

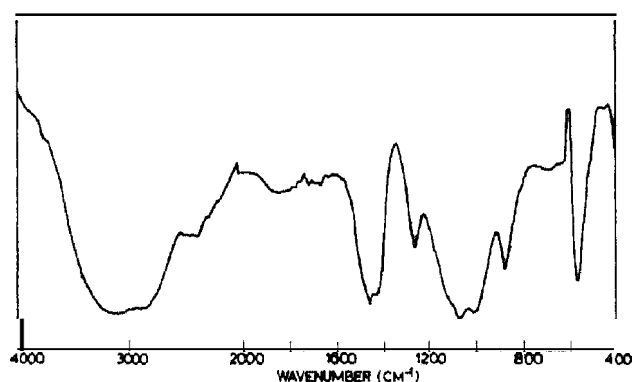
**Figure 2.** Raman spectra of the low frequency region of TAAP.

carried out separately, Here the internal modes are analysed to establish the symmetry of the polyatomic groups and their distortion to relate the structure with the ferroelectricity in TAAP.

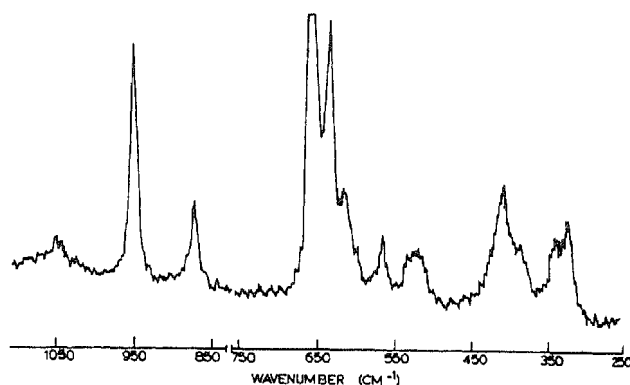
Figure 3 shows the IR spectrum of TAAP while figure 4 shows the Raman spectra of the internal modes.

#### *Te(OH)<sub>6</sub> vibrations*

The Te(OH)<sub>6</sub> group consists of vibrations due to TeO<sub>6</sub> octahedron and that of the O-H bonds. The octahedral TeO<sub>6</sub> has six vibrational modes:  $\nu_1(A_{1g})$  symmetric stretching,  $\nu_2(E_g)$  and  $\nu_3(F_{1u})$  asymmetric stretchings,  $\nu_4(F_{1g})$  asymmetric bending,  $\nu_5(F_{2g})$  symmetric bending and  $\nu_6(F_{2u})$  asymmetric bending. While  $\nu_1$ ,  $\nu_2$  and  $\nu_3$  are Raman active,  $\nu_3$  and  $\nu_4$  are IR active.  $\nu_6$  is inactive both in IR and Raman



**Figure 3.** Infrared spectra of internal mode region of TAAP.



**Figure 4.** Raman spectra of internal mode region of TAAP.

spectra. The TeO<sub>6</sub> symmetric stretching ( $\nu_1$ ) vibration is expected at 600–700 cm<sup>-1</sup>. The very strong line at 653 cm<sup>-1</sup> in the Raman spectrum is therefore assigned to this vibration. The doubly degenerate asymmetric stretching vibration ( $\nu_2$ ) is split into two lines and are observed at 610 and 632 cm<sup>-1</sup>. The asymmetric and symmetric bending modes  $\nu_4$  and  $\nu_5$  are observed in the region 300–350 cm<sup>-1</sup>. The asymmetric stretching mode ( $\nu_3$ ) vibration and asymmetric bending vibration by O–P–O of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and HPO<sub>4</sub><sup>2-</sup> lie in the same region and could not be identified unambiguously. It can be noticed that none of these lines are observed in IR spectra.

#### *Phosphate group vibrations*

The P–O(H) stretching vibrations of HPO<sub>4</sub><sup>2-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> are expected<sup>3</sup> in the region 800–1000 cm<sup>-1</sup>. The Raman lines observed at 948 and 878 cm<sup>-1</sup>, and the IR lines observed at 850, 970 cm<sup>-1</sup> are attributed to these vibrations. The Raman lines observed at 1048, 1060 cm<sup>-1</sup> and in IR at 1040 cm<sup>-1</sup> correspond to the P–O stretching vibrations of HPO<sub>4</sub><sup>2-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. A line at 1230 cm<sup>-1</sup> in IR is attributed to the P–O–H bending vibrations of the two phosphate groups. The lines observed in the Raman spectra in the region 382–410 cm<sup>-1</sup> and 510–560 cm<sup>-1</sup> are due to the asymmetric, symmetric and OPO bending mode vibrations. The O–H stretch is observed in the region 2600–3300 cm<sup>-1</sup>.

#### *NH<sub>4</sub> group vibrations*

The NH<sub>4</sub><sup>+</sup> ion is a tetrahedron having four vibrational modes and all the four appear in Raman and IR spectra due to its general position in the crystal. The symmetric and asymmetric stretching modes  $\nu_1$  and  $\nu_3$  appear as broad bands in the region 2800–3300 cm<sup>-1</sup> along with the O–H vibrations of

**Table 1** Vibrational frequencies of internal modes and their assignment to different groups

Raman	IR	Assignment
cm <sup>-1</sup>	cm <sup>-1</sup>	
320	-	$\nu_4(\text{TeO}_6)$ &
340		$\nu_5(\text{TeO}_6)$
382		OPO asy. bending modes of
410	-	$\text{H}_2\text{PO}_4^-$ , $\text{HPO}_4^-$
520		OPO sy. bending modes
535	540	of $\text{H}_2\text{PO}_4^-$ ,
564		$\text{HPO}_4^-$ & $\nu_3(\text{TeO}_6)$
610		
632	-	$\nu_2(\text{TeO}_6)$
653	-	$\nu_1(\text{TeO}_6)$
878	850	P-O(H) stretching vib. of
948	970	$\text{H}_2\text{PO}_4^-$ , $\text{HPO}_4^-$
1048	1040	P-O stretching vib. of $\text{HPO}_4^-$ ,
1060		$\text{H}_2\text{PO}_4^-$
1410	1390	
		$\nu_4(\text{NH}_4^+)$
1436	1440	
1682	1640	
		$\nu_2(\text{NH}_4^+)$
1789	1690	
2600	2400	$\nu_1$ & $\nu_3(\text{NH}_4^+)$
to	to	& $\nu(\text{N-H-O})$
3300	3400	stretching mode.

other groups present. The symmetric bending mode appears as two lines in the region 1682–1780 cm<sup>-1</sup> in Raman and 1640–1690 cm<sup>-1</sup> in IR. The asymmetric bending mode appears at 1410 and 1436 cm<sup>-1</sup> in Raman, and at 1390 and 1440 cm<sup>-1</sup> in IR. Table 1 shows the different frequencies observed in Raman and IR spectra and their assignment to different groups.

The structural analysis of this crystal<sup>1</sup> indicates that the PO<sub>4</sub> tetrahedron is distorted with relatively

large deviations in the P–O distances from the average values. These deviations have been suggested to be due to the possible presence of hydrogen bonds. The bands observed both in IR and Raman corresponding to the asymmetric bending mode of NH<sub>4</sub><sup>+</sup> show an upward shift of as much as 39 cm<sup>-1</sup> from the free ion frequency 1397 cm<sup>-1</sup>. This as well as the presence of a broad band in the region 2600–3300 cm<sup>-1</sup> in Raman and IR confirms the existence of hydrogen bonds of the type N–H–O corresponding to the N–O distances reported in the crystal structure.

The temperature variation of internal modes across the phase transition has been studied to look for any change in the spectra as a result of phase transition. However no significant changes have been observed. The resemblance of the properties of TAAP with TGS<sup>4</sup> predicts interesting temperature behaviour of lattice modes<sup>5</sup>. The detailed studies of polarized Raman spectra and the temperature variation of lattice modes and hydrogen bond region are in progress.

#### ACKNOWLEDGEMENT

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