

RAMAN AND INFRARED SPECTRA OF AMMONIUM SELENATE AND LITHIUM AMMONIUM SELENATE

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ABSTRACT

The Raman and infrared absorption spectra of $(\text{NH}_4)_2\text{SeO}_4$, $(\text{ND}_4)_2\text{SeO}_4$ and $\text{Li}(\text{NH}_4)\text{SeO}_4$ have been recorded at 300°K ; while the spectra of the non-deuterated compounds have been recorded at 110°K also. $(\text{NH}_4)_2\text{SeO}_4$ crystal exhibits 33 Raman lines, while $\text{LiNH}_4\text{SeO}_4$ shows 30 Raman lines at 300°K . Proper assignments have been given to the observed vibration frequencies. The SeO_4^{--} ions and the $(\text{NH}_4)^+$ ions are found to be highly distorted in these selenates. There is lowering of the N-H vibration frequencies due to hydrogen bonding. The present spectroscopic investigations do not reveal the existence of any phase transition in these selenates in the temperature region investigated.

1. INTRODUCTION

AMMONIUM compounds are known to exhibit interesting physical properties and have formed the subject-matter for detailed spectroscopic investigations. Simple compounds like the ammonium halides possess a λ -type transition point and studies on their Raman and infrared spectra have thrown considerable light on the behaviour of the NH_4^+ ions in the neighbourhood of the transition temperature. Some ammonium compounds show dielectric anomalies as the temperature is lowered. Ammonium sulphate is a classic example of such a compound possessing a ferroelectric transition. Although many of the crystalline sulphates have been shown to be isomorphous with the analogous crystalline selenates, ammonium selenate is an exception. At room temperature ammonium sulphate crystallises in the orthorhombic system, while the corresponding selenate crystallises in the monoclinic system and is not known to exhibit ferroelectric properties at low temperatures. A detailed spectroscopic study of ammonium selenate crystal at different temperatures would be of great interest. Although the infrared spectrum of ammonium selenate has been recorded by Borenzelli *et al.* (1965) its Raman spectrum has so far not been investigated. The Raman and infrared absorption spectra of a single crystal of ammonium selenate and

also of its deuterated analogue have therefore been recorded at room temperature and at liquid nitrogen temperature and the results are presented here.

Like sulphates, selenates form many double selenates of the general formula $AA'SeO_4$ or $A_2B(SeO_4)_2$ with or without water of crystallisation, where A and A' are monovalent cations and B is a divalent cation. The infrared spectra of many double selenates of the formula $A_2B(SeO_4)_2 \cdot nH_2O$ including those containing ammonium ion have recently been reported by Brown and Ross (1970). The Raman effect data are available only for one crystalline double selenate, namely, $[Na_2Zn(SeO_4)_2]$ Brown and Ross (1970). The infrared and Raman spectra of $NaNH_4SeO_4 \cdot 2H_2O$ a double salt belonging to the group $AA'SeO_4 \cdot nH_2O$ have been studied recently by one of us (Sankaranarayanan, 1972). In continuation of this work, we have now studied the Raman and infrared absorption spectra of a single crystal of lithium ammonium selenate ($LiNH_4SeO_4$) both at room temperature and at liquid nitrogen temperature and the results are also presented here.

2. EXPERIMENTAL DETAILS

Transparent crystals of ammonium selenate of size, $3 \times 2 \times 2$ mm., were prepared by the method of slow evaporation from aqueous solutions of the salt. Single crystals of the double salt ($LiNH_4SeO_4$) was prepared by slow evaporation of a mixture of the saturated solutions of the individual selenates containing the component salts in their molar proportions. Deuteration of the samples were carried out by repeated crystallisation from solutions of the ordinary crystals in heavy water.

The Raman spectra of $(NH_4)_2SeO_4$, and $LiNH_4SeO_4$ were recorded with λ 2537 Å mercury resonance radiation as exciter both at 300° K and at 110° K, while that of $(ND_4)_2SeO_4$ was recorded at 300° K, only.

The infrared absorption spectra of the selenates at 300° K and 110° K and of $LiND_4SeO_4$ at 300° were recorded using a Carl-Zeiss UR-10 instrument. The lattice spectrum could not be recorded with this instrument and therefore the region covered was from 400 to 4000 cm^{-1} only. The solid samples were imbedded in KBr pellets for absorption measurements.

For low temperature work, the specimen in the form of a plate for Raman effect studies, and in the form of a KBr pellet for infrared studies was placed in the cavity of a copper block which was screwed on to the bottom of the inner jacket of a metal dewar which was provided with suitable

windows for illumination and observation. Cooling was achieved by conduction from the coolant liquid to the specimen through the copper block. With liquid nitrogen as the coolant the specimen attained a temperature of 110° K only when the exciting radiation was turned on.

3. RESULTS

Microphotometric records of Raman spectra of $(\text{NH}_4)_2\text{SeO}_4$ and $\text{LiNH}_4\text{SeO}_4$ taken at 300° K and 110° K are reproduced in Figs. 1 and 3. The spectrum of ND_4SeO_4 taken at 300° K is given in Fig. 2. The posi-

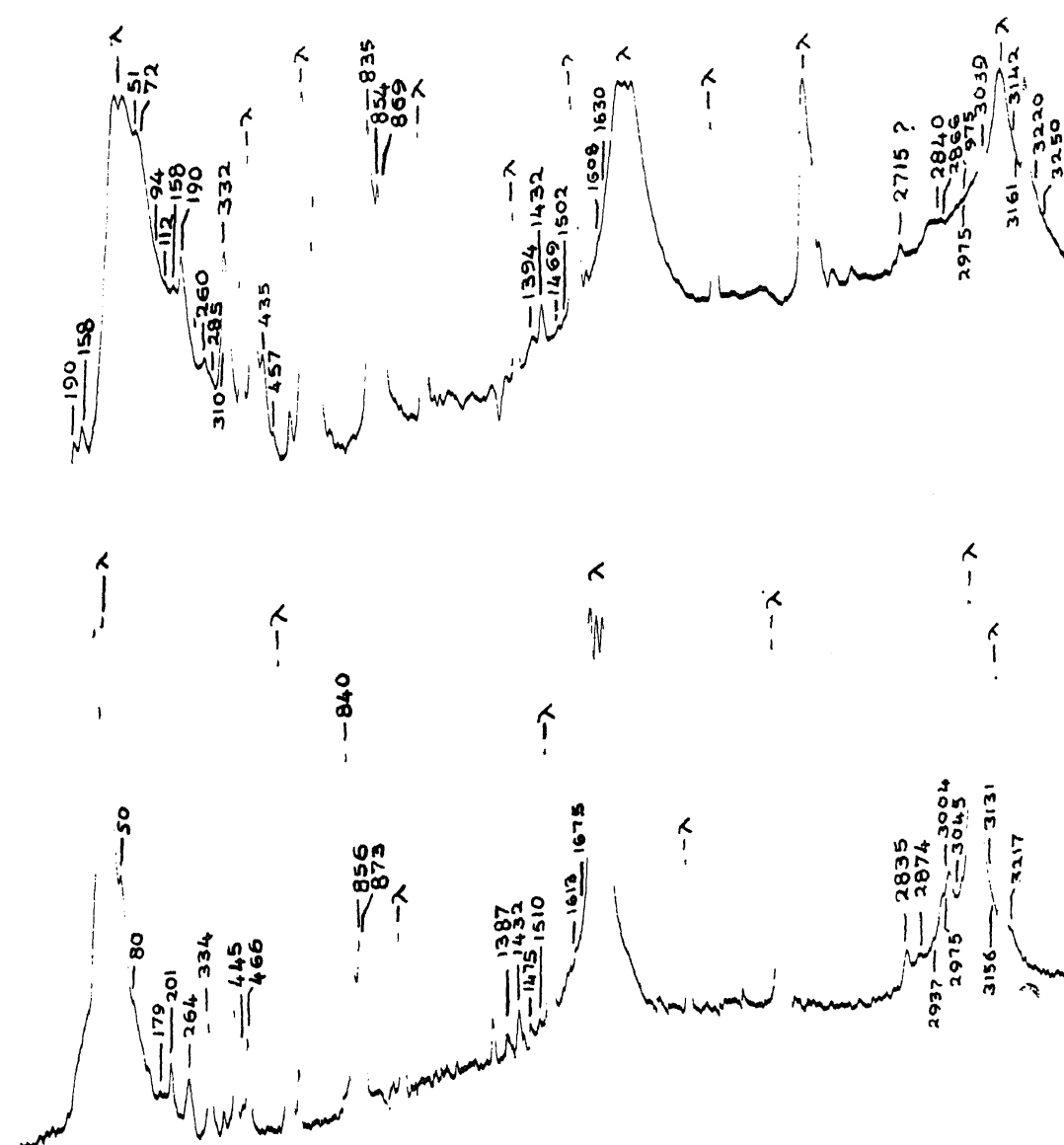


FIG. 1. Raman spectrum of ammonium selenate: (a) at Room temperature, (b) at Low temperature.

tions of the Raman lines together with the frequency shifts from the exciting line are marked in Figs. 1 to 3. The infrared absorption spectra of the selenates are reproduced in Fig. 4.

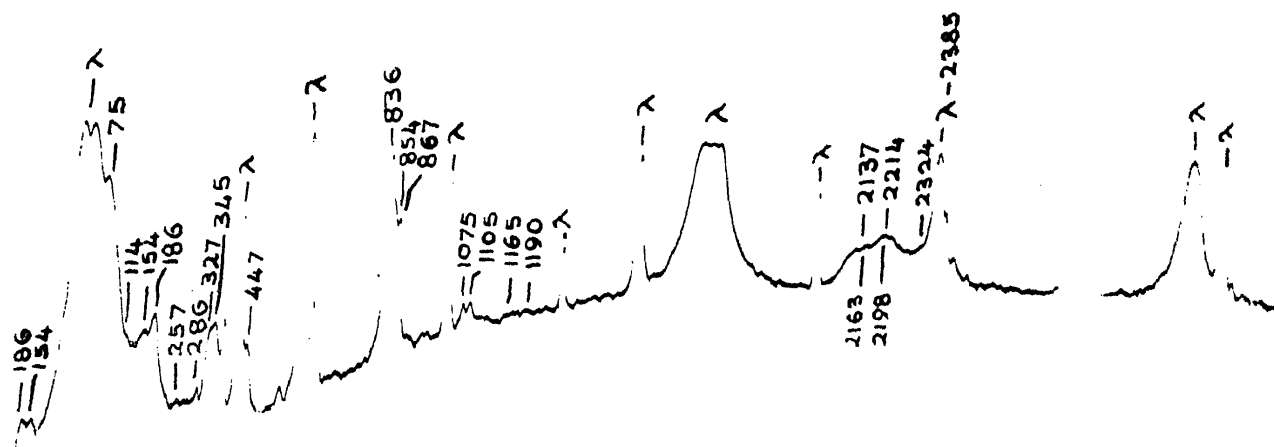


FIG. 2. Raman spectrum of deuterated ammonium selenate

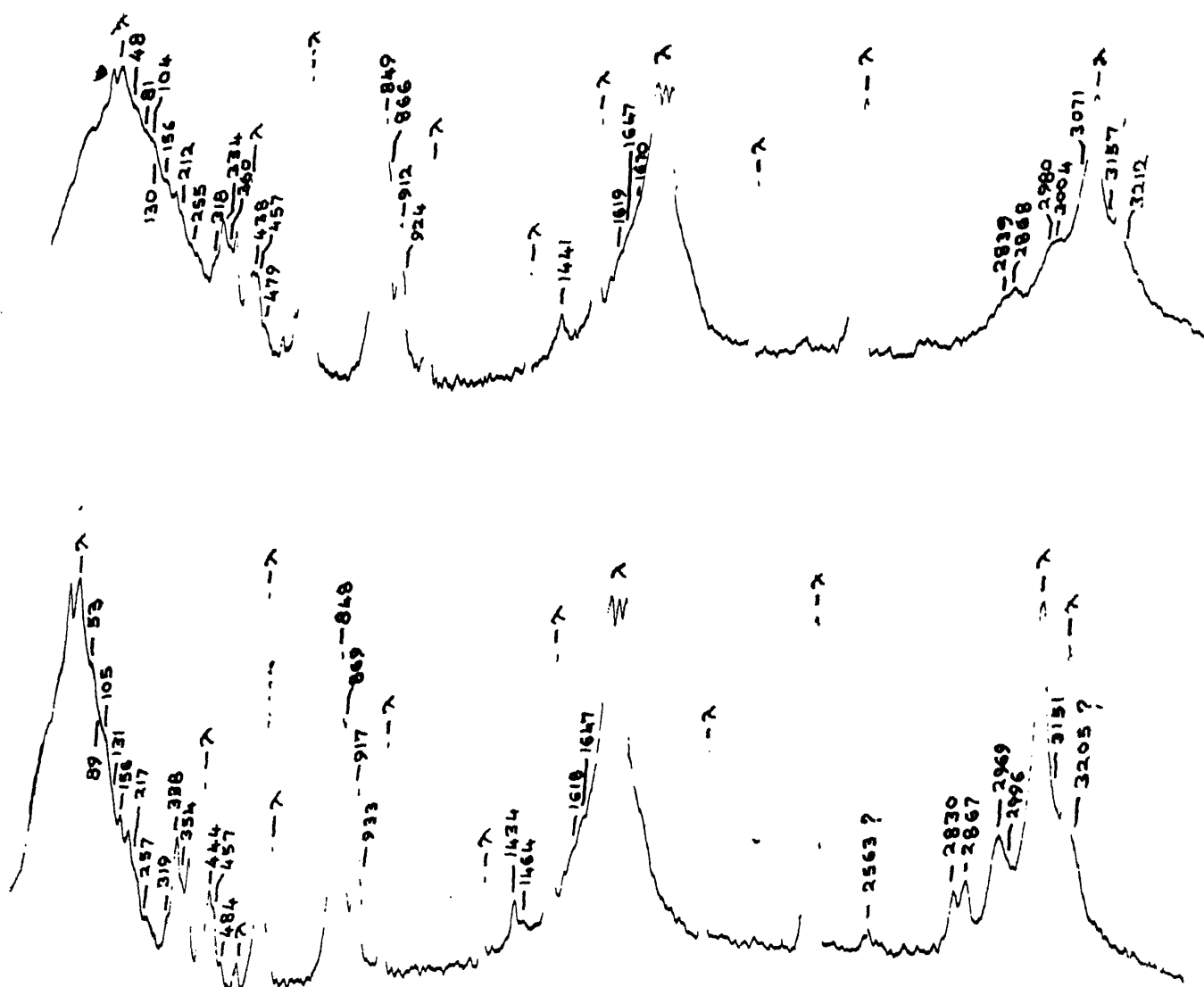


FIG. 3. Raman spectrum of lithium ammonium selenate: (a) at Room temperature, (b) at Low temperature.

The Raman frequency shifts and the frequencies corresponding to the peaks in the infrared absorption spectra are listed in Tables I and II. The figures given within brackets are visual estimates of the relative intensities of the lines. The spectrum of NH_4SeO_4 exhibits 33 Raman lines at 300°K , while $\text{LiNH}_4\text{SeO}_4$ shows only 30 Raman lines. The Raman line with frequency shift of 411 cm^{-1} was identified on the anti-Stokes side as it fell near a mercury line on the Stokes side.

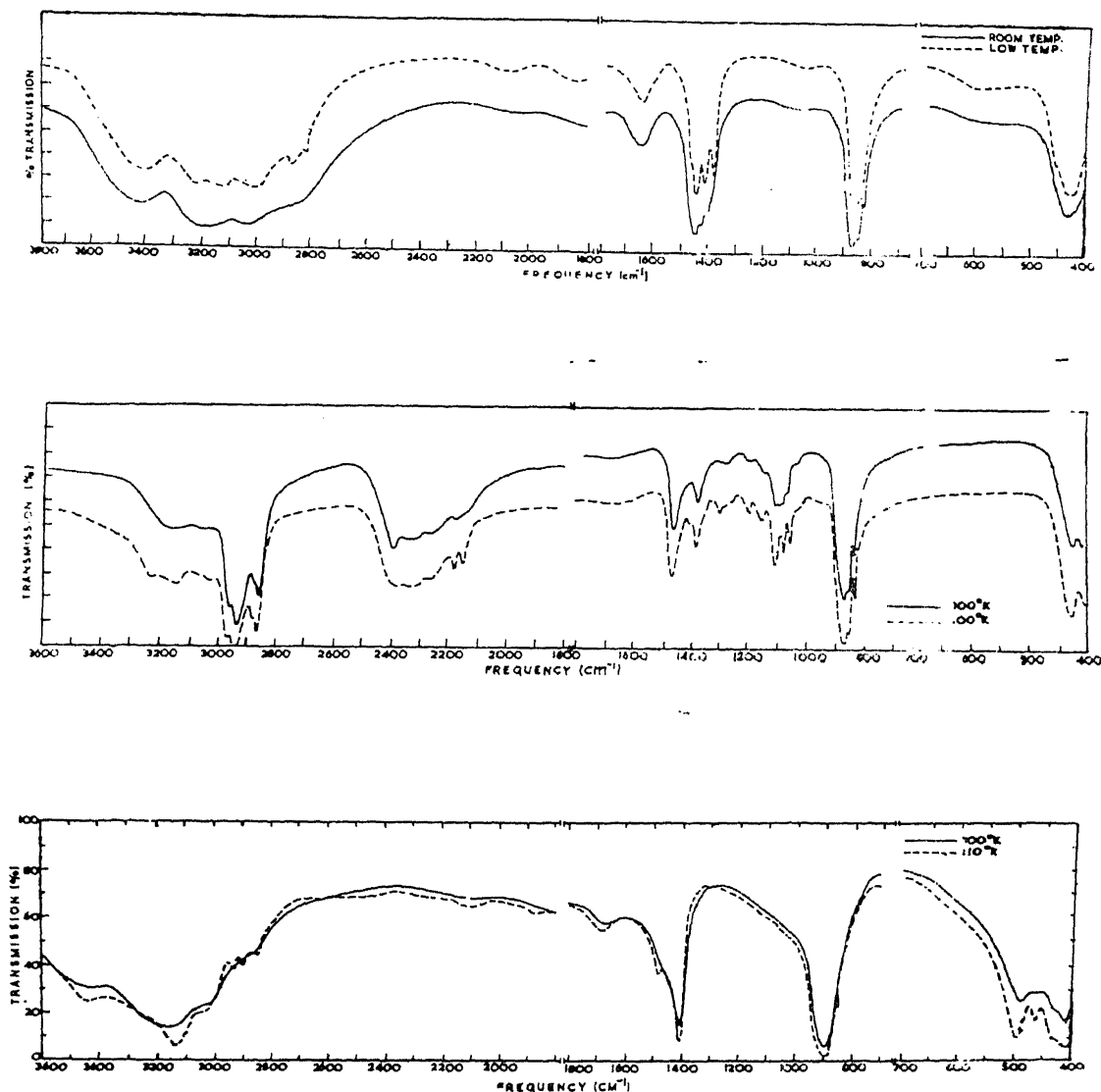


FIG. 4. Infrared spectra of (a) Ammonium selenate, (b) Deuterated ammonium selenate, (c) Lithium ammonium selenate.

4. DISCUSSION

The crystal structure of $(\text{NH}_4)_2\text{SeO}_4$ was analysed by Hasegawa *et al.* (1963). It belongs to the space group $C2/m$ with $a = 12.30\text{ \AA}$, $b = 6.37\text{ \AA}$,

TABLE I
Vibrational frequencies of ammonium selenate (in cm⁻¹)

Raman			Infrared			110° K (Deuterated)	Assignments
300° K	110° K	300° K (Deuterated)	300° K	110° K	300° K (Deuterated)		
51 (1)	50 (2)						
72 (2)	80 (1)	75 (1)					
94 (0)							
112 (0)		114 (1)					
158 (2)	179 (1)	154 (2)					
190 (3)	201 (2)	186 (2)					
260 (2)	264 (2)	257 (0) ?					NH ₄ ⁺ torsion
285 (0)		286 (0)					
310 (2)		327 (1)					
332 (7)	334 (5)	345 (3)					ν ₂ SeO ₄
411 (1)			415 (s)	417 (s)	410 (s)	408 (s)	
435 (3)	445 (1)	447 (2)	428 (s)	427 (s)	428 (s)	430 (s)	ν ₄ SeO ₄
457 (2)	466 (3)		450 (m)	455 (m)			
835 (10)	840 (10)	836 (10)	835 (m)	840 (m)	836 (m)	838 (m)	ν ₁ SeO ₄
854 (4)	856 (5)	853 (5)	855 (s)	858 (s)	855 (s)	855 (s)	
869 (6)	873 (6)	867 (6)	877 (s)	880 (s)	880 (s)	875 (s)	ν ₃ SeO ₄
					1065 (m)	1060 (m)	
		1075 (2)			1080 (m)	1080 (m)	
					1092 (m)	1092 (m)	ν ₄ ND ₄ ⁺
		1105 (2)			1100 (m)	1111 (m)	
		1165 (0)			1160 (m)	1160 (m)	
		1190 (0)			1205 (m)	1205 (m)	
					1280 (m)	1280 (m)	ν ₂ ND ₄ ⁺
						1303 (m)	
1394 (2)	1387 (2)		1410 (s)	1402 (s)			
1432 (3)	1442 (3)		1432 (s)	1432 (s)			
1469 (1)	1473 (1)		1459 (s)	1465 (s)			ν ₄ NH ₄ ⁺
1502 (1)	1510 (1)			1485 (m)			
1608 (0)	1613 (0)						
1630 (0)	1675 (0)		1655 (w)	1670 (w)			ν ₂ NH ₄ ⁺
				1860 (w)			
				2100 (w)			Combinations
		2137 (3)			2150 (s)	2145 (s)	
		2163 (3)				2175 (s)	
		2198 (4)					N-D stretching
		2214 (3)					
		2324 (2)			2262 (2)	2250 (s)	
		2385 (0) ?			2320 (s)	2325 (s)	
					2392 (s)	2385 (s)	
2462 ?							
2535 ?							
2715 ?							
2840 (3)	2835 (3)			2830 (s)			
2866 (3)	2874 (2)		2880 (s)	2870 (s)			
				2895 (s)			
	2937 (2)		2940 (s)				
2975 (4)	2975 (3)						
	3004 (5)						N-H stretching (Hydrogen bonded)
3039 (5)	3045 (2)		3040 (s)	3020 (s)			
3142 (3)	3131 (2)		3140 (s)	3080 (s)			
3161 (2)	3156 (1)		3170 (s)	3130 (s)			
3220 (2)	3217 (2)		3230 (s)	3180 (s)			
3250 (2)				3220 (s)			

TABLE II

Vibrational frequencies of lithium ammonium selenate (in cm^{-1} .)

RAMAN		INFRARED		ASSIGNMENTS
300° K	110° K	300° K	110° K	300° K (deuterated)
48 (1)	53 (1)			
81 (0)	89 (0)			
104 (1)	105 (1)			
130 (0)	131 (0)			
156 (2)	156 (2)			
212 (2)	217 (2)			
255 (2)	251 (1)			NH ₄ ⁺ torsion
318 (2)	319 (2)			
334 (5)	338 (5)			ν_2 SeO ₄
360 (3)	354 (3)			
411 (0)	411 (0)	410 (s)	412 (s)	413 (2)
438 (3)	444 (3)	430 (s)	435 (s)	430 (s) ν_4 SeO ₄
457 (3)	457 (2)	460 (s)	465 (s)	463 (s)
479 (2)	484 (2)	492 (s)	500 (s)	487 (s) Li-O stretching
849 (10)	848 (10)	857 (m)	858 (m)	858 (m) ν_1 SeO ₄
866 (8)	869 (8)	870 (s)	870 (s)	882 (s)
912 (6)	917 (6)	895 (s)	895 (s)	897 (s) ν_3 SeO ₄
924 (5)	933 (5)	923 (s)	920 (s)	920 (s)
				1072 (m)
				1115 (m) ν_4 ND ₄ ⁺
				1155 (w)

TABLE II—*Contd.*

RAMAN		INFRARED		ASSIGNMENTS
300° K	110° K	300° K	110° K	300° K (deuterated)
				1248 (w)
				1335 (w) ν_2 ND ₄ ⁺
1412 (1)		1410 (s)	1410 (s)	1401 (w)
1441 (2)	1434 (3)	1442 (s)	1453 (s)	1443 (w) ν_4 NH ₄ ⁺
	1464 (2)	1480 (s)	1487 (s)	
1619 (0)	1618 (0)			1538 (w)
1647 (0)	1647 (0)			ν_2 NH ₄ ⁺
1670 (0)		1680 (w)	1680 (w)	
		1860 (w)	1880 (w)	combinations
		2070 (w)	2100 (w)	
				2160 (m)
				2240 (s)
				2320 (s) N-D stretching
				2362 (s)
				2412 (s)
	2563 (3) ?			
2839 (2)	2830 (3)	2860 (m)	2847 (m)	
2868 (2)	2867 (4)		2905 (m)	
2980 (4)	2969 (6)	2940 (m)	2932 (m)	
3004 (4)				N-H vibrations (hydro-
3071 (6)		3030 (s)	3050 (s)	gen bonded)
3157 (3)	3151 (3)	3170 (s)	3135 (s)	
3212 (2) ?	3205 (3) ?		3230 ?	

s = strong;

m = medium;

w = weak.

$c = 7.74 \text{ \AA}$ and $\beta = 115.5^\circ$ and $Z = 4$. The structure of $\text{LiNH}_4\text{SeO}_4$ has not been analysed so far. Preliminary X-ray diffraction studies carried out in this laboratory indicated that it belonged to the orthorhombic system. Because of the low symmetry of the crystal structures of the selenates studied here, one finds in general a one to one correspondence between the Raman lines and the infrared absorption maxima.

Vibrations of the SeO_4^{--} ions

The free SeO_4^{--} ion in solution has four Raman frequencies (Siebert, 1954), namely, $\nu_1 = 832 \text{ cm}^{-1}$, $\nu_2(2) = 345 \text{ cm}^{-1}$, $\nu_3(3) = 879 \text{ cm}^{-1}$ and $\nu_4(3) = 412 \text{ cm}^{-1}$. The figures inside brackets indicate the corresponding degeneracies. The Raman frequencies corresponding to the internal vibrations of the SeO_4^{--} ion observed in the crystal spectra are grouped into ν_1 , ν_2 , ν_3 and ν_4 modes and are given in Table III.

TABLE III
Raman frequencies of SeO_4^{--} ion

Mode	Free State	$(\text{NH}_4)_2\text{SeO}_4$		$(\text{ND}_4)_2\text{SeO}_4$		$\text{LiNH}_4\text{SeO}_4$	
		300° K	110° K	300° K	300° K	110° K	
ν_1	832	835	840	836	849	848	
		310		327	318	319	
$\nu_2(2)$	345	332	334	345	334	338	
					360	354	
$\nu_3(3)$	879	854	856	853	866	869	
		869	873	867	912	917	
					924	913	
$\nu_4(3)$	412	411			411	411	
		435	445	447	438	444	
		457	466		457	457	

The general appearance of the selenate spectrum is in good agreement with the low site symmetry of the SeO_4^{--} ion, namely, C_1 in these compounds. In many alkaline earth selenates Brown and Ross (1970) reported additional

bands in infrared absorption spectra in the ν_3 ($\sim 870 \text{ cm}^{-1}$) region due to correlation splitting as well as due to $2\nu_4$. Similar correlation splitting is not observed in the Raman and infrared spectra of $(\text{NH}_4)_2\text{SeO}_4$, $(\text{ND}_4)_2\text{SeO}_4$ and $\text{LiNH}_4\text{SeO}_4$. In the case of $(\text{NH}_4)_2\text{SeO}_4$, the frequencies of ν_2 and ν_3 are lower than the corresponding frequencies of the free ion, whereas they are higher in the double selenate. The mean frequencies of the four modes in the double selenate are appreciably higher than those in ammonium selenate and also in sodium ammonium selenate (Sankaranarayanan, 1972). This behaviour can be attributed to the strong interaction of the Li^+ ions on the oxygen atoms of the SeO_4^{--} ions.

As is to be expected, there is a slight increase in the values of the frequencies as the temperature is lowered; but there is no indication of any change in site symmetry at the low temperature. As the temperature is lowered there is a reversal of intensities of the Raman lines at 435 and 457 cm^{-1} in $(\text{NH}_4)_2\text{SeO}_4$. The infrared spectra at 110° K exhibit more fine structure as compared to those at 300° K (see Fig. 4). Deuteration does not change the values of the SeO_4^{--} frequencies appreciably. The number of Raman lines recorded with the deuterated sample is less than that with the ordinary sample. This is attributed to the poor spectrogram obtained with the former as the crystals were very small in size.

Spectrum of the $\text{NH}_4^+/\text{ND}_4^+$ Ions

All the Raman lines with frequency shifts greater than 1350 cm^{-1} appearing in the spectra of $(\text{NH}_4)_2\text{SeO}_4$ and $\text{LiNH}_4\text{SeO}_4$ and above 1050 cm^{-1} in the spectra of the deuterated compounds have been attributed to the internal oscillations of the $\text{NH}_4^+/\text{ND}_4^+$ group. The Raman lines corresponding to the vibrations of the NH_4^+ ion appearing in the spectra of $(\text{NH}_4)_2\text{SeO}_4$ and $\text{LiNH}_4\text{SeO}_4$ are grouped under the modes ν_1 , ν_2 , ν_3 and ν_4 of the free ion and are listed in Table IV. The Raman lines corresponding to the symmetric and antisymmetric N-H oscillations (ν_1 and ν_3 modes) fall on either side of two fairly intense mercury lines. Consequently their frequency shifts and intensities could not be accurately estimated.

In the spectra of $(\text{NH}_4)_2\text{SeO}_4$ and of $\text{LiNH}_4\text{SeO}_4$, the degeneracies of ν_1 , ν_3 and ν_4 modes of NH_4^+ ion are completely removed. In these selenates the NH_4 tetrahedra should be highly distorted unlike those in $(\text{NH}_4)_2\text{SO}_4$ (Torrie *et al.*, 1972) and in ammonium halides. The fact that the ν_1 and ν_3 modes of NH_4^+ ion appear as broad bands and that there are Raman lines with frequency shifts as low as 2840 cm^{-1} suggests the presence of strong

TABLE IV
Raman frequencies of KH_4^+/ND_4^+ ion

Mode	Free State	$(NH_4)_2SeO_4$		$(ND_4)_2SeO_4$		$LiNH_4SeO_4$	
		300° K	110° K	300° K	300° K	110° K	
ν_1		2840	2835	2137	2839		
		2866	2874	2163	2868		
	3033		2937				
	(2114)	2975	2975	2198	2980	2969	
			3004	2214	3004		
ν_2 (2)		3039	3045		3045		
	1685	1608	1613	1165	1619	1618	
	(1215)	1630	1675	1190	1647	1647	
					1670		
		3142	3131				
ν_3 (3)	3135	3161	3156	2324	3157	3151	
	(2346)	3220	3217	2385	3212	3205	
		3250					
ν_4 (3)		1394	1387	1075	1412	1434	
	1397	1432	1442	1105	1441		
	(1065)	1469	1475			1464	
		1502	1510				

(N-H...O) hydrogen bonds in these selenates. Although correlation curve of N-H frequency *versus* N...O distance for the quadrivalent N is not available in the literature, on the basis of the known curve for NH_3^+ ion (Krishnan and Krishnan, 1964) one can assign the Raman line at about 2840 cm^{-1} to a N...O distance of about 2.8 \AA . The existence of three such Raman lines below 3033 cm^{-1} is indicative of the presence of hydrogen bonds of different lengths. The appearance of Raman lines above 3200 cm^{-1} is attributable to the possible existence of Fermi resonances of ν_3 and $2\nu_2$.

The general conclusions arrived at regarding NH_4^+ ions in the ordinary selenates are applicable to the deuterated selenates also.

On lowering the temperature there is no appreciable change in the NH_4^+ spectrum.

Li-O Mode

The spectrum of the double selenate exhibits an extra Raman line at 479 cm^{-1} at 300° K and there is a corresponding line in the infrared absorption spectrum which is absent in the spectrum of $(\text{NH}_4)_2\text{SeO}_4$. This line gains in intensity at low temperature and does not show any change on deuteration. It is therefore assigned to Li-O stretching vibration. Similar modes have been observed by Tarte (1965) in the infrared spectra of lithium carbonate and molybdenate. Since the structure of $\text{LiNH}_4\text{SeO}_4$ has not been analysed so far, one cannot give a quantitative estimate of the Li-O stretching frequency.

Lattice Spectrum

There are a large number of low frequency lattice vibrations in both the compounds, which are not much affected by temperature. The line at 158 cm^{-1} in $(\text{NH}_4)_2\text{SeO}_4$ and the one at 156 cm^{-1} in $\text{LiNH}_4\text{SeO}_4$ are the intense ones. These two should be attributed to the librational mode of SeO_4^{--} . There is a line at about $250\text{--}260\text{ cm}^{-1}$ in all the Raman spectra, which is assigned to NH_4^+ torsional mode.

In conclusion, the present spectroscopic investigations do not reveal the existence of any phase transition in $(\text{NH}_4)_2\text{SeO}_4$ and $\text{LiNH}_4\text{SeO}_4$ in the temperature region investigated here.

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