

Vibrational Spectroscopic Studies of Amino acid p-toluenesulfonic acid NLO Crystals

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ABSTRACT

In the present work, a comparative study on the vibrational spectrums recorded on some newly synthesized amino acid p- toluenesulfonic acid NLO crystals are discussed. Infrared spectral measurements of all the grown crystals were made in the range of 4000–400 cm^{-1} using Jasco Spectrometer FT-Raman spectra of the grown crystals were recorded in the BRUKER RFS 27, Stand alone FT-Raman Spectrometer in the range of 4000 – 400 cm^{-1} The Nd: YAG laser source was operated at 1064 nm. FT-IR and FT-Raman spectral analyses shows the different functional groups present in the studied compounds. Its intensities and positions are analyzed. The high intensity vibrational bands observed around 2950 cm^{-1} which is assigned to N- H...O vibrations shows the influence of hydrogen bonds in the analyzed compounds.

Keywords: NLO crystal, Organic single crystal, FTIR, FTRAMAN.

1 Introduction

Vibrational spectroscopy is the branch of science that measures the exact wavelength of light absorbed by the molecule. This can be used as a fingerprint for identifying the different functional groups present in the molecule and their vibrational behavior when subjected to external radiation of energy. This technique could be used to identify an unknown molecule by comparing its absorption to that of other molecules. Vibrational spectroscopy could be used to understand further the physical properties of an unknown molecule. The present compounds have various functional groups such as -OH, -CH (aliphatic and aromatic), -NH₃, -CH₃, C-N, C-C, COOH and -SO₃. These groups are affected both in intensity and position with respect to their surroundings and the hydrogen bonding interactions. In the present work, the vibrational spectral analysis (FT-IR and FT-Raman) of the newly grown NLO crystals viz, L- Alaninium p- toluenesulfonate (LAPT), L-Histidinium p- toluenesulfonate (LHPT), L-Valinium p- toluenesulfonate monohydrate (LVPT), L- Leucinium p – toluenesulfonate monohydrate (LLPT), L- Isoleucinium p – toluenesulfonate monohydrate (LIPT) and β - Alaninium p- toluenesulfonate (BAPT) were discussed.

2 Experimental

2.1 Synthesis and Crystal Growth

Crystals of the compound under study were obtained by the addition of p-toluenesulfonic acid monohydrate to the solutions of L- Alanine for LAPT, L-Histidine for LHPT, L-Valine for LVPT, L- Leucine for LLPT, L- Isoleucine for LIPT and β - Alanine for BAPT as per the reactions in the literature [1, 2, 3, 4, 5 & 6] & prepared with starting materials taken in the equimolar ratio (1:1) in distilled water. Calculated amount of compounds were dissolved in distilled water and stirred well for about 2 hours using magnetic stirrer to obtain the homogenous mixers for single crystal growth. The obtained solutions were filtered and kept undisturbed for crystallization to take place. Good quality single crystals of the compound under study were obtained after about a week time. Obtained crystals are confirmed by single crystal XRD and taken for further analysis for vibration spectroscopic measurements.

2.2 Vibrational studies

The Infrared spectral measurements of all the grown crystals were made in the range of 4000–400 cm^{-1} using Jasco Spectrometer (FT-IR, model 410) by KBr pellet technique with the resolution of $\pm 2 \text{ cm}^{-1}$. FT-Raman spectra of the grown crystals were recorded in the BRUKER RFS 27, Stand alone FT-Raman Spectrometer in the range of 4000 – 400 cm^{-1} with the resolution of $\pm 2 \text{ cm}^{-1}$. The Nd: YAG laser source was operated at 1064 nm. The comparative representation of FT-IR and FT-RAMAN spectra of grown crystals are shown in figure. 1 & 2.

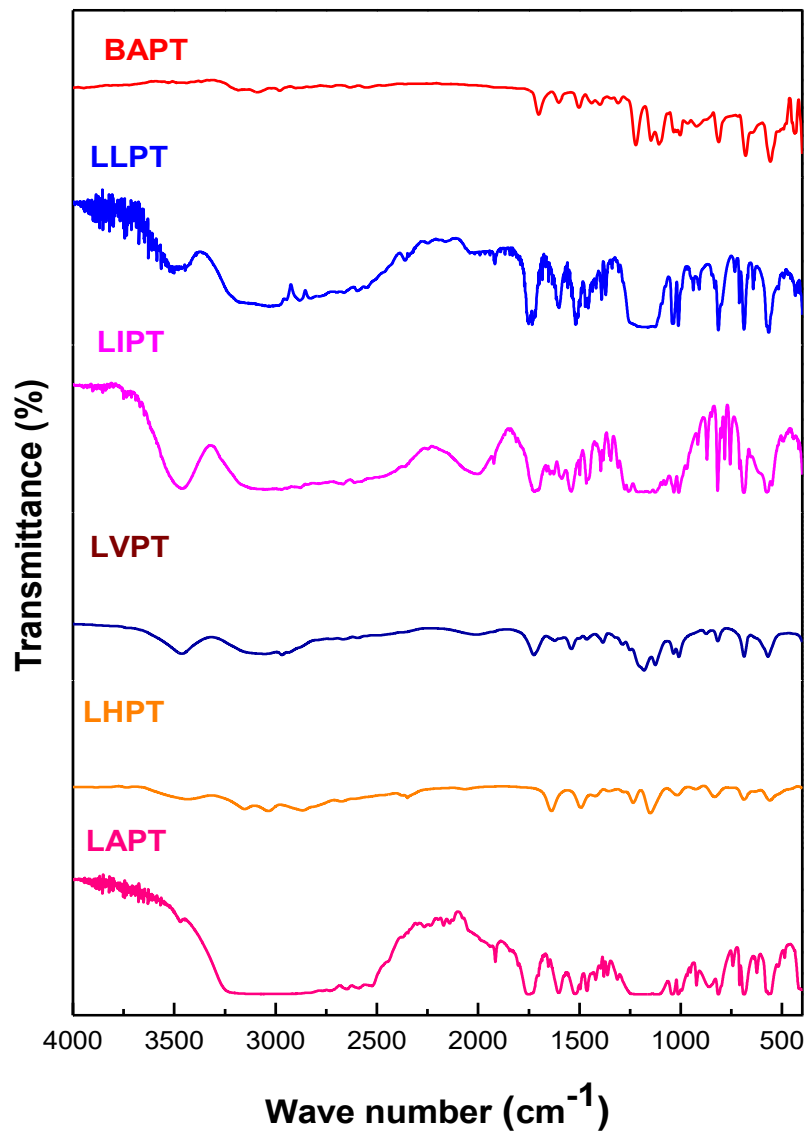


Figure 1 Comparative representation of FTIR spectra of grown crystals

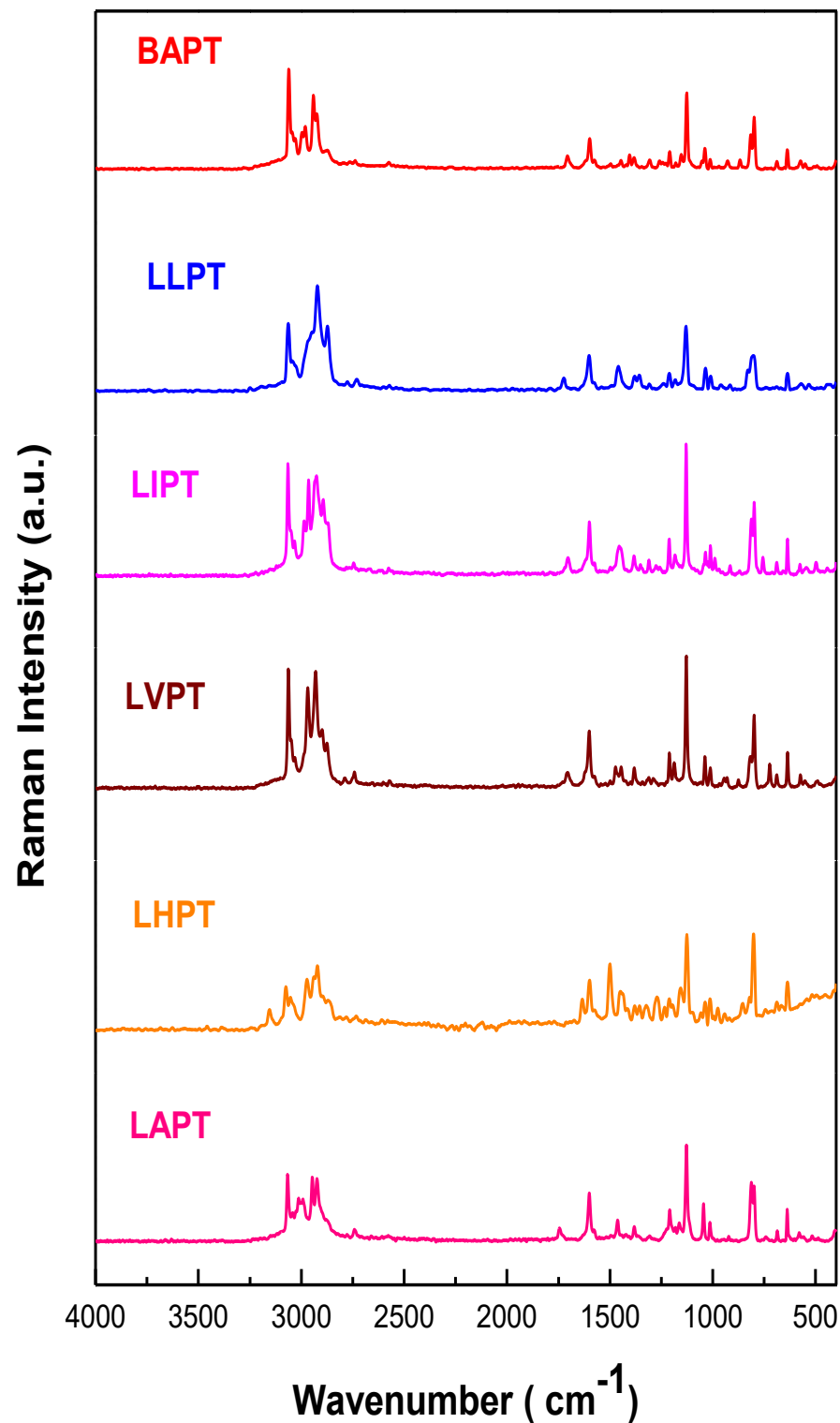


Figure 2 Comparative representations of FT- RAMAN spectra

3 Results and discussions

3.1 Vibrations of the –NH₃⁺ group

The hydrogen bonds of NH₃⁺ group play an important role in asymmetric crystal structure which favors NLO activity of the material. For the amino group, the asymmetric and symmetric stretching modes are expected in the region of 3150-3000 cm⁻¹ and it is also expected to have asymmetric and symmetric bending in the range of 1625 – 1560 cm⁻¹, and 1550 – 1505 cm⁻¹, respectively [7,8]. Further the charged amino species stretching wave numbers are observed in the region of 3300-3500 cm⁻¹ and these stretching vibrations are broader than those arising from the uncharged group. In the present study the asymmetric stretching vibrations of NH₃ are observed as a broad band at 3210 cm⁻¹ for LAPT and observed as a medium band at 3153 cm⁻¹ for LHPT in IR spectrum of the compounds. This vibration is observed at 3152 cm⁻¹ for LHPT in Raman spectrum and is Raman inactive for the case of LAPT compounds. Further the above said vibrations are inactive both in IR and Raman spectrum of LVPT, LLPT, LIPT and BAPT. The symmetric stretching vibrations of NH₃ are observed as a broad peak at 3052 cm⁻¹ for LVPT, 3068 cm⁻¹ for LLPT and as a weak peak at 3088 cm⁻¹ for BAPT in the IR spectrum. These vibrations are not observed in the IR spectrum of LHPT, LAPT and LIPT. The vibrations of the above said group are observed as a strong band around 3063 cm⁻¹ in the Raman spectra of all the compounds.

The influence of strong hydrogen bonds on the nonlinear optical properties of crystals with the dipole-dipole orientations of H-bonded chiral molecules forms molecular pairs in parallel fashion which in turn results in non zero first order hyperpolarizability [9]. This dipole-dipole interaction or hydrogen bonding interaction lead to strong intensity intermolecular peak, shifting of band positions and broadening of higher wave number region.

A broad peak observed at 2944 cm⁻¹ for LAPT, a strong peak at 2866 cm⁻¹ for LHPT, a strong peak at 2972 cm⁻¹ for LVPT, a broad peak at 2995 cm⁻¹ for LLPT, a broad peak at 2978 cm⁻¹ for LIPT and a broad peak at 2981 cm⁻¹ for BAPT in the IR spectrum are attributed to the N–H...O intermolecular hydrogen bond vibrations. These high intensity band confirms the strong hydrogen bonding tendency occur between the cation and anion in all the compounds under study. These vibrations are observed as a strong band at 2944 cm⁻¹ for LAPT, a very strong band at 2972 cm⁻¹ for LHPT, a strong peak at 2972 cm⁻¹ for LVPT, a very strong peak at 2928 cm⁻¹ for LLPT, a very strong peak at 2964 cm⁻¹ for LIPT and a strong peak at 2947 cm⁻¹ for BAPT in the Raman spectrum of the respective compounds.

The strong peak observed at 1610 cm^{-1} in the IR spectrum and a strong peak at 1601 cm^{-1} in the Raman spectrum of LAPT is assigned to NH_3^+ asymmetric deformation. These vibrations are observed at 1605 cm^{-1} in the Raman spectrum of LHPT. Further, these vibrations are observed as a medium peak at 1607 cm^{-1} in the IR spectrum and at 1598 cm^{-1} in the Raman spectrum of BAPT.

A very strong band observed at 1122 cm^{-1} in the Raman spectrum of LAPT is assigned to NH_3 rocking vibration. These vibrations are observed as a medium peak at 1150 cm^{-1} in the IR spectrum and at 1154 cm^{-1} in the Raman spectrum of LHPT. The above said vibrations are observed as a very strong peak around 1126 cm^{-1} both in IR and Raman spectrums of LVPT. The peak around 1126 cm^{-1} in the Raman spectrum of LLPT and LIPT are also assigned to NH_3 rocking vibration. In BAPT the NH_3^+ rocking vibrations are observed in 1110 cm^{-1} in the IR spectrum and at 1119 cm^{-1} in Raman spectrum.

3.2 Vibrations of COOH group

Generally monocarboxylic acids are exhibited three strong bands at 655 , 635 & 620 cm^{-1} due to in plane vibration of the O-C=O group, which are not resolved in the region $665\text{-}610\text{ cm}^{-1}$ [262]. The stretching vibration of the C=O bond is a nonionized carboxylic (COOH) group usually appear in the wave number $1755\text{-}1700\text{ cm}^{-1}$. The OH stretching vibration of monomeric carboxylic acids (liquids) observes sharp and a weak band at $3550\text{-}3500\text{ cm}^{-1}$ and somewhat higher in the vapour phase. The carboxylic acids are usually characteristic in the condensed state by a strongly bonded, very broad OH stretching band centered in the region at 3000 cm^{-1} . This stretching vibration is superimposed on the CH stretching band ($3100\text{-}2800\text{ cm}^{-1}$). The carboxyl monomer infrared band at $1380\text{-}1280\text{ cm}^{-1}$ (medium) and $1190\text{-}1075\text{ cm}^{-1}$ (strong) involve O-H deformation in-plane and C-O stretching [10]

In the present studies for LAPT, a strong vibrational band at 1754 cm^{-1} (in IR) and a weak band at 1745 cm^{-1} (in Raman) is assigned to C=O stretching vibrations. C-O stretching is observed around 1378 cm^{-1} in Raman spectrum as a weak peak. A strong band observed at 676 cm^{-1} (in IR) is assigned to COOH rocking. In the case of LHPT, C-O stretching vibrations are observed as a weak peak at 1376 cm^{-1} in Raman spectrum.

For LVPT, a very strong vibrational band at 1729 cm^{-1} (in IR) and a weak band at 1694 cm^{-1} (in Raman) is assigned to C=O stretching vibrations. C-O stretching is observed around 1383 cm^{-1} in both IR and Raman spectrum as medium and weak peak respectively. A strong band observed at 671 cm^{-1} (in IR) is assigned to COOH rocking and a shoulder peak at 496 cm^{-1} (in Raman) is assigned to C-O bending.

For LLPT, a very strong vibrational band at 1739 cm^{-1} (in IR) and a strong band at 1724 cm^{-1} (in Raman) are assigned to C=O stretching vibrations. A strong peak at 693 cm^{-1} (in IR) is assigned to COOH rocking. The weak peaks at 442 cm^{-1} in the Raman spectrum of compound is assigned to C-O bending.

In the vibrational spectrums of LIPT, a medium vibrational band at 1722 cm^{-1} (in IR) and a strong band at 1702 cm^{-1} (in Raman) are assigned to C=O stretching vibrations. C-O stretching is observed around 1358 cm^{-1} in the IR spectrum as strong peak. A strong band observed at 685 cm^{-1} (in IR) and a weak peak at 689 cm^{-1} (in Raman) is assigned to COOH rocking. The weak peak at 497 cm^{-1} in Raman spectrum is assigned to C-O bending.

In BAPT, a medium vibrational band at 1695 cm^{-1} (in IR) and a strong vibrational band at 1705 cm^{-1} (in Raman) is assigned to C=O stretching vibrations.. A strong band observed in 675 cm^{-1} (in IR) and weak peak at 685 cm^{-1} (in Raman) is assigned to COOH rocking.

3.3 Vibrations of C- H group

Most of the aromatic compounds have several peaks in the region $3100\text{--}3000\text{ cm}^{-1}$ and they are being due to the stretching vibrations of the ring C-H bonds. The C-H stretching vibrations are overlapped with the NH_3^+ vibrations and observed in the range of $3026\text{--}3107\text{ cm}^{-1}$ in IR and $3065\text{--}3094\text{ cm}^{-1}$ in Raman. In the present studies the strong vibrational bands around 2926 cm^{-1} in the Raman spectrum for LAPT, LHPT, LVPT and LIPT are assigned to C-H stretching vibrations. The vibrational bands identified around 3021 cm^{-1} in the Raman spectrum of LAPT and LIPT, a medium peak at 2991 cm^{-1} (Raman) for BAPT and 2892 cm^{-1} (Raman) for LVPT are also assigned to C-H stretching vibrations

Normally, the C- H in plane bending vibrations occur in the range of $1300\text{--}1000\text{ cm}^{-1}$. In the present observations the peaks at 1310 cm^{-1} & 1011 cm^{-1} in the Raman spectrum of LAPT, the peaks at 1323 cm^{-1} & 1014 cm^{-1} , 802 cm^{-1} in Raman spectrum and a weak peak at 1013 cm^{-1} , 833 cm^{-1} in IR spectrum of LHPT, a vibrational band at 1010 cm^{-1} both in IR and Raman spectrum and a peak at 816 cm^{-1} in the IR spectrum of LVPT, a peaks at 1009 cm^{-1} , 802 cm^{-1} in Raman spectrum and a strong band at 1021 cm^{-1} , 809 cm^{-1} in IR spectrum for LLPT, a medium peak at 1310 cm^{-1} , 1212 cm^{-1} and 812 cm^{-1} in Raman spectrum and peaks at 1004 cm^{-1} and 817 cm^{-1} in the IR spectrum of LIPT, a strong peak at 1004 cm^{-1} in the IR spectrum for BAPT are assigned to C-H in plane bending. The peaks observed at 1184 cm^{-1} , 1182 cm^{-1} in the Raman spectrum of LIPT and LLPT respectively is assigned to C-H out of plane deformation. The vibrational peaks observed

around $1154 - 1190 \text{ cm}^{-1}$ in the IR spectrum of all the compound except LAPT and BAPT are assigned to C-H out of plane deformation.

The band observed at 1456 cm^{-1} , 1472 cm^{-1} , 1458 cm^{-1} and 1454 cm^{-1} in the Raman spectrum for LAPT, LVPT, LLPT and LIPT respectively are assigned to CH_3 asymmetric deformation. The corresponding peaks are observed at 1492 cm^{-1} , 1463 cm^{-1} , 1456 cm^{-1} , 1465 cm^{-1} in the IR spectrum for LHPT, LVPT, LLPT and LIPT respectively. The peaks identified at 959 cm^{-1} , 974 cm^{-1} , 931 cm^{-1} , 959 cm^{-1} and 924 cm^{-1} in the Raman spectrum for LAPT, LHPT, LVPT, LIPT and BAPT are assigned to CH_3 rocking vibration. The corresponding peaks are observed at 920 cm^{-1} and 924 cm^{-1} in the IR spectrum of LHPT and BAPT & LIPT. For all other compounds the above vibrations are IR inactive.

3.4 Vibrations of C–C group

The vibrational bands observed at 1521 cm^{-1} , 1543 cm^{-1} , 1518 cm^{-1} , 1545 cm^{-1} & 1500 cm^{-1} in IR spectra for LAPT, LVPT, LLPT, LIPT and BAPT respectively is attributed to C- C stretching. The above said vibrations are observed at 1501 cm^{-1} is observed in the Raman spectrum of LHPT. Addition to above, the peaks identified around 1638 cm^{-1} (both in Raman & IR) for LHPT is also assigned to C-C stretching. For all the other compounds these vibrations are Raman inactive. The peaks around 629 cm^{-1} to 640 cm^{-1} in Raman spectra of all the compounds are assigned to C- C in plane bending. These vibrations are IR inactive except LIPT. A shoulder peak at 631 cm^{-1} (in IR) for LIPT is assigned to C-C in plane deformation. The vibrational peaks observed at 727 cm^{-1} for LVPT, at 756 cm^{-1} for LIPT in Raman spectrum and a strong peak at 755 cm^{-1} in the IR spectrum for LIPT are assigned to C- C torsional deformation. Additionally the weak peaks observed around 532 cm^{-1} and 544 cm^{-1} in the Raman spectrum of LLPT and LIPT respectively are assigned to C-C deformation.

3.5 Vibrations of C- N group

The vibrational peaks at 811 cm^{-1} , 798 cm^{-1} , 798 cm^{-1} and 809 cm^{-1} in the Raman spectra for LAPT, LVPT, LIPT and BAPT are assigned to C- N deformation. Corresponding vibration is identified in the IR spectrum at 799 cm^{-1} for LAPT. The weak vibrational peaks identified at 1445 cm^{-1} and 1439 cm^{-1} in the Raman spectrum of LVPT and LHPT respectively are assigned to C- N stretching. This vibration is observed around 1403 cm^{-1} in the IR spectrum for LIPT.

3.6 Vibrations of SO_3 group

In general, the SO_3 group shows four normal modes of vibration such as asymmetric stretching at 1291 cm^{-1} , symmetric stretching at 1053 cm^{-1} , asymmetric deformation at 551 cm^{-1} and symmetric deformation at 535 cm^{-1} . In the presents studies the SO_3 asymmetric stretching vibrations are assigned to the bands identified at 1211 cm^{-1} , 1273 cm^{-1} , 1206 cm^{-1} , 1212 cm^{-1} , 1212 cm^{-1} and 1206 cm^{-1} in the Raman spectrum for LAPT, LHPT, LVPT, LLPT, LIPT and BAPT respectively. The corresponding vibrations are observed at 1232 cm^{-1} , 1234 cm^{-1} , 1252 cm^{-1} and 1216 cm^{-1} in the IR spectrum for LAPT, LHPT, LIPT and BAPT respectively. These vibrations are IR inactive for LVPT and LLPT. The symmetric stretching vibrations of SO_3 group are observed in the compounds at 1045 cm^{-1} , 1033 cm^{-1} , 1038 cm^{-1} , 1039 cm^{-1} , 1035 cm^{-1} and 1039 cm^{-1} to in the Raman spectrum of LAPT, LHPT, LVPT, LLPT, LIPT and BAPT respectively. The peak observed at 1048 cm^{-1} in the IR spectrum for LIPT is assigned to the SO_3 group symmetric stretching vibrations. In all other compounds the above vibrations are IR inactive. The vibrational peaks observed at 578 cm^{-1} (Raman) for LAPT, 560 cm^{-1} (IR) for LHPT and at 589 cm^{-1} (Raman) & at 560 cm^{-1} (IR) for BAPT are assigned to SO_3 asymmetric deformation.

3.7 Vibrations of OH & H_2O group

The stretching vibrational modes of water molecules are usually expected in the region 3450 cm^{-1} – 3250 cm^{-1} . As evident Characteristics bands originating from O-H stretching vibrations which are not involved in a hydrogen bond occurs at much higher frequencies, whereas the bands at lower frequency is observed for O-H bonds engaged in hydrogen bonds. Generally, the O-H stretching vibration is observed in the wave number region at $3600\text{--}3200\text{ cm}^{-1}$. In the IR spectra of the compounds of present studies a medium peak at 3433 cm^{-1} for LHPT, a very strong peak at 3459 cm^{-1} for LVPT, a broad peak at 3496 cm^{-1} for LLPT, and a strong peak at 3460 cm^{-1} for LIPT are assigned to O-H asymmetric stretching vibration. Further, these vibrations may be overlapped with NH_3 asymmetric stretching. These vibrations are Raman inactive for all the compounds and for LAPT & BAPT these vibrations are both IR inactive. The weak vibrational bands observed at 915 cm^{-1} , 916 cm^{-1} , 915 cm^{-1} and 879 cm^{-1} in the Raman spectrum of LAPT, LLPT, LIPT and BAPT respectively are assigned to OH out of plane deformation. These vibrations are observed at 869 cm^{-1} and 871 cm^{-1} in the IR spectrum of LVPT and LIPT respectively.

The wave numbers of bands originating from scissoring deformation type of vibrations of water molecule are observed at 1614 cm^{-1} , 1607 cm^{-1} and 1589 cm^{-1} in IR spectrum and at 1605 cm^{-1} , 1600 cm^{-1} and 1598 cm^{-1} in Raman spectrum for LVPT, LLPT and LIPT respectively. These modes occur in the range of protonated amino group vibrations therefore may overlapped with NH_3^+ group vibrations. The bands near

600cm^{-1} can be assigned to wagging vibrations of water molecules and is sufficiently described in the literature [11]. Hence, the vibrational bands at 567 cm^{-1} both in IR and Raman spectrum of LVPT, the bands at 560 cm^{-1} in the IR spectrum and at 569 cm^{-1} in Raman spectrum of LLPT, the band at 577 cm^{-1} in IR spectrum and at 575 cm^{-1} in Raman spectrum are assigned to wagging vibrations of H_2O molecule. However, these vibrations may be overlapped with SO_3 asymmetric deformation.

4 Conclusion

The vibrational spectra of compounds are recorded for the range of $4000 - 400\text{ cm}^{-1}$. It is FT-IR and FT-Raman spectral analyses confirm the different functional groups present in the studied compounds. Its intensities and positions were discussed. The high intensity vibrational bands around 2950 cm^{-1} which is assigned to N- H...O vibrations are the evidence for the influence of hydrogen bonds in the analyzed structures.

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