NORMAL COORDINATE ANALYSIS OF POLY VINYL ACETATE

K.B. Renuka Devi
Department of Physics,
Rajiv Gandhi College of Engineering and Technology,
Puducherry-607402, India.
renuakshaya@gmail.com

R.Madivanane
Department of Physics
Bharathidasan Govt. College for Women,
Puducherry -605003, India.
madivanane_r@yahoo.com

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 molecules 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 transducers. 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 far [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.

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 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–CH₃ group is considered as point mass and lies in the plane of the molecule, then PVA belongs to Cₛ point group. Cₛ symmetry leads to two types of vibrations namely a' (in-plane) and a'' (out-of-plane) and are distributed as

\[
\Gamma_{\text{vib}} = 22a' + 10a'' \quad (1)
\]
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 valence 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 valence 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-CH₃ group within a reasonable limit (± 10 cm⁻¹) and with an acceptable potential energy distribution.

![Fig-2: FTIR Spectrum of Poly Vinyl Acetate](image)

![Fig-3: FT Raman Spectrum of Poly Vinyl Acetate](image)

**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 in 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 3100 cm⁻¹ which originate from the ring carbon C-H stretch. It is 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 is 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

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Species</th>
<th>Observed Wave Number &amp; Rel. Intensity</th>
<th>Calculated wave Number cm⁻¹</th>
<th>Assignments</th>
<th>PED %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Infrared cm⁻¹</td>
<td>Raman cm⁻¹</td>
<td>Raman cm⁻¹</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>a'</td>
<td>2973 m</td>
<td>2973 m</td>
<td>2970</td>
<td>C-H asym stretching in CH₃</td>
</tr>
<tr>
<td>2</td>
<td>a'</td>
<td>2933 ms</td>
<td>2940 vs</td>
<td>2933</td>
<td>C-H asym stretching in CH₂</td>
</tr>
<tr>
<td>3</td>
<td>a'</td>
<td>2853 w</td>
<td>2853 w</td>
<td>2856</td>
<td>C-H sym stretching in CH₃</td>
</tr>
<tr>
<td>4</td>
<td>a'</td>
<td>2733 vw</td>
<td>2728</td>
<td>2728</td>
<td>C-H sym stretching in CH₂</td>
</tr>
<tr>
<td>5</td>
<td>a'</td>
<td>2546 vw</td>
<td>2537</td>
<td></td>
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<tr>
<td>6</td>
<td>a'</td>
<td>2466 vw</td>
<td>2458</td>
<td></td>
<td>C-H stretching</td>
</tr>
<tr>
<td>7</td>
<td>a'</td>
<td>1740 vs</td>
<td>1733 m</td>
<td>1736</td>
<td>C=O stretching</td>
</tr>
<tr>
<td>8</td>
<td>a''</td>
<td>1493 w</td>
<td>1490</td>
<td>88νas(CH)</td>
<td>CH asym deformation</td>
</tr>
<tr>
<td>9</td>
<td>a''</td>
<td>1433 ms</td>
<td>1443 ms</td>
<td>1442</td>
<td>CH₂ asym deformation</td>
</tr>
<tr>
<td>10</td>
<td>a''</td>
<td>1373 vs</td>
<td>1383 m</td>
<td>1381</td>
<td>CH₃ asym deformation</td>
</tr>
<tr>
<td>11</td>
<td>a'</td>
<td>1357 m</td>
<td>1350</td>
<td></td>
<td>CH₂ sym deformation</td>
</tr>
<tr>
<td>12</td>
<td>a'</td>
<td>1240 vs</td>
<td>1300 w</td>
<td>1289</td>
<td>CH₃ sym deformation</td>
</tr>
<tr>
<td>13</td>
<td>a'</td>
<td>1127 s</td>
<td>1133 m</td>
<td>1129</td>
<td>C-O stretching</td>
</tr>
<tr>
<td>14</td>
<td>a'</td>
<td>1087 vw</td>
<td>1081</td>
<td></td>
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</tr>
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<td>15</td>
<td>a''</td>
<td>1040 s</td>
<td>1032</td>
<td></td>
<td>CH₂ wagging</td>
</tr>
<tr>
<td>16</td>
<td>a''</td>
<td>1027 vs</td>
<td>1023 m</td>
<td>1026</td>
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</tr>
<tr>
<td>17</td>
<td>a''</td>
<td>947 ms</td>
<td>947 vw</td>
<td>938</td>
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</tr>
<tr>
<td>18</td>
<td>a''</td>
<td>933 vw</td>
<td>926</td>
<td></td>
<td>CH₃ twisting</td>
</tr>
<tr>
<td>19</td>
<td>a'</td>
<td>900 vw</td>
<td>891</td>
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<td>C-C stretching</td>
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<tr>
<td>20</td>
<td>a'</td>
<td>887 m</td>
<td>880</td>
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</tr>
<tr>
<td>21</td>
<td>a'</td>
<td>830 w</td>
<td>820</td>
<td></td>
<td>C-O-C in plane bending</td>
</tr>
<tr>
<td>22</td>
<td>a'</td>
<td>800 m</td>
<td>806</td>
<td></td>
<td>CH₃ rocking</td>
</tr>
<tr>
<td>23</td>
<td>a'</td>
<td>740 vw</td>
<td>734</td>
<td></td>
<td>CH₂ rocking</td>
</tr>
<tr>
<td>24</td>
<td>a'</td>
<td>660 w</td>
<td>656</td>
<td></td>
<td>C=O in plane bending</td>
</tr>
<tr>
<td>25</td>
<td>a'</td>
<td>633 m</td>
<td>633 ms</td>
<td>628</td>
<td>C=O out of plane bending</td>
</tr>
<tr>
<td>26</td>
<td>a''</td>
<td>577 w</td>
<td>568</td>
<td></td>
<td>C-CH₃ in plane bending</td>
</tr>
<tr>
<td>27</td>
<td>a'</td>
<td>477 vw</td>
<td>475</td>
<td></td>
<td>C-CH₃ in plane bending</td>
</tr>
<tr>
<td>28</td>
<td>a''</td>
<td>407 w</td>
<td>401</td>
<td></td>
<td>C-H out of plane bending</td>
</tr>
<tr>
<td>29</td>
<td>a''</td>
<td>347 vw</td>
<td>337</td>
<td></td>
<td>C-CH₂ out of plane bending</td>
</tr>
<tr>
<td>30</td>
<td>a''</td>
<td>313 vw</td>
<td>308</td>
<td></td>
<td>C-CH₃ out of plane bending</td>
</tr>
<tr>
<td>31</td>
<td>a''</td>
<td>160 vw</td>
<td>168</td>
<td></td>
<td>C-C torsion</td>
</tr>
</tbody>
</table>

Notations: vs-very strong; s- strong; ms- medium strong; m-medium; w- weak; vw-very weak; v- 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 CH3 [29,30]. Similarly, the bands at 2853 cm^{-1} in infrared and Raman are attributed to C-H symmetric stretching in CH3 [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 CH3 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 CH3 asymmetric deformation mode of vibration [18, 33]. Similarly, the bands at 1300 cm^{-1} in Raman are attributed to CH3 symmetric deformation mode of vibration [19, 32]. The medium intensity band 800 cm^{-1} in FT-IR is attributed to the CH3 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) CH2 group Vibrations: The CH2 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]. CH2 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 1433 cm^{-1} in FT-IR and 1443 cm^{-1} in FT-Raman are assigned to the CH2 asymmetric deformation mode of vibration [40]. Similarly, the band at 1357 cm^{-1} in Raman is attributed to CH2 symmetric deformation in mode of vibration [41]. The strong band at observed at 1040 cm^{-1} in FT-IR are assigned to CH2 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 CH2 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 coordinate 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-CH3 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-CH2 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-CH2 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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AUTHORS PROFILE

K.B.Renukadevi has completed her M. phil in Pondicherry University and doctrate degree in Physics at the Mannnoim Sundaranar University, TN. She is working as the Prof and Head of the department of physics for more than a decade at the Rajiv Gandhi College of Engineering and Technology, Puducherry, India.

R. Madivanane has completed both his M.Phil and Doctorate degree in physics at the Pondicherry university. He has more than twenty years of teaching experience and more than ten years of research experience. He has guided more than five M.phil students and presently guiding three Ph.d scholars and published around seven papers in both international and national level.