads to two types of vibrations namely *a'* (in-plane) and *a''* (out-of-plane) and are distributed as

$$\Gamma_{vib}=22a'+10a''$$

All the vibrations are active both in Infrared and Raman. The normal co-ordinate analysis program of Fuhrer et al. [28] was used after suitable modification to calculate the vibrational frequencies and potential energy distribution (PED). This program follows the Wilson's FG matrix method [29] of vibrational analysis in which the normal co-ordinates are defined with respect to a set of molecular coordinates.

Table 1. Observed and calculated frequencies and potential energy distribution for poly vinyl acetate.

Species	**Observed Wave Number & Rel. Intensity**		**Calculated wave Number cm^{-1}**	**Assignments**	**PED %**
	Infrared cm^{-1}	**Raman cm^{-1}**			
	3453 w				
a'	2973 m	2973 m	2970	C-H asym stretching in	$88\nu_{asy}$ CH
a'	2933 ms	2940 vs	2933	C-H asym stretching in	$92\nu_{asy}$ CH
a'	2853 w	2853 w	2856	C-H sym stretching in	$90\nu_{sym}$ CH
a'	2733 vw'		2728	C-H sym stretching in	$89\nu_{sym}$ CH
a'	2546 vw		2537	C-H stretching	95ν CH
a'	2466 vw		2458	C-H stretching	96ν CH
a'	1740 vs	1733 m	1736	C=O stretching	84ν C=O
a''		1493 w	1490	CH asym deformation in CH_3	$88\nu_{asy}$ CH
a''	1433 ms	1443 ms	1442	CH_2 asym deformation	$79\delta_{asy}$ CH
a''	1373 vs	1383 m	1381	CH_3 asym deformation	$69\delta_{asy}$ CH+21β CH
a'		1357 m	1350	CH_2 sym deformation	$74\delta_{sym}$ CH+14β CH
a'		1300 vw	1289	CH_3 sym deformation	$68\delta_{sym}$ CH+28β CH
a'	1240 vs		1233	C-H in plane bending	71β CH+19δ CH
a'	1127 s	1133m	1129	C-O stretching	79ν C-O+11ν CH_3
a'		1087 vw	1081	C-O stretching	84ν C-O+10ν CH_3
a''	1040 s		1032	CH_2 wagging	74ω CH_2+19τ CH_2
a''	1027 vs	1023 m	1026	CH_2 twisting	59τ CH_2+28ω CH_2
a''	947 ms	947 vw	938	CH_3 wagging	68ω CH_3+30τ CH_3
'a''		933 vw	926	CH_3 twisting	60τ CH_3+24ω CH_3
a'		900 vw	891	C-C stretching	78ν C-C+28γ CH
a'		887 m	880	C-C stretching	69ν C-C+14 ν C-O
a'		830 w	820	C-O-C in plane bending	71β C-O-C+19ρ CH_3
a'	800 m	800 w	806	CH_3 rocking	68 ρ CH_3+22β C-O-C
a'		740 vw	734	CH_2 rocking	79 ρ CH_2+11β C-O-C
a'	660 w		656	C=O in plane bending	88β C=O +10β C-CH_3
a''	633 m	633 ms	628	C=O out of plane	69 η C=O +14 η C-CH_3
a'		577 w	568	C-CH_2 in plane bending	74β C-CH_2 +16β CH
a'		477 vw	475	C-CH_2 in plane bending	80β C-CH_3 +10β CH
a''		407 w	401	C-H out of plane bending	66 η CH +19 η C-O
a''		347 vw	337	C-CH_2 out of plane	71 η C-CH_2 +24 η C=O
a''		313 vw	308	C-CH_3 out of plane	68 η C-CH_3 +30 η C=O
a''		160 vw	168	C-C torsion	51 η C-C +22 η C-O

Notation: vs, very strong; s, strong; ms, medium strong; m, medium; w, weak; vw, very weak; ν, stretching; δ, deformation; β, in-plane bending; η, out-of-plane bending; ρ, rocking; ω, wagging; *τ*, twisting

The structural parameters necessary for the compound were taken from Sutton table [30] and-similar molecules. The simple valance force field (SVFF) was adopted for both in-plane and out-of-plane vibrations and the force constants were refined by the damped least square technique keeping few interaction constants fixed throughout the refinement process to obtain a close fit between the obtained and calculated frequencies. This set of force constants is subsequently used to calculate potential energy distribution. The SVFF is shown to be very effective in the normal co-ordinate analysis because of the valance force constants can be transferred between the structurally related molecules which is found very useful in the NCA of similar molecules. The salient feature of simple valence force field calculations has been that it should reproduce the frequencies associated with the skeletal rings as well as the C-CH_3 group within a reasonable limit ±10cm^{-1}) with an acceptable potential energy distribution.

3. Results and discussion

The observed frequencies of Polyvinyl Acetate (PVAc) with their relative intensities and probable assignments are given in the Table 1 along with the calculated frequencies. Potential energy distribution (PED) obtained using the final set of force constants are also given the Table 1. Spectra of hetero aromatic compounds result primarily from the same vibrational modes as observed for aromatics. Assignments have been made on the basis of relative intensities and results of normal co-ordinate analysis. Addition to the above, the assignments of the spectrum has also been made in analogy with the available literature values, The general agreement between the calculated and observed frequencies for both the in-plane and out-of-plane seems to encouraging. The vibrational assignments are discussed the following paragraphs. The vibrations of the molecule under study are generally divided into two groups (1) skeletal vibrations and (2) group vibrations due to the substituent.

Skeletal vibrations

C-H Stretching Vibration

According to Dollish et al [31] all vinyl functional structures have Rama bands between 3000 and 3100cm^{-1} which originate from the ring carbon C-H stretch. It is a established fact that C-H stretch due to Benzene structures lies in the region 3100-3000 cm^{-1} [32, 33]. Using the above facts the IR bands seen at 2546 cm^{-1} and 2466cm^{-1} are assigned to C-H stretching vibrations.

Carbon – Oxygen Stretching

Symmetrical bands such as C=O and C-O manifest themselves by giving the most intense bands in Raman spectra [34-37], thus the very strong infrared band at 1740 cm^{-1} is assigned to C = O stretch [38, 39]. The Raman counter part of this band is at 1733 cm^{-1} but it is medium. The Raman peaks present at 1133 and 1087 cm^{-1} are also assigned to C-O stretching modes. Similarly a band at 1127 cm^{-1} in infrared spectrum is assigned to C-O stretching. All the assignments are in line with pervious work [39, 40].

C-C Stretching

C-C Stretching modes dominate in Raman Spectrum. The intense Raman lines are due to the stretching of CC bonds [34]. In line with the above conclusion, the medium band at 887 cm^{-1} and very weak band at 900 cm^{-1} is assigned to C-C – stretching vibration.

In-plane and out-of-plane bending

C-H in plane bending vibrations

C-H in-plane bending vibrational mode in Poly Vinyl Acetate are assigned to the frequency 1240 cm^{-1} in FT-IR. This assignments are in line with piaggio [41] and Zhang [42]. The C-H deformation mode are weak in Raman spectra of polymers. The weak Raman band at 1493 cm^{-1} are assigned to C-H deformation mode.

C-H out-of-plane vibrations

Proposing the assignment become cumbersome in the low frequency region as the infrared and Raman peaks are complex mixtures of different internal coordinates or mixing of low lying deformations and they are not pure fundamental vibrational modes. The Raman bands at 407w cm^{-1} are identified as C-H out-of-plane vibrations using the results of the normal coordinate analysis. All these assignments are in line with previous works [38].

Carbon – Oxygen bending Vibration:

The C=O in plane bending vibration are assigned at 660 cm^{-1} while C=O out of plane bending vibration are assigned at 633 cm^{-1}. These are good agreement with [43-45].

C-O-C in-plane bending

C-O-C in-plane bending are assigned to IR band at 830 cm-1 which agrees well with calculated values 820 cm^{-1} [46].

Group Vibrations (Methylene Modes)

CH_3 Vibration

The asymmetric and symmetric stretching vibration of a methyl group usually occur at about 2965 and 2880 cm^{-1}, respectively. If the C-H band is adjacent to an aromatic ring, the C-H stretching frequency and absorption between 3100 and 3000 cm^{-1} can be expected. Always the asymmetric vibration shift to a higher wave number. In the light of the above facts, the bands at 2973 cm^{-1} in FT-IR and in FT-R are attributed to C-H asymmetric stretching in CH_3 [47,48]. Similarly, the bands at 2853

cm^{-1} in infrared and Raman are attributed to C-H symmetric stretching in CH_3 [35, 49, 50]. These C-H stretching modes of vibrations are considered to be absolutely pure modes since the PED contribution of these modes are high. The CH_3 in plane bending vibrations, that is, the deformation and rocking modes of vibrations are assigned for this molecule as follows. The very strong band observed at 1373 cm^{-1} in FT-IR and the medium band at 1383 cm^{-1} in FT-R are assigned to the CH_3 asymmetric deformation mode of vibration [36, 51]. Similarly, the bands at 1300 cm^{-1} in Raman are attributed to CH_3 symmetric deformation mode of vibration [37, 50]. The medium intensity band 800 cm^{-1} in FT-IR is attributed to the CH_3 rocking mode vibration [52]. The out-of-plane vibration of methyl group are also assigned in the present table. The medium strong intensity band at 947 cm^{-1} in FT-IR and very weak intensity band of the same frequency in Raman are assigned to the wagging mode of vibration [53]. The very weak intensity band at 933 cm^{-1} in Raman has been assigned to the twisting mode of vibrations [54].

CH_2 vibration

The CH_2 group has got asymmetric and symmetric type of vibration. The very strong bands in Raman at 2940 cm^{-1} in FT-Raman and 2933 cm^{-1} in FT-IR are assigned to asymmetric vibration [55] and the symmetric vibrational frequencies are observed at 2733 cm^{-1} in FT-IR spectra [56]. These assignments agree well with the earlier work [55-57]. CH_2 in-plane bending vibrations, that is, the deformation and rocking mode of vibration are assigned for this molecules as follows. The medium strong band observed at 1433cm^{-1} in FT-IR and 1443cm^{-1} in FT-Raman are assigned to the CH_2 asymmetric deformation mode of vibration.[58] Similarly, the band at 1357 cm^{-1} in Raman are attributed to CH_2 symmetric deformation in mode of vibration. [59]. The strong band at observed at 1040 cm^{-1} in FT-IR are assigned to CH_2 wagging mode [60]. The very strong band observed at 1027 cm^{-1} in FTIR and the strong of the same frequency in Raman are assigned to the twisting mode of vibration [61]. The CH_2 rocking mode is identified with the very weak Raman band at 740 cm^{-1} [54]. The out-of-plane vibration of methyl group are also assigned in the Table 5.1.

C-C torsion

C-C torsion bending are assigned to IR band at 160 cm^{-1} which agrees well with calculated values 168 cm^{-1}[53].

Potential energy distribution

To check whether the chosen set of assignments contribute maxiimum to the potential energy associated with normal co-ordinate of the molecules, the potential energy distribution has been calculated. The higher PEDs contribution corresponding to each of the observed frequencies is reported in Table 5.1. The PED contribution less than 10% are not reported in the table 5.1.

From the normal co-ordinate analysis, the calculation of potential energy distribution of the fundamental vibrational modes shows that almost all skeletal as well as group vibrations of the compound contributes maximum to the potential energy associated with the respective bonds. From PED calculation, it's observed that a few skeletal carbon-carbon stretching vibrations are coupled slightly with C-H stretching vibrations. The C-H stretching vibrations are considered to be absolutely pure modes, since the PED contributions of these modes are almost 90%. CH in-plane bending vibrations are moderately pure while-the out-of-plane bending vibrations are coupled with C-CH_2 out-of-plane bending modes.

From the NCA it is also observed that maximum number of fundamental vibrations are obtained below 800 cm^{-1} significantly mixed with the neighbouring modes. Considerable mixing of the C-CH_2 in-plane and out-of-plane pending vibrations are observed with that of C=O in-plane and out-of-plane bending vibrations, respectively. Also the C-H in-plane and out-of-plane bending vibrations are mixed with C-CH_2 in-plane and out-of-plane bending vibrations, respectively. Twenty-one percent contribution of the C=O deformation mode to the deformation mode of C-CH_2 group is also observed.

4. Conclusion

In the present work, a complete vibrational assignments and analysis have been performed for Poly Vinyl Acetate (PVAc) on the basis of normal coordinate calculations using the FT-IR and FT-Raman spectra.

Reference

[1] J. I. Kroschwitz, Encyclopedia of Polymer Sci and Engg. **17** (John Wiley, New York), 1989.

[2] J. N. Kim, W. J. Cho, Ha C. S., J Poly Sci Poly Phy Ed, **40**, 19 (2002).

[3] J. Barry, Holland, N. James. Hay, Polymer, **43**(8), 2207 (2002).

[4] Sumin Kim, Hyun – J. Joong Kim. Adhesion Sci, Technol, **20**(2-3), 209 (2006).

[5] S. Kim, H. J. Kim, Int. J. Adhesion Adhesives **25**, 456 (2005).

[6] S. Kim, H. J. Kim, Indoor Air **15**, 317 (2005).

[7] S. Kim, H. J. Kim, Bioresource Technol **96**, 1457 (2005).

[8] S. K Verma, S. C. Bisarya, J. Appl. Polymer Sci. **31**, 2675 (1986).

[9] D. Turnar, H. Salim, Building Environment **39**, 1199 (2004).

[10] O. Yolun; A. Musa, O. Ayhan, J. Appt Polym. Sc. **76**, 1472-14, 79 (2006).

[11] Samy A. Madbouly, Ashraf. A. Mansowa, Nahed European Polymer Journal **43**(9), 3933 (2007).

[12] F. J. Boerio, J. L. Koenig, J. Polymer Sci, **A-2**, 7 1989 (1969).

[13] F. J. Boerio, J. L. Koenig, Polym Sci, **A-2**, 9, 1517 (1971).

[14] G. L. Cessac, J. G. Curro, J Poly Sci, Polym Phys Ed, **12**, 695 (1974).

[15] L. Lauchlan, J. F. Rabolt, Macromolecules, **19**, 1049

(1986).
[16] K. Tashiro, Y. Itoh, M. Kobayashi, H. Tadokoro, Macromolecules, 18 (1985).
[17] A. Armenyaud, J. L. Ramonja, M. Abenoza, J Raman Spectrosc, **18**, 109 (1987).
[18] M. Kobayashi, K. Tashiro, H. Tadokoro, Macromolecules, **8**, 158 (1975).
[19] M. A. Bachmann, W. L. Gordon, J. L. Koening, J. B. Lando, J Appl Phys, **50**(10), 6106 (1979).
[20] M. W. Huang, S. W. Kuo, H. D. Wu, F-C.Chang, S. Y. Fany, Polymer **41**, 2479 (2000).
[21] N. Mekhilef, P. Hadjiandreou, Polymer **36**, 2165 (1995).
[22] C.-C. M. Ma, H.-D Wu, P. Pchu, H. – T. Tseny, Macromolecules **30**, 5443 (1997).
[23] L. A. Utracki, Polymer Alloys and Blends, Hanser, Munich (1989).
[24] E. E. Shafee, Polymer **43**, 921 (2002).
[25] A. R. Prabakran, Spectroscopic Investigations of some polymers and organic molecues, Ph.D Thesis, Pondicherry University, pondicherry, 1990.
[26] F. J. Lu, S. L. Hsu, Macromolecules, **19**, 326 (1986).
[27] J. N. Kim, J. Chow, C. S. Ha, J. Poly Sci Poly Phy Ed, **40**, 19 (2002).
[28] H. Furhrer, V. B. Kartha, K. L Kidd, P. J. Kruger, H. H. Mantsch, Complete Program for Infrared Spectrometry – Normal Co-Ordinate Analysis Vol. **5**, National Research Council, Ottawa, Canada 1976.
[29] E. B. Wilson, J. C. Decius, P. C. Cross, Molecular Vibrations, Mc Graw Hill, New York, 1955.
[30] L. E. Sutton, The Interatomic Bond Distance and Bond Angles in molecule and Ions, London Chem. Soc., London, 1958.
[31] F. R. Dolish, W. G. Fately, F. F. Bently, characteristic Raman frequency of organic compounds, 1st Ed., Wiley, New York (1994)
[32] George Socrates, Infrared and Raman characteristic group frequencies – Tables and charts, 3rd ed., 5 John Wiley and Sons Ltd., England, (2001).
[33] W. O. Geroge, P. S. Mcintyre, Infrared Spectroscopy, John Wiley & Sons, London, 1987.
[34] A. H. Kuptson, G. N. Zhizhim Handbook of fourier transform Raman and infrared spectra of polymers, Elsivier, Arunsterdam, (1998).
[35] C. A. Indira Chary, K. Venkata Ramiah, Proc. Indian Acad. Sci, **69**, 18, (1969).
[36] G. Durgaprasad, D. N. Satyanarayana, C. C. Patel, Bull. Chem.. Soc. Japan, **44**, 316 (1971).
[37] G. Durgaprasad, D. N. Satyanarayana, C. C. Patel, H. S. Randhawa, Abha Goel, C. N. R. Rao, Spectrochim. Acta, **28A**, 2311 (1972).
[38] Srinivasan etal, Indian J. Pure & Applied Physic, **43** June 2005.
[39] Gunasekaran & Abitha Indian J. Pure & Applied phys. Vol **43**, May 2005.
[40] Varsanyi, Vibrational Spectra of Benzene Derivative 1969.
[41] P. Piaggio, C. Cuniberti, G. Dellepiane, E. Campini, G. Gorini, etal. Spectrochim. Acta, **45A** 3, 347 (1989).
[42] Zhang, Guizhong: Wang, Qingyue: Yu, Xiaogan: Su, Dazhao; Li, Zengfa; Zhang, Guangyin, Spectrochim, Acta, **47A**, 6, 737 (1991).
[43] E. Tatsch, B. Schrader, K. Raman Spectrosc., **26**, 467, (1995).
[44] S. F. Parker, S. M. Mason, K. P. J. Williams, Spectrochim Acta. **46A**, 2, 315 (1990).
[45] G. A. Neville, H. F. Shurvell, J. Raman skutrosc., 22, 35, (1991).
[46] N. Puviyarasan, FTIR and FIR Investigation on some amino Compounds, Ph. D, Thesis, Pondicherry University, Pondicherry, April 2001.
[47] J. C. Morris J. Chem Phys. **11**, 230 (1943).
[48] K. A. Jensen, B. M. Dahl, Niclson, G. Bosch, Acta Chem, Scand, **26**, 2241 (1972).
[49] J. J. Fox, A. E. Martin Proc. Roy. Soc. [London] **A175**, 208 (1940).
[50] V. Vekachalapathi, K. Venkata Ramiah, Proc. Indian Acad. Sci. **68**,109 (1968).
[51] V. Anthoni, L. Henriksen, P. H. Nielson, S. Prwochim. Acta, **30A**, 1351 (1974).
[52] M. C. Tobin, J.Phys. chem.. **64**, 216 (1960)].
[53] R. Mathivanane, Vibrational Spectra and Analysis of some substituted Benzonitrile, Phenols, Puridine Molecules and Phenylene Polymers, Ph.D Thesis, Pondicherry University, Pondicherry Dec. 2002.
[54] Sujin P. Josse, Vibrational Spectra, Assignments and Analysis of some Bologically important N-Hetrocyclic compounds, Ph.d, Thesis Manonmaniam Sundaranar University, Tirunelveli, Sept, 2005.
[55] H. W. Tompson, G. P. Harris, Trans. Faraday Soc, **38**, 37 (1942).
[56] C. Y. Liang, S. Krimm, J. Chem. Phys. **25**, 563 (1956).
[57] A. Blnidar, R. L. Doucen, J. C. Guillemin, O. Mo, M. Yanex, J. Phys. Chem., A(2002).
[58] M. M. Bobayashi, K. Tashiro, H. Tandokoro Mauyo Molecules **8**, 158 (1975).
[59] V. Arjunan, etal., Turk.J.Chem **27**, 423 (2003).
[60] F. J. Boerio, J. L. Koenig J.Chem. Phys. **52**, 4826 (1970).
[61] R. J. Petcavich, M. M. Coleman, J. Polym. Sci. Polym. Phys. Ed.**18**, 2097 (1980).

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