# Raman and X-ray Investigations of Ferroelectric Phase Transition in NH<sub>4</sub>HSO<sub>4</sub>

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Supporting Information

**ABSTRACT:** Temperature-dependent Raman spectroscopy and X-ray diffraction studies have been carried out on NH<sub>4</sub>HSO<sub>4</sub> single crystals in the temperature range 77–298 K. Two structural transitions driven by the molecular ordering and change in crystal symmetries are observed below 263 and 143 K. These phase transitions are marked by the anomalies in the temperature dependence of wavenumber and fwhm of several internal vibrational modes. The Raman spectra and X-ray data enable us to understand the nature of the molecular ordering resulting in the ferroelectric phase below 263 K, sandwiched between two nonferroelectric phases. The crystal structure of the ferroelectric phase is determined correctly as *Pc*, which has



been earlier solved in *Ba* symmetry. The temperature dependent Raman and X-ray results suggest that the disorder to order transition leading to lower symmetry below 263 K is driven by the change in  $HSO_4^-$  ions and that below 143 K is driven by the change in both  $HSO_4^-$  and  $NH_4^+$  ions.

## INTRODUCTION

Ferroelectric materials have been a central theme in both fundamental sciences as well as in electronics in recent times.<sup>1</sup> Ferroelectricity is observed in numerous materials<sup>2-7</sup> including hydrogen bonded systems.<sup>8–13</sup> NH<sub>4</sub>HSO<sub>4</sub> belongs to the family of the hydrogen sulfate compound  $AHSO_4$ , where, A = Cs,  $NH_4$ , Rb, K, Na, which are interesting for their fast ion conducting property,<sup>14–17</sup> ferroelectricity, and structural phase transitions with temperature.<sup>18–20</sup> These materials are characterized by a strong  $O-H \cdots O$  hydrogen bond between  $HSO_4^-$  ions forming dimer and chain structures. From early dielectric measurements, it was surmised that at normal pressure, NH4HSO4 undergoes two phase transitions, one at  $T_{c1} = 270$  K and the other at  $T_{c2} = 154$  K, respectively.<sup>20</sup> The first transition is associated with a large anomaly in dielectric constant, whereas a small anomaly was observed at the second transition temperature. At T<sub>c1</sub>, NH<sub>4</sub>HSO<sub>4</sub> undergoes paraelectric to ferroelectric transition and is second order in nature, whereas at  $T_{c2}$ , it goes through ferroelectric to nonferroelectric transition and is first order in nature as explained by Pepinsky et al.<sup>20</sup> The values of coercive field and spontaneous polarization were about 150 V/cm and  $0.4 \,\mu\text{C/cm}^2$  at 260 K, respectively.<sup>20</sup> The maximum value of spontaneous polarization was about 0.8  $\mu$ C/cm<sup>2</sup> just above 154 K, and it dropped to zero at that temperature, interestingly the compound showed a piezoelectric property until 77 K.<sup>20</sup> However, the mechanism of the transitions was not proposed by

Pepinsky et al. from their dielectric measurements. These phase transitions in NH<sub>4</sub>HSO<sub>4</sub> were also observed from specific heat measurements<sup>21</sup> and modulated differential scanning calorimetry.<sup>22</sup> The mechanism of the ferroelectric transition was explained as only due to the orientation of NH4<sup>+</sup> ions below the transition temperature.<sup>22</sup> It was also believed that the presence of hydrogen bonding in the crystal structure is also responsible for the ferroelectric transition in NH<sub>4</sub>HSO<sub>4</sub>.<sup>19</sup> The single crystal structures of NH<sub>4</sub>HSO<sub>4</sub> were solved at 293 and 192 K.<sup>23,24</sup> At 293 K, NH<sub>4</sub>HSO<sub>4</sub> is monoclinic, space group  $P2_1/c_1^{23}$ with eight formula units per unit cell. The asymmetric unit contains two crystallographically independent NH<sub>4</sub>HSO<sub>4</sub> units in which one HSO<sub>4</sub><sup>-</sup> ion is ordered, while the other is disordered. The structure has long polymeric  $O-H \cdots O$  hydrogen bonds between HSO<sub>4</sub><sup>-</sup> ions. The 192 K structure is also monoclinic, space group Ba, with sixteen formula units per unit cell and  $\hat{eta} \approx 90^\circ$  depicting pseudo orthorhombic features as explained by Nelmes.<sup>24</sup> The asymmetric unit contains four independent NH<sub>4</sub>HSO<sub>4</sub> units. While the structure in ferroelectric phase below 243 K was indexed by Pepinsky et al. to be monoclinic, space group *Pc*, with a = 14.26 Å, b = 4.62 Å, c = 14.80 Å, and  $\beta = 121.30^{\circ}$ , the structure below 154 K was also indexed in triclinic system, space

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**Figure 1.** (a, b, and c) Packing diagram of NH<sub>4</sub>HSO<sub>4</sub> at 293 K, 200 K, and 125 K (D = disordered, O = ordered). (d, e, and f) Showing O-H···O hydrogen bonds at 293 K, 200 K, and 125 K. NH<sub>4</sub><sup>+</sup> ions are in the layer formed by the O-H···O hydrogen bonds and are removed for the clarity of the figure.

group P1, with a = 14.24 Å, b = 4.56 Å, c = 15.15 Å,  $a \approx 90^{\circ}$ ,  $\beta = 123.40^{\circ}$ ,and  $\gamma \approx 90^{\circ}$  but remained unsolved.<sup>20</sup>

Raman spectroscopy is an ideal tool for capturing the dynamics and local structural changes in the viewpoint of vibrational frequencies whereas X-ray diffraction establishes the detail estimation of symmetry and periodicity in a crystal during phase transition. Although the phase transitions in NH<sub>4</sub>HSO<sub>4</sub> were established from various experimental techniques,<sup>20–22</sup> the mechanism and dynamics of transitions were not understood very well. In this article, we have studied the internal vibrations of molecular units and the crystal structures of NH<sub>4</sub>HSO<sub>4</sub> as a function of temperature by using temperature dependent Raman spectroscopy and X-ray diffraction to understand the dynamics of the structural phase transition across the transition temperatures. Earlier reported structures<sup>24</sup> suggest strong orthorhombic pseudo symmetry in ferroelectric phase; however, we report the crystal structure of NH<sub>4</sub>HSO<sub>4</sub> in ferroelectric phase below the first transition temperature to be Pc showing conventional monoclinic symmetry and the lowest temperature phase to be *P*1 showing triclinic symmetry.

## EXPERIMENTAL SECTION

Single crystals of  $NH_4HSO_4$  were grown by slow evaporation from aqueous solution containing equimolar quantities of  $(NH_4)_2SO_4$  and  $H_2SO_4$ . The quality of the crystal used for the experiment was checked under a polarized optical microscope. The temperature evolution of the Raman spectra of  $NH_4HSO_4$ was recorded in the  $180^\circ$  backscattering geometry, using a 532 nm excitation from a diode pumped frequency doubled Nd:YAG solid state laser (model GDLM-5015 L, Photop Suwtech Inc., China) and a custom-built Raman spectrometer equipped with a SPEX TRIAX 550 monochromator and a liquid nitrogen cooled CCD (Spectrum One with CCD 3000 controller, ISA Jobin Yovn).<sup>25</sup> Laser power at the sample was  $\sim$ 8 mW, and a typical spectral acquisition time was 3 min. The spectral resolution chosen was 2 cm<sup>-1</sup>. The temperature was controlled with an accuracy of (±0.1 K) by using a temperature-controller (Linkam TMS 94) equipped with a cooling stage unit (Linkam THMS 600). The spectral profile was fitted using Lorentzian functions with the appropriate background.

For single crystal X-ray data collections, the crystal was mounted inside a close-ended Lindemann glass capillary. X-ray diffraction data were collected on a Bruker AXS SMART APEX CCD diffractometer. The X-ray generator was operated at 50 kV and 35 mA using Mo  $K_{\alpha}$  radiation. For all of the measurements, 606 frames per set were collected using SMART<sup>26</sup> in four different settings of  $\varphi$  (0°, 90°, 180°, and 270°) with an  $\omega$  scan at  $-0.3^{\circ}$  intervals and with a counting time of 5s, while keeping the sample to detector distance at 6.054 cm and  $2\theta$  value fixed at  $-25^{\circ}$ . The data were processed using the SAINT-PLUS<sup>26</sup> protocol, and an empirical absorption correction was applied using the package SADABS<sup>27</sup> followed by XPREP<sup>26</sup> to determine the space group. The structures were solved and refined by using the SHELX-97<sup>28</sup> program present in the WinGX<sup>29</sup> suite. The conventional R factor, the weighted R factor wR, and the goodness of fit *S* are based on  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is

Table 1. Crystallographic Data

temp	293 K (disorder)	200 K (order)	125 K (order)
chemical formula	NH <sub>4</sub> HSO <sub>4</sub>	NH <sub>4</sub> HSO <sub>4</sub>	$NH_4HSO_4$
formula weight (mr)	115.12	115.12	115.12
a (Å)	14.393(5)	14.288(3)	14.096(5)
b (Å)	4.600(2)	4.571(1)	4.5953(2)
c (Å)	14.416(5)	14.305(3)	14.381(3)
$\alpha$ (deg)	90	90	89.980(1)
$\beta$ (deg)	117.997(5)	117.842(3)	117.149(5)
$\gamma$ (deg)	90	90	90.028(2)
crystal system	monoclinic	monoclinic	triclinic
space group	P21/c	Pc	P1
volume (Å <sup>3</sup> )	842.7(5)	826.1(3)	824.8(5)
Z	8	8	8
density (g cm $^{-3}$ )	1.815	1.851	1.856
radiation type	X-ray Mo K $_{\alpha}$	X-ray Mo ${\rm K}_{\alpha}$	X-ray Mo K $_{\alpha}$
crystal form, color	block, colorless	block, colorless	block, colorless
crystal size (mm)	$0.50 \times 0.50 \times 0.40$	0.50  imes 0.50  imes 0.40	0.50  imes 0.50  imes 0.40
diffractometer	Bruker SMART CCD area detector	Bruker SMART CCD area detector	Bruker SMART CCD area detector
data collection method	heta and $arphi$ scans	heta and $arphi$ scans	heta and $arphi$ scans
absorption correction	SADABS	SADABS	SADABS
R <sub>int</sub>	0.0367	0.0368	0.0366
$\theta_{\min,\max}$	1.65, 26.35	1.66, 26.37	1.59, 26.37
$R[F^2 > 2\sigma(F^2)]$	0.0509	0.0350	0.0843
goof (S)	1.108	1.051	1.149

used only for calculation of the *R* factor and is not relevant to the choice of reflections for refinements. In situ low-temperature measurements were carried out with an attached OXFORD cryosystem, maintaining a cooling rate of 60 K/h by using a temperature controller with liquid-N<sub>2</sub> flow.

## RESULTS AND DISCUSSION

Crystal Structure. The structure of NH<sub>4</sub>HSO<sub>4</sub> determined at 293 K confirms the details of the earlier report<sup>23</sup> and is isostructural to RbHSO<sub>4</sub><sup>11,19,30,31</sup> and belongs to the monoclinic crystal system, space group  $P2_1/c$  with Z = 8 [see Figure 1a, Supporting Information S1, and Table 1]. All atoms in the structure are at general crystallographic positions (4e; Wyckoff), with two crystallographically independent NH<sub>4</sub>HSO<sub>4</sub> units in the asymmetric unit, among which one NH<sub>4</sub>HSO<sub>4</sub> unit has disorder in the HSO<sub>4</sub><sup>-</sup> moiety. The sulfate ions have the usual tetrahedral coordination; however, the angles have small deviations from the tetrahedral values for the ordered  $SO_4^{2-}$  unit, while that for the disordered  $SO_4^{2-}$  unit, the deviations are large. There are extensive strong  $O-H\cdots O$  hydrogen bond networks between HSO<sub>4</sub><sup>-</sup> ions forming long polymeric chain structures in both the ordered and disordered units [Figure 1d]. In fact, the hydrogen-bonded chains are formed along the *b* crystallographic axis by translational symmetry. In addition to O-H···O hydrogen bonds, there are also  $N-H\cdots O$  hydrogen bonds present in the structure, which help in stabilizing the crystal packing. Upon cooling to 200 K in situ on the single-crystal X-ray diffractometer at a ramp rate of 60 K/h, keeping the temperature steady for 30 min and checking the CCD images at regular intervals, a structural phase transition to a space group Pc is observed, with Z = 8 [Figure 1b, Supporting Information S2, and Table 1]. It is of interest to note that RbHSO<sub>4</sub>, which is



Figure 2. Room temperature Raman spectra of  $NH_4HSO_4$  in the frequency range 350-3500 cm<sup>-1</sup>.

analogous to NH<sub>4</sub>HSO<sub>4</sub>, also exhibits a ferroelectric phase transition to space group *Pc* below 258 K.<sup>11,19,31</sup> The asymmetric unit contains four independent NH<sub>4</sub>HSO<sub>4</sub> units, with all atoms at general crystallographic positions (2a; Wyckoff). The hydrogen bonding features remain similar to the room temperature structure, infinite polymeric chains; however, all the NH<sub>4</sub>HSO<sub>4</sub> units are ordered in the low temperature phase [Figure 1e]. It is to be noted that the structure at 192 K was earlier solved by Nelmes<sup>24</sup> in the monoclinic system, with space group *Ba* by considering a = 24.48(4) Å, b = 4.58(2) Å, c = 14.75(3) Å, and  $\beta = 90.00^{\circ}(5)$ showing pseudo symmetry; however, we have determined it in the conventional monoclinic symmetry with a = 14.288(3) Å, b = 4.571(1) Å, c = 14.305(3) Å, and  $\beta = 117.842^{\circ}(3)$ . With further cooling to 125 K, we observed another phase transition to a space



Figure 3. (a) Temperature evolution of S-O-H and O-S-O bending mode frequencies of  $NH_4HSO_4$  and (b) fwhm of the respective bending modes in the temperature range 77–298 K.

group *P*1, with Z = 8 [Figure 1c and Table 1]. The asymmetric unit contains eight ordered NH<sub>4</sub>HSO<sub>4</sub> units. The hydrogen bonding features remain similar to the room temperature and 200 K structures [Figure 1f].

**Raman Scattering.** The sulfate and ammonium ions, with tetrahedral  $(T_d)$  symmetry, have four Raman active normal modes each, namely, symmetric stretching mode  $v_1$ , the doubly degenerate symmetric bending mode  $v_2$ , the triply degenerate asymmetric stretching mode  $v_3$ , and the triply degenerate asymmetric bending mode  $v_4$ .<sup>32</sup> The room temperature Raman modes of NH<sub>4</sub>HSO<sub>4</sub> were reported only in the frequency range 350–1300 cm<sup>-1</sup>.<sup>37</sup> Here, we recorded the Raman spectra of NH<sub>4</sub>HSO<sub>4</sub> in the range 350–3600 cm<sup>-1</sup> at room temperature, which is shown in Figure 2. All the Raman active modes in NH<sub>4</sub>HSO<sub>4</sub> at 298 K are assigned based on the information available in the literature.<sup>32–36</sup> The internal modes in these regions are divided into five groups of frequencies: (i) S–O–H, O–S–O bending (400–850 cm<sup>-1</sup>), (ii) symmetric S–OH

stretching  $(850-900 \text{ cm}^{-1})$ , (iii) symmetric and asymmetric S-O stretching  $(950-1350 \text{ cm}^{-1})$ , (iv) symmetric and asymmetric N-H bending  $(1350-1800 \text{ cm}^{-1})$ , and (v) symmetric and asymmetric N-H stretching  $(3000-3200 \text{ cm}^{-1})$ . Along with these above fundamental group frequencies, we also observed frequencies that are arising from  $O-H\cdots O$  hydrogen bonds as well as combination modes and overtones of the S-O and N-H vibrations. These frequencies are derived by considering  $SO_4^{2-}$  and  $NH_4^+$  as distorted tetrahedra. It is established that, at room temperature, the structure contains two crystallographically independent NH4HSO4 units of which one unit is disordered at the HSO<sub>4</sub><sup>-</sup> moiety. This phenomenon is well reflected in the symmetric S–O stretching region of the Raman spectra collected at room temperature [Figure 2]. The symmetric S-O stretching region has two intense and well-defined Raman peaks centered at 1013 and 1042 cm<sup>-1</sup> and a plateau centered at  $1033 \text{ cm}^{-1}$  at 298 K. The frequencies at 1013 and 1033 cm<sup>-1</sup> are assigned to the symmetric S–O stretching of the disordered unit because of its two different possible orientations, whereas the 1041  $\text{cm}^{-1}$  mode is assigned to the S–O stretching frequency of the ordered unit.

Temperature evolutions of the Raman spectra of NH<sub>4</sub>HSO<sub>4</sub> for all the regions in the temperature range 77–298 K are shown in Figures 3-7. Significant changes are observed in the spectral features around phase transition temperatures ( $T_{c1} = 263$ K and  $T_{c2}$  = 143K) and are in agreement with the structural phase transition observed in the single crystal X-ray diffraction reported in the present work and also with the earlier dielectric studies by Pepinsky et al.<sup>20</sup> Here, we present the temperature dependence of the vibrational frequencies and a few selected full width at half maximum (fwhm) of different molecular subunits of NH4HSO4 to explain the dynamics driving the phase transitions. Figure 3 represents the temperature evolution of S-O-H and O-S-O bending modes of HSO4- ions in the spectral range 400- $850 \text{ cm}^{-1}$ . This spectral range consists of six frequencies centered at 405, 416, 444, 573, 582, and 609 cm<sup>-1</sup> at room temperature. With a decrease in temperature from 298 K approaching the first transition temperature  $T_{c1} = 263$  K, very small changes in the vibrational frequencies are observed, whereas at  $T_{c2}$  = 143 K, an abrupt increase in the frequencies at 416, 444, and 609  $\text{cm}^{-1}$  and an abrupt decrease in the frequency at 582 cm<sup>-1</sup> are observed [Figure 3a]. Similarly, the fwhm of all the six normal modes exhibit very small changes around the first transition temperature; however, significant changes are observed around the second transition temperature [see Figure 3b]. Figure 4 represents the temperature dependent symmetric S-OH and S-O stretching mode frequencies and their fwhm in the spectral range 850-1350 cm<sup>-1</sup>. As the temperature is lowered, the symmetric S-OH mode centered at 800 cm<sup>-1</sup> slowly hardens, and in addition to that, a new mode appeared at 886 cm<sup>-1</sup> around  $T_{c1}$ . Both these modes harden as the temperature is lowered from  $T_{c1}$ toward  $T_{c2}$ . At  $T_{c2}$ , we observe a slight deviation in the temperature dependence of modes but no discontinuities.

The 970 cm<sup>-1</sup> mode could be arising from the combination of the S–O–H and O–S–O bending modes and is based on the observation of Moreira et al.<sup>33</sup> The temperature dependence of the wavenumber of this mode presents a small anomaly near  $T_{c1}$ , and above  $T_{c2}$ , we observed an appearance of a new mode at 984 cm<sup>-1</sup>. Both the frequencies harden until the temperature approached 77 K. A very interesting behavior is displayed by the symmetric S–O stretching modes. The 1033 cm<sup>-1</sup> mode, which arises from the disordered S–O bonds, abruptly decreased and



Figure 4. (a and b) Temperature evolution of symmetric S-OH and S-O stretching mode frequencies of NH<sub>4</sub>HSO<sub>4</sub> and (c and d) fwhm of the respective stretching modes in the temperature range 77-298 K.

tends toward the 1013 cm<sup>-1</sup> mode at the same time the mode at 1042 cm<sup>-1</sup> shows a discontinuous jump at  $T_{c1}$ . As the temperature is lowered to  $T_{c2}$ , the mode due to the disordered S–O unit softens and gets closer to the counterpart (the other disorder mode) without merging, while the frequency from the ordered S–O unit hardens and continues the trend until 143 K. The second transition is spread over a temperature range of 20 K and is observed for all the modes. It is observed that the stretching modes of the ordered S–O units and disordered one behave differently; mainly, the difference in frequency increases as it approaches the  $T_{c2}$ . Before  $T_{c2}$  itself, we observe the appearance

of a new mode, and beyond  $T_{c2}$ , the three modes are now reduced to two modes with a much lesser frequency difference. The fwhm of the three modes rapidly decreases from  $T_{c1}$  to  $T_{c2}$  before they disappear to give rise to two modes.

In the case of the asymmetric stretching modes of sulfate ions, very small to no change are observed at  $T_{c1}$  at the same time large changes are observed at  $T_{c2}$ . The temperature dependent Raman spectra, the vibrational frequencies, and the fwhm of the asymmetric S–O stretching modes are shown in the Figure 5. Four Raman active mode frequencies centered at 1162, 1207, 1246, and 1279 cm<sup>-1</sup> are observed for the asymmetric S–O stretching



Figure 5. (a and b) Temperature evolution of asymmetric S–O stretching mode frequencies of  $NH_4HSO_4$  and (c) fwhm of the respective stretching modes in the temperature range 77–298 K.

vibration. At  $T_{c2}$ , we also observe the appearance of four new modes centered at 1152, 1190, 1223, and 1294 cm<sup>-1</sup>. The temperature dependent bending modes of ammonium ions are shown in Figure 6. In this region, we observed two frequencies centered at 1444 and 1675 cm<sup>-1</sup> at room temperature. In this case, we also observe very small anomalies in both the frequencies at  $T_{c1}$ , but large anomalies are observed at  $T_{c2}$ . Similarly, the fwhm also showed a large change around  $T_{c2}$  [See Figure 6b]. Here, too, we observe the appearance of two new modes centered at 1461 and 1692 cm<sup>-1</sup> at  $T_{c2}$ .

Raman spectra collected in the region  $2000-3600 \text{ cm}^{-1}$  are assigned as N–H and O–H group vibrations (Figure 7). The interpretation of unpolarized Raman spectra in this region is difficult because it contains the superposition of broad bands due to the hydrogen bonding and are hard to deconvolute. Vibrational frequencies in the range 2200 to  $2600 \text{ cm}^{-1}$  could be due to the coupling of the stretching modes of (SO)–H with the external modes of SO3–O(H) groups and are not very sensitive to the temperature, which is based on the earlier report on RbHSO<sub>4</sub>.<sup>34</sup> With a decrease in temperature, the frequencies in this region decreased slightly and split across the transition temperature  $T_{c2}$ . The spectral region  $2600-3000 \text{ cm}^{-1}$  contain

peaks that could be due to the  $\nu(OH) \cdots O$  mode and the first overtone of ammonium bending mode  $\nu_2(NH_4^+)$  at 1444 cm<sup>-1</sup>, which is based on the reports on KHSO<sub>4</sub><sup>17</sup> and NaNH<sub>4</sub> SO<sub>4</sub>·2H<sub>2</sub>O.<sup>33</sup> With the lowering in the temperature, the frequencies gradually decreased until 77 K. Raman modes in the region 3000–3600 cm<sup>-1</sup> are probably due to the symmetric and asymmetric ammonium stretching modes as well as the first overtone of the ammonium bending mode  $\nu_4(NH_4^+)$  at 1675 cm<sup>-1</sup>, again based on the report on NaNH<sub>4</sub>SO<sub>4</sub>·2H<sub>2</sub>O.<sup>33</sup> When the temperature is lowered, these regions have interesting changes. There is evolution of new modes across the transition temperatures, and the modes are sharp. The modes generally soften with a decrease in temperature.

On the basis of the Raman and single crystal X-ray studies presented here, we observed three phases of NH<sub>4</sub>HSO<sub>4</sub> evolving with decreasing temperature. Above  $T_{c1}$ , the phase is  $P2_1/c$ , between  $T_{c1}$  and  $T_{c2}$ , it is Pc, and below  $T_{c2}$ , it is P1. In this, we discuss the temperature dependence of the wavenumber and fwhm of the vibrational modes showing substantial changes in the vicinity of the ferroelectric phase transition at  $T_{c1} = 263$  K and nonferroelectric transition at  $T_{c2} = 143$  K. The changes in the temperature behavior of some of the internal modes and their





Figure 6. (a) Temperature evolution of N–H bending mode frequencies of  $NH_4HSO_4$  and (b) fwhm of the respective bending modes in the temperature range 77–298 K.

fwhm associated with the HSO4<sup>-</sup> and NH4<sup>+</sup> ions certainly disclose the existence of structural modifications that occur at  $T_{c1}$  and  $T_{c2}$ . In the paraelectric phase  $(P2_1/c)$ , the total polarization of the crystal is zero due to the presence of the center of inversion. Below  $T_{c1}$ , there is a transition from  $P2_1/c$  to Pcleading to a nonzero polarization arising due to the lack of a center of inversion. An interesting observation is that symmetric stretching modes show a substantial change across  $T_{c1}$ , whereas the bending and asymmetric stretching modes do not show changes or show subtle changes at this temperature. Interestingly the converse is true across  $T_{c2}$ . This is important as it demonstrates that  $T_{c1}$  introduces changes in the covalency of the bonds because of ordering across the transition. In general, the effect of covalency on the vibrational parameters of symmetric stretching modes is significant when compared to the other modes.  $T_{c2}$ is more due to tilting of the tetrahedra because of further lowering of the crystal symmetry to P1 and hence would affect bending and asymmetric stretching and increasing the number of modes. The ordering in the structure below the first and second



Figure 7. Temperature evolution of Raman bands associated with the N-H and O-H region.

transition temperatures can be seen clearly from the fwhm of the vibratonal modes. From our Raman and X-ray data, it is ruled out that the ferroelectric phase transition is not due to the orientation of  $\rm NH_4^+$  ions as we did not observe any anomaly in the temperature dependent N-H vibrational mode frequencies and their fwhm [see Figures 6 and 7]. By analyzing the symmetric S-O stretching modes [Figure 4b], it is evident that the disordered sulfate groups are becoming similar in their orientation, which increases the ordering beyond the first transition temperature leading to the ferroelectric property. The abrupt decrease in the fwhm [Figure 4d] signifies the ordering across the ferroelectric transition.

The second phase transition below  $T_{c2}$  where the material lost the ferroelectric property could be explained by analyzing the temperature dependent symmetric S–O stretching frequency of the HSO<sub>4</sub><sup>-</sup> ion. In the paraelectric phase, the difference between the symmetric S–O stretching frequency occurring from two different crystallographically HSO<sub>4</sub><sup>-</sup> ions is less. As the temperature is lowered below  $T_{c1}$ , the compound attained the ferroelectric phase, and the difference between the symmetric S–O stretching frequency increases gradually until the second transition temperature, which could be due to strong coupling of modes. Below  $T_{c2}$ , the compound lost its ferroelectricity; hence, the difference between the symmetric S–O stretching frequency reduced drastically, which could be due to less coupling of modes leading to only the piezoelectric property.

We have tried solving and refining the 125 K structure in both P1 and P1 symmetry. However, the structure could be solved and refined only with space group P1. The earlier piezoelectric study by Pepinsky et al.<sup>20</sup> reported that the NH<sub>4</sub>HSO<sub>4</sub> showed piezoelectric current until 77 K ;the structure was indexed to the P1 space group similar to that of our observation. From group theoretical analysis, it is known that the point group P1 shows the piezoelectric property, while P1 does not. There are two crystallographically independent formula units in the asymmetric unit of the  $P2_1/c$  space group; however, when the temperature is reduced to the first transition temperature ( $T_{c1}$ ), the space group changes to *Pc*, and the number of independent formula units in

the asymmetric unit are now 4, leading to the appearance of a new Raman active mode in the S-OH symmetric stretching region [see Figure 4a,b]. The compound in the *Pc* phase has four different crystallographically independent formula units in the asymmetric unit similar to the case of  $P\overline{1}$ . We have noticed the appearance of new Raman active peaks in the S-O asymmetric stretching region [see Figure 5a,b], NH<sub>4</sub> bending region [see Figure 6a], and symmetric and asymmetric NH<sub>4</sub> stretching region [see Figure 7], which indicates that there is an increase in the number of independent formula units in the asymmetric unit. Since in the case of P1 the asymmetric unit contains 8 independent formula units, it would have more Raman modes compared to the Pc phase. Conversely, if we assume the structure is  $P\overline{1}$ , we do not expect an increase in Raman active modes as the number of formula units in the asymmetric unit remain the same for both the Pc and  $P\overline{1}$  space groups.

The appearance of new Raman bands [Figures 5a,b, 6a, and 7] below  $T_{c2}$  is interpreted as deformations within the crystallographically independent molecular units because of symmetry breaking. The analysis of the Raman spectra also provides evidence for proton ordering in O–H···O and N–H···O hydrogen bonds, which can be noticed by analyzing the O–H and N–H vibration of the temperature dependent Raman spectra. The decrease in frequency with a decrease in temperature suggests that the hydrogen atoms are moving away from the O and N atoms toward acceptor atoms. The sharp peaks at lower temperatures suggest that protons are ordered and are fixed in space. This induced splitting of modes due to a reduction in symmetry.

# CONCLUSIONS

The temperature-dependent Raman and X-ray investigation are able to explain the dynamics of the phase transitions in NH<sub>4</sub>HSO<sub>4</sub>. The appearance of new Raman modes and anomaly in both vibrational frequencies and fwhm at transition temperatures are attributed to the structural changes in the crystal during the transitions. The ferroelectric phase transition in NH<sub>4</sub>HSO<sub>4</sub> at T<sub>c1</sub> is mainly driven by ordering in the  $HSO_4^-$  ions. It is clear that the internal S-OH and S-O symmetric stretching modes and their fwhm throw light on the ordering mechanism during the ferroelectric phase transition, whereas the large changes in asymmetric stretching and bending vibrational modes in addition to symmetric S-O stretching modes suggest the lowering of symmetry in the nonferroelectric phase transition. The Raman and X-ray studies are able to capture the three phases of NH<sub>4</sub>HSO<sub>4</sub> with the lowering of temperature and suggest a role of hydrogen bonding and proton ordering, contrary to what had been proposed by earlier experiments.

# ASSOCIATED CONTENT

**Supporting Information.**  $P2_1/c$  and Pc *hkl* plots. This material is available free of charge via the Internet at http://pubs. acs.org.

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