NORMAL COORDINATE ANALYSIS OF POLY VINYL ACETATE

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Abstract—**Fourier transform infrared and Raman spectra of poly 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. A normal coordinate analysis was also carried out using simple valence force field. A complete vibrational analysis is presented here for these molecule and results are briefly discussed**

Keywords- FTIR spectra, FT-Raman spectra, Poly Vinyl Acetate, PED, Normal coordinate analysis, SVFF.

I. INTRODUCTION

Poly Vinyl Acetate (PVA) is an important polymer, exhibiting piezoelectric, pyro-electric and ferroelectric properties [1]. The typical advantages of PVA are flexibility, formability and low density. Polyvinyl acetate is a rubbery synthetic polymer and 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.

PVA is a common copolymer with more expensive acrylics, used extensively in paper, paint and industrial coatings, referred to as vinyl acrylics. PVA is also commonly recommended for use in making leather handcrafted works and papier-mâché. PVA is used in the manufacture of electronic devices - dielectrics to transductors. The most important industrial applications of PVA are long lasting architectural metal finishes [2]. Poly vinyl acetate -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 [3].

The PVA polymers are found to have wide applications but only limited studies have been reported so for [4-9]. Thus in this work a complete vibrational analysis is attempted and in the present study the FTIR and FT Raman spectra of the PVA were recorded and normal coordinate analysis was carried out. Using their results various modes of vibrations and their probable assignment have been discussed.

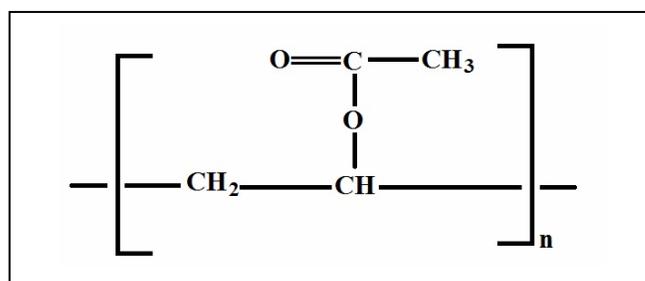Fig-1: Molecular structure of Poly Vinyl Acetate

II. EXPERIMENTAL DETAILS

The compound PVA 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 the molecule under study is shown in Fig-1. The FT-IR and FT-Raman spectra are given in the Fig-2 and Fig-3.

III. NORMAL CO-ORDINATE ANALYSIS (NCA)

To present a complete picture of the molecular forces holding the PVA 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 PVA 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

$$\Gamma_{vib} = 22a' + 10a'' \qquad (1)$$

All the vibrations are active both in Infrared and Raman. The normal co-ordinate analysis program of Fuhrer et al. [10] was used after suitable modification to calculate the vibrational frequencies and potential energy distribution (PED). This program follows the Wilson's FG matrix method [11] of vibrational analysis in which the normal co-ordinates are defined with respect to a set of molecular coordinates.

The structural parameters necessary for the compound were taken from Sutton table [12] 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 are 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 ($\pm$ 10 cm^{-1}) and with an acceptable potential energy distribution.
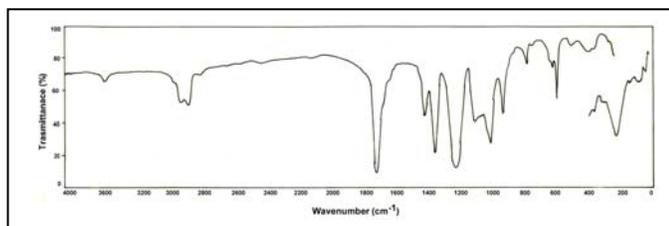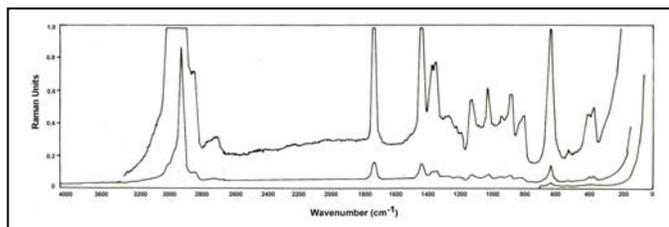

Fig-2: FTIR Spectrum of Poly Vinyl Acetate

Fig-3: FT Raman Spectrum of Poly Vinyl Acetate

IV. RESULTS AND DISCUSSION

The observed frequencies of PVA 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 was 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 substituents.

A. Skeletal Vibrations

1) C-H Stretching Vibrations: According to Dollish et al [13] 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} [14, 15]. Using the above facts the IR bands seen at 2546 cm^{-1} and 2466 cm^{-1} are assigned to C-H stretching vibrations.

2) Carbon-oxygen Stretching Vibrations: Symmetrical bands such as C=O and C-O manifest themselves by giving the most intense bands in Raman spectra [16-19], thus the very strong infrared band at 1740 cm^{-1} is assigned to C = O stretch [20,21]. 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 previous work [21, 22].

3) C-C Stretching Vibrations: C-C Stretching modes dominate in Raman Spectrum. The intense Raman lines are due to the stretching of CC bonds [16]. 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.

4) 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 and this assignment are in line with piaggio [23] and Zhang [24]. The C-H deformation mode are weak in Raman spectra of polymers and hence the weak Raman band at 1493 cm^{-1} are assigned to C-H deformation mode.

5) C-H Out-Of-Plane Bending 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 407 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 [20].

6) Carbon-Oxygen Bending Vibrations: 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} and these are good agreement with [25-27].

7) C-O-C in-Plane Bending Vibrations: C-O-C in-plane bending are assigned to IR band at 830 cm-1 which agrees well with calculated values 820 cm^{-1} [28].

Table-1: Observed and Calculated Frequencies and Potential Energy Distributions of Poly Vinyl Acetate

| Sl. No. | Species | Observed Wave Number & Rel. Intensity | | Calculated wave Number cm^{-1} | Assignments | PED % |
		Infrared cm^{-1}	Raman cm^{-1}			
1	a'	2973 m	2973 m	2970	C-H asym stretching in CH$_3$	88ν_{asy} CH
2	a'	2933 ms	2940 vs	2933	C-H asym stretching in CH$_2$	92ν_{asy} CH
3	a'	2853 w	2853 w	2856	C-H sym stretching in CH$_3$	90ν_{sym} CH
4	a'	2733 vw'		2728	C-H sym stretching in CH$_2$	89ν_{sym} CH
5	a'	2546 vw		2537	C-H stretching	95ν CH
6	a'	2466 vw		2458	C-H stretching	96ν CH
7	a'	1740 vs	1733 m	1736	C=O stretching	84ν C=O
8	a"		1493 w	1490	CH asym deformation in	88ν_{asy} CH
9	a"	1433 ms	1443 ms	1442	CH$_2$ asym deformation	79δ_{asy} CH
10	a"	1373 vs	1383 m	1381	CH$_3$ asym deformation	69δ_{asy} CH+21β CH
11	a'		1357 m	1350	CH$_2$ sym deformation	74δ_{sym} CH+14β CH
12	a'		1300 vw	1289	CH$_3$ sym deformation	68δ_{sym} CH+28β CH
13	a'	1240 vs		1233	C-H in plane bending	71β CH+19δ CH
14	a'	1127 s	1133m	1129	C-O stretching	79ν C-O+11ν CH$_3$
15	a'		1087 vw	1081	C-O stretching	84ν C-O+10ν CH$_3$
16	a"	1040 s		1032	CH$_2$ wagging	74ω CH$_2$+19τ CH$_2$
17	a"	1027 vs	1023 m	1026	CH$_2$ twisting	59τ CH$_2$+28ω CH$_2$
18	a"	947 ms	947 vw	938	CH$_3$ wagging	68ω CH$_3$+30τ CH$_3$
19	a"		933 vw	926	CH$_3$ twisting	60τ CH$_3$+24ω CH$_3$
20	a'		900 vw	891	C-C stretching	78ν C-C+28γ CH
21	a'		887 m	880	C-C stretching	69ν C-C+14 ν C-O
22	a'		830 w	820	C-O-C in plane bending	71β C-O-C+19ρ CH$_3$
23	a'	800 m	800 w	806	CH$_3$ rocking	68 ρ CH$_3$+22β C-O-C
24	a'		740 vw	734	CH$_2$ rocking	79 ρ CH$_2$+11β C-O-C
25	a'	660 w		656	C=O in plane bending	88β C=O +10β C-CH$_3$
26	a"	633 m	633 ms	628	C=O out of plane bending	69 η C=O +14 η C-CH$_3$
27	a'		577 w	568	C-CH$_2$ in plane bending	74β C-CH$_2$ +16β CH
28	a'		477 vw	475	C-CH$_2$ in plane bending	80β C-CH$_3$ +10β CH
29	a"		407 w	401	C-H out of plane bending	66 η CH +19 η C-O
30	a"		347 vw	337	C-CH$_2$ out of plane bending	71 η C-CH$_2$ +24 η C=O
31	a"		313 vw	308	C-CH$_3$ out of plane bending	68 η C-CH$_3$ +30 η C=O
32	a"		160 vw	168	C-C torsion	51 η C-C +22 η C-O

Notations: 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.

B. Group Vibrations (Methylene Modes)

1) Methyl Group Vibrations: 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 [29,30]. Similarly, the bands at 2853 cm-1 in infrared and Raman are attributed to C-H symmetric stretching in CH_3 [17, 31, 32]. 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 [18, 33]. Similarly, the bands at 1300 cm-1 in Raman are attributed to CH_3 symmetric deformation mode of vibration [19, 32]. The medium intensity band 800 cm-1 in FT-IR is attributed to the CH_3 rocking mode vibration [34]. The out-of-plane vibrations 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 [35]. The very weak intensity band at 933 cm-1 in Raman has been assigned to the twisting mode of vibrations [36].

2) CH_2 group Vibrations: 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 [37] and the symmetric vibrational frequencies are observed at 2733 cm^{-1} in FT-IR spectra [38]. These assignments agree well with the earlier work [37-39]. 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 [40]. Similarly, the band at 1357 cm^{-1} in Raman is attributed to CH_2 symmetric deformation in mode of vibration [41]. The strong band at observed at 1040 cm^{-1} in FT-IR are assigned to CH_2 wagging mode [42]. 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 [43]. The CH_2 rocking mode is identified with the very weak Raman band at 740 cm^{-1} [36]. The out-of-plane vibration of methyl group are also assigned in the table-1.

3) C-C Torsion Vibrations: C-C torsion bending are assigned to IR band at 160 cm^{-1} which agrees well with calculated values 168 cm^{-1}[35].

V. POTENTIAL ENERGY DISTRIBUTION

To check whether the chosen set of assignments contribute maximum 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 1 and the PED contribution less than 10% are not reported.

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-CH2 out-of-plane bending modes.

From the NCA it is also observed that maximum numbers of fundamental vibrations are obtained below 800 cm^{-1} significantly mixed with the neighboring 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.

VI. CONCLUSION

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

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