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Infrared, Single Crystal Raman, and SERS Spectra of $CH_3NH_3NaSeO_4 \cdot 6X_2O$ and $NaNH_4SeO_4 \cdot 2X_2O$ (X = H,D)

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IR and polarized Raman spectra of $CH_3NH_3NaSeO_4 \cdot 6H_2O$ (MASS), $NaNH_4SeO_4 \cdot 2H_2O$ (SAS), and their deuterated analogues are recorded and analyzed. In both the crystal symmetry of SeO_4^{2-} is lower than T_d. The symmetry of $CH_3NH_3^+$ is lower than C_{3v} and hydrogen bonding is strong in MASS. NH_4^+ is not rotating freely in the crystal lattice of SAS. SERS spectra are recorded in two types of silver colloids. Colloid 1 adsorbs MASS through the nitrogen atom of CH_3NH_3 group. There are two different adsorption sites for MASS in colloid 2. SAS is chemisorbed by colloid 2 through the oxygen atom of SeO_4^{2-}. Shifting and splitting observed for the internal modes of SeO_4^{2-} on adsorption are due to the reduced local symmetry of the ion. © 1994 Academic Press, Inc.

INTRODUCTION

At room temperature methyl ammonium sodium selenate hexahydrate (MASS), $CH_3NH_3NaSeO_4 \cdot 6H_2O$, is pyroelectric whereas sodium ammonium selenate dihydrate (SAS), $NaNH_4SeO_4 \cdot 2H_2O$ is ferroelectric (1). Dielectric studies on phase transitions in MASS have been carried out earlier (1). There are several reports (2–7) on the vibrational spectra of compounds containing ($CH_3NH_3^+$). In most of them phase transitions are governed by this group. Some physical properties of the crystal group $NaNH_4XO_4 \cdot 2H_2O$ (X = S, Se) have also been investigated (8–11).

Surface enhanced Raman scattering (SERS) spectra of inorganic acid radicals adsorbed on silver colloids have been reported by Greaves and Griffith (12). They observed rapid sol aggregation on addition of an aqueous solution of $K_3PO_4 \cdot H_2O$ or $Na_2HAsO_4 \cdot 7H_2O$. The color of the colloid changed from yellow through brown to blue with the Ag–O stretching band at 237 cm^{-1}. Also, an additional band appeared in the electronic spectrum at 560 nm. Although there is a recent report (13) on the SERS spectrum of SO_4^{2-} adsorbed on silver surface, the related selenate group is not yet studied. SERS spectral studies of MASS and SAS are expected to give information regarding the nature of adsorption and orientation of the adsorbed species on the metal surface. To elucidate the vibrational energy levels of MASS and SAS, their IR and polarized Raman spectra are also recorded and analyzed.

EXPERIMENTAL

Single crystals of MASS are synthesized by the chemical reaction of CH_3NH_2, H_2SeO_4, and Na_2SeO_4 in the stoichiometric ratio (1). Crystals of SAS are grown by the evaporation of an aqueous solution of sodium selenate and ammonium selenate (8). The 5145-Å line of a Spectra Physics model 165 Ar^+ laser (power 100 mW) is used to record the polarized Raman spectra of MASS (Fig. 1) for the four orientations $a'(cc)a$, $b(cb)a$, $b(ab)a$, and $b(ac)a$. Polarized Raman spectra of SAS (Fig. 2) are recorded for the four orientations $z(yy)x$, $z(yz)x$, $z(xz)x$, and $z(xy)x$ where x, y, and z coincide with the crystallographic axes a, b, and c. A Spex Ramalog instrument with a double monochromator 1401 has been used throughout. IR spectra are recorded using a PE 882 (4000–400 cm^{-1}) and PE 983 (4000–200 cm^{-1}) spectrophotometers with the samples in KBr and nujol. IR and Raman spectra of deuterated samples obtained by repeated recrystallization from D_2O are also recorded.

A silver colloid for SERS measurements has been prepared by two different methods. A greenish-yellow colloid (colloid 1) having a sharp absorption band at 400 nm is prepared (14) by adding a 1 mM solution of $AgNO_3$ drop-

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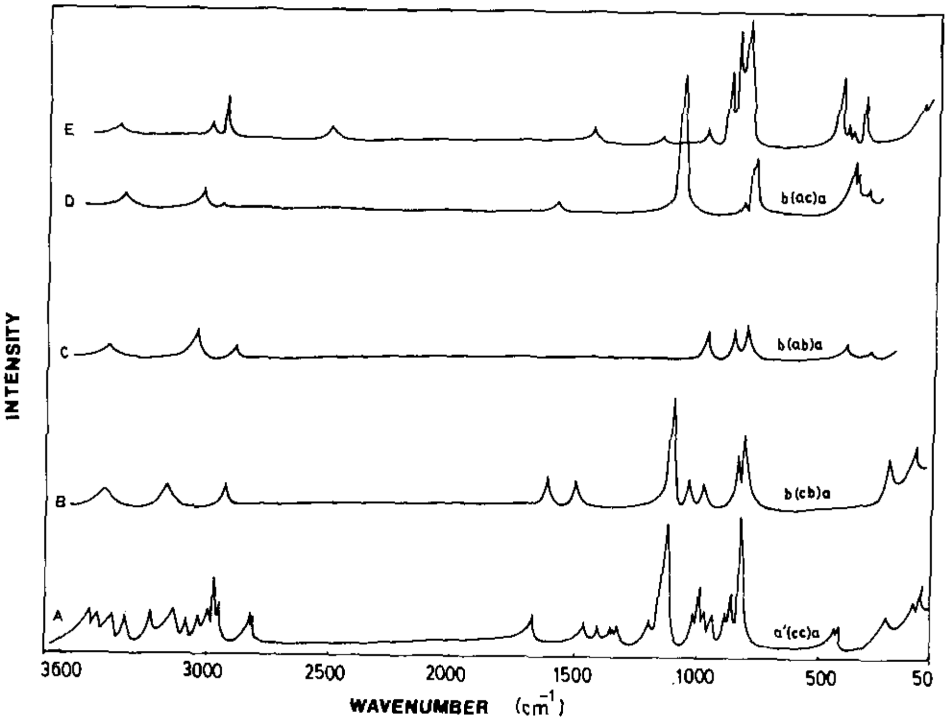


FIG. 1. (A), (B), (C), and (D) Raman spectrum of MASS single crystal and (E) deuterated MASS.

wise to a 2 m*M* solution of $NaBH_4$ with vigorous stirring until the volume ratio is 1 : 3. This colloid is stable and does not show precipitation or color change on standing for three months. A greenish-gray colloid (colloid 2) having a somewhat broad absorption band around 430 nm has been prepared (15) by adding 10 ml of a 1% solution of sodium citrate to a boiling solution of $AgNO_3$ (90 mg in 500 ml). This colloid is stable for two weeks. Chemicals

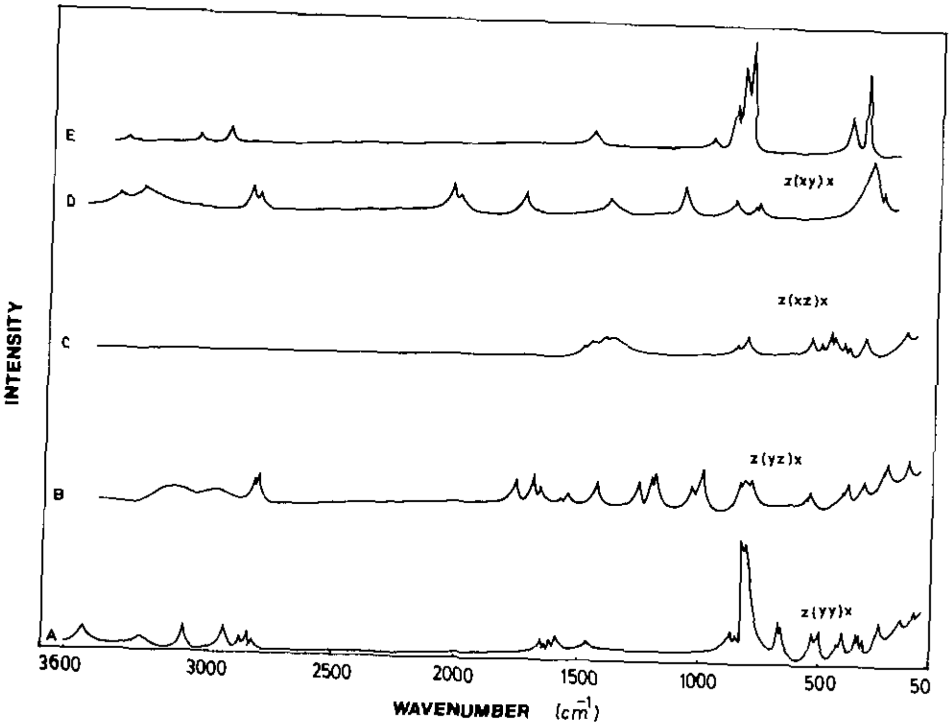


FIG. 2. (A), (B), (C), and (D) Raman spectrum of SAS single crystal and (E) deuterated SAS.

are procured from Sigma, St. Louis, MO, and deionized water has been used throughout.

Absorption spectra of silver colloids, MASS, SAS, and adsorbed MASS and SAS have been recorded on a UV-240 Shimadzu UV–Visible recording spectrophotometer. When MASS and SAS are adsorbed onto colloid 1, the color changes to light pink, the absorption band at 400 nm becomes broadened and shifts to 410 nm. Further, an additional very broad band for SAS and shoulder for MASS appears around 490 nm. In the case of colloid 2, the color changes to gray and the broad band around 430 nm becomes more broadened with center around 450 nm (SAS)/485 nm (MASS).

To record the SERS spectra, equal volumes of 10^{-3} *M* MASS (or SAS) and colloid 1 are mixed. The resulting solution is taken in a rectangular quartz cell and the Raman spectra have been recorded on a Dilor GMBH Z24 spectrometer with 40 mW laser power. In the case of colloid 2, a 1 : 2 mixture of 10^{-3} *M* MASS (or SAS) and the colloid are taken.

FACTOR GROUP ANALYSIS

MASS crystallizes in the hexagonal system $P6mm$ (C_{6v}^1) having two formula units in the unit cell (1). The tetramolecular unit cell (8) of SAS is orthorhombic $P2_12_12_1(D_2^4)$. The factor group analysis (16) predicts the distribution of irreducible representations at $k = 0$ as

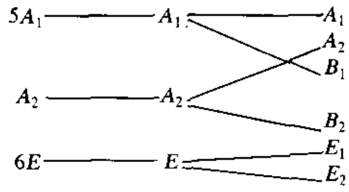
$$\Gamma_{\text{MASS}} = 20A_1(\text{R,IR}) + 11A_2(\text{IA}) + 21B_1(\text{IA}) + 11B_2(\text{IA}) + 31E_1(\text{R,IR}) + 32E_2(\text{R})$$

and

$$\Gamma_{\text{SAS}} = 51A(\text{R}) + 50B_1(\text{R,IR}) + 50B_2(\text{R,IR}) + 50B_3(\text{R,IR})$$

(R, Raman active; IR, infrared active; IA, inactive).

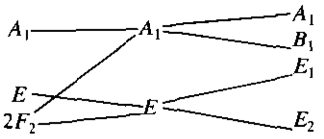
TABLE 1
Correlation Scheme for the Internal Vibrational Modes of $CH_3NH_3^+$ in MASS



f^r	Free ion symmetry C_{3v}	Site symmetry C_{3v}	Factor group symmetry C_{6v}	a_ξ	
10	$5A_1$	A_1	A_1	5	$(5A_1)$
			A_2	1	$(1A_2)$
			B_1	5	$(5A_1)$
2	A_2	A_2			
			B_2	1	$(1A_2)$
			E_1	6	$(6E)$
24	$6E$	E	E_2	6	$(6E)$

intramol.
$\Gamma_{CH_3NH_3^+} = 5A_1 + A_2 + 5B_1 + B_2 + 6E_1 + 6E_2$

TABLE 2
Correlation Scheme for the Internal Modes of SeO_4^{2-} in MASS



f^r	Free ion symmetry T_d	Site symmetry C_{3v}	Factor group symmetry C_{6v}	a_ξ	
			A_1	3	$(A_1 + \frac{2}{3} F_2)$
2	A_1	A_1	B_1	3	$(A_1 + \frac{2}{3} F_2)$
			E_1	3	$(E + \frac{4}{3} F_2)$
4	E				
12	$2F_2$	E	E_2	3	$(E + \frac{4}{3} F_2)$

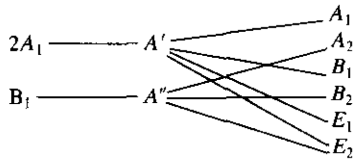
intramol.
$\Gamma_{SeO_4^{2-}} = 3A_1 + 3B_1 + 3E_1 + 3E_2$

($CH_3NH_3^+$), SeO_4^{2-} and Na atoms occupy C_{3v} site in MASS. Water molecules are in two different C_s sites. In SAS, all the atoms are in general sites. Therefore, the effects of lower site symmetry such as activation of inactive modes and splitting of degenerate modes are expected. Correlation schemes for the internal vibrational modes of $CH_3NH_3^+$, SeO_4^{2-}, H_2O in MASS and NH_4^+, SeO_4^{2-}, H_2O in SAS are given in Tables 1–5.

IR AND POLARIZED RAMAN SPECTRA OF MASS

Unambiguous assignment of bands above 3000 cm^{-1} is difficult as the vibrational frequencies of CH_3, NH_3^+, and H_2O occur in this region. Both correlation field splitting and Fermi resonance with overtones of δH_2O and δNH_3^+ may also add to this complexity. However, water bands could be separated by comparing with the spectra of the deuterated sample (Table 6). The bending modes of NH_3^+ observed at 1570 and 1510 cm^{-1} in IR have not shown an isotopic shift on deuteration which leads to the assumption that the NH_3^+ portion of MASS is unaffected by deuteration. The bands above 3100 cm^{-1} in both Raman (Fig.

TABLE 3
Correlation Scheme for the Internal Vibrational Modes of H_2O in MASS



f^r	Molecular symmetry $C_{2v} \xrightarrow{\sigma(yz)}$	Site symmetry $C_s \xrightarrow{\sigma_v}$	Factor group symmetry C_{6v}	a_ξ	
			A_1	4	$(4A_1)$
24	$2A_1$	A'	A_2	2	$(2B_1)$
			B_1	4	$(4A_1)$
12	B_1	A''	B_2	2	$(2B_1)$
			E_1	6	$(8A_1 + 4B_1)$
			E_2	6	$(8A_1 + 4B_1)$

intramol.
$\Gamma_{H_2O} = 4A_1 + 2A_2 + 4B_1 + 2B_2 + 6E_1 + 6E_2$

TABLE 4
Correlation Scheme for the Internal Vibrational Modes of NH_4^+/SeO_4^{2-} in SAS

f^r	Free ion symmetry T_d	Site symmetry C_1	Factor group symmetry D_2	a_ξ	
			A_1	9	$(A_1 + E + 2F_2)$
4	A_1		B_1	9	$(A_1 + E + 2F_2)$
8	E	A	B_2	9	$(A_1 + E + 2F_2)$
			B_3	9	$(A_1 + E + 2F_2)$
24	$2F_2$				

intramol.
$\Gamma_{NH_4^+/SeO_4^-} = 9A_1 + 9B_1 + 9B_2 + 9B_3$

1) and IR show a decrease in intensity and a new band appears at 2550 cm^{-1} in Raman on deuteration. Therefore, the bands above 3100 cm^{-1} are assigned to stretching modes of water. The ν_{as} NH_3^+ in this region could not be located in the deuterated spectrum.

The highest symmetry $(CH_3NH_3)^+$ can have is C_{3v}. Of the 18 internal vibrational modes, $5A_1 + A_2 + 6E$, the A_1 and E species are active in both Raman and IR and A_2 is inactive. Assignments are done by comparing with earlier reports on $(CH_3NH_3)^+$ vibrations (2–7). Stretching modes of CH_3 group usually occur in the region 2850–3000 cm^{-1}. In the present case as the methyl group is attached to a nitrogen atom the C–H bands may appear much below the expected region (17). Hence the IR band at 2700 cm^{-1} and Raman bands at 2825 and 2817 ($a'(cc)a$ orientation) are assigned to νCH_3. Also, $\delta_s CH_3$ may get shifted to higher values from the usually observed range 1370–1385 cm^{-1}. The splittings observed in the $a'(cc)a$ orientation (Table 6) for the vibrational modes $\nu_{as}CH_3(\nu_8)$, ρNH_3^+ (ν_{11}) and $\rho CH_3(\nu_{12})$ which belong to the E species indicate the symmetry of $CH_3NH_3^+$ is lower than C_{3v} in the crystal.

The presence of librational modes of water appearing at 620 and 640 cm^{-1} in IR which get shifted/reduced in intensity on deuteration shows that hydrogen bonding is fairly strong between the water molecules and NH_3^+ and oxygen atoms of SeO_4^{2-}. The presence of four Raman bands in the spectrum of the polycrystalline sample and six in the single crystal $a'(cc)a$ orientation are possibly due to the factor group splitting (Table 3).

The polarized Raman band around 835 cm^{-1} in Raman (Fig. 1) and the strong IR band at 850 cm^{-1} are assigned to the $\nu_1(A_1)$-symmetric stretching mode of SeO_4^{2-}. The splitting of 4 cm^{-1} observed in the $b(ac)a$ orientation for this nondegenerate mode is due to a correlation field effect. The $\nu_2(E)$-symmetric bending mode cannot split due to the lower site symmetry C_{3v} of the ion as can be seen from the correlation scheme (Table 2). Therefore, its splitting at about 45 cm^{-1} in both Raman [$b(ac)a$] and IR is also due to the correlation field effect. This comparatively large correlation field splitting may be due to strong hydrogen bonding (18). $\nu_3(F_2)$-asymmetric stretching and $\nu_4(F_2)$-asymmetric bending modes may split into two each due to lower site symmetry and into a maximum of four components due to both site symmetry and correlation field effects (Table 2). In the IR spectrum (Table 6), ν_3 mode is split into three components. The deuteration study does not show any decrease in intensity/shift of these components. These are therefore not due to the liberational modes of water. For the ν_4 mode no splitting is observed in IR.

TABLE 5
Correlation Scheme for the Internal Vibrational Modes of H_2O in SAS

f^r	Molecular symmetry C_{2v}	Site symmetry C_1	Factor group symmetry D_2	a_ξ	
			A_1	6	$(4A_1 + 2B_1)$
16	$2A_1$	A	B_1	6	$(4A_1 + 2B_1)$
8	B_1		B_2	6	$(4A_1 + 2B_1)$
			B_3	6	$(4A_1 + 2B_1)$

intramol.
$\Gamma_{H_2O} = 6A_1 + 6B_1 + 6B_2 + 6B_3$

IR AND POLARIZED RAMAN SPECTRA OF SAS

In the spectra of SAS also the assignment of bands above 3000 cm^{-1} is difficult as the vibrations of both NH_4^+ and H_2O appear in this region. The assignments are given based on the spectra of the deuterated sample and the results (19) of the isostructural $NaNH_4SO_4 \cdot 2H_2O$. The bands above 3100 cm^{-1} show either a decrease in intensity or a shift in frequency on deuteration (Table 6). In the bending mode region the band at 1690 disappears on deuteration. The assignment of the IR bands at 670 and 720 cm^{-1} to libration modes of water is justifiable as they disappear on deuteration. The downward shift of the stretching modes along with the appearance of a rocking mode of water shows that water molecules are hydrogen bonded.

$\nu_1 SeO_4^{2-}$ is split into a maximum of four components (Raman) in SAS (Fig. 2), whereas in MASS into two only. These are the maximum number of split components expected by correlation field effect. The ν_3 mode is split into three components in IR similar to that of MASS. These bands do not show a shift on deuteration. Therefore, they are the split components of ν_3. The assignments are given in Table 6. In both the compounds, activation of inactive modes, if any, is due to lower site symmetry of the ion (Tables 2 and 4).

TABLE 6
Vibrational Spectral Data (cm^{-1}) and Band Assignments[a]

MASS								SAS								
Raman						IR		Raman						IR		
$a'(cc)a$	$b(cb)a$	$b(ab)a$	$b(ac)a$	Powder hydrated	Powder deuterated	Hydrated	Deuterated	$z(yy)x$	$x(yz)x$	$z(xz)x$	$z(xy)x$	Powder hydrated	Powder deuterated	Hydrated	Deuterated	Assignment
3490w 3460w 3400w 3335w	3450wbr	3450wbr	3400wbr	3459mbr 3400sh 3283w 3142w	3461wbr 2550wbr	3460sbr		3530wbr 3290wbr 3112w	3200–3100wbr		3425wbr 3325wbr	3393wbr 3038wbr	3390vwbr	3240s	3380vwbr 2490w 2265w 2240w	$\nu H_2O/D_2O$
3245w 3142wbr 3102w	3190wbr	3090w	3072w			3140sh	3140m	2945w 2872vw	3100–3000wbr		2885w	3140w	3100w	3100s	3100s	ν_1 and ν_3 NH_4^+
								2845vw 2827vw	2827w 2814w		2850w	2860w	2978w	2880m	2935m	$\nu_7 - \nu_{as}NH_3^+$
3040w				3053w	3048w	3050s	3050s									$\nu_1 - \nu_s NH_3^+$
2997w 2973m	2960w		2998vw	2989s	2988m	2900sbr	2980s									$\nu_8 - \nu_{as}CH_3$
2968w		2930vw		2919w			2935m									$\nu_2 - \nu_s CH_3$
2825w 2817w				2838w		2700m	2700w									$\nu(N)$ CH_3, combination
						2580w 2450w 2170s 1730wbr					2065w 2035w			2220mbr 2040mbr		$\nu_2 + \nu_6 NH_4^+$ combinations of ν_4, ν_{11}, $\nu(C-N)$ of $CH_3NH_3^+$ and $2\nu_3 SeO_4^{2-}$
1668w	1636w		1630vw	1640vw	1200vw	1675s 1640s 1620sh	1235m 1155w	1662vw 1640vw 1620vw	1768w 1699w 1668w		1770w			1690m 1670m 1630w	1235m 1650wbr	$\nu_2 NH_4^+$ $\delta H_2O/D_2O$
						1570m	1560mbr									$\nu_9 - \delta_{as}NH_3^+$
	1520w					1510s		1596vw 1465vw	1592w 1565w	1520wbr	1425wbr			1540w 1450vs	1525wbr 1470sh	$\nu_3 - \delta_s NH_3^+$
							1485s		1560w 1550w 1438w	1485wbr 1430wbr 1400wbr	1405w		1480w	1410s 1390sh	1385vs	$\nu_4 NH_4^+$
1460w				1477w	1486w	1450s										$\nu_{10} - \delta_{as}$ CH_3

1410w						1375s	1390s									$\nu_4 - \delta_s CH_3$
1364w 1345w 1329w				1264vw					1266w 1262w 1251vw 1212w 1208w							$\nu_{11} - \rho\ NH_3^+$ combination
1198w 1120vs 1020w	1120vs 1054w		1120vvs	1002w	1200vw 1021w	1250m 1120m 1100m	1235m 1115m 1105m 1085w		1049w 1006w		1119w		1012w	1150w	1150w 1110w 1085sh 985w	ν(C–N) combination
996m 970w 942w	996w	997w					990w									$\nu_{12} - \rho CH_3$
889w 863m	857m	884w	860w	920w 890s	924s 890vs	930s 910s 870m	915vs 865vs	872w	849w	885w	910w	873m	920m 887s	920s 900m 880m	915vs 855vs	$\nu_3 SeO_4^{2-}$
833vs	833s	835w	837sh 833m	839vs	859vs	850vs	835m	843w 832vs 829vs	833w 830w 820w 808w	835w	825w	824vs	847vs	845s	835m	$\nu_1 SeO_4^{2-}$
						640vw 620m	600w	675w 660w 531w 505w	577vw 558vw	575w 525w 490w 472w				720m 670m	600w	RH_2O
442w 438w		443vw	408m	445wbr 407m	475s 446w 420w	420m	410sh 400vs	432w 413w	416vw 410w 403w	430w 420w		407m	435mbr	425s	410vs	$\nu_4 SeO_4^{2-}$
		335vw	400w 355w	358s	376s	385s 340sh		348w 336w 327w	341w	349w	340mbr	333s	368s	390m 350m	395vs	$\nu_2 SeO_4^{2-}$ $\nu_6 NH_4^+$
235w 118w 79w	235w 120w			127w	140w		240sh 225m	248w 161w 110w	252w 245w 150w	181w	292w	156w		240w	235m	External modes

[a] Relative intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

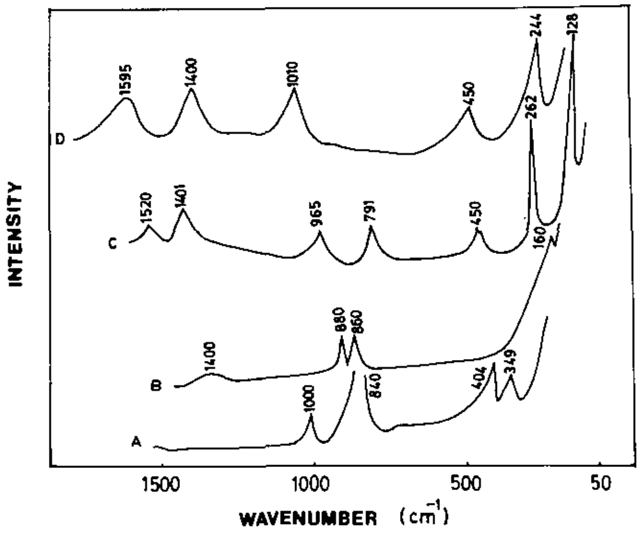


FIG. 3. (A) Raman spectrum of saturated aqueous solution of MASS. (B) SERS spectrum of MASS in colloid 1. (C) SERS spectrum of MASS in colloid 2. (D) SERS spectrum of SAS in colloid 2.

From a detailed analysis of the IR spectra of NH_4^+ in crystals, Oxton *et al.* (20) have established that the ammonium ion does not rotate if the spectrum contains medium intense bands due to combination modes involving the torsional mode (ν_6) with ν_2 and ν_4. These usually occur (21) in the regions 1900–2000 cm^{-1} ($\nu_2 + \nu_6$) and 1700–1800 cm^{-1} ($\nu_4 + \nu_6$). The torsional mode (ν_6) of NH_4^+ is usually IR inactive and shows up as combinations or overtones such as $\nu_2 + \nu_6$ or $\nu_4 + \nu_6$ or $2\nu_6$. In different compounds ν_6 is found to have values ranging from 200 to 390 cm^{-1} (19). In SAS, it is difficult to identify the torsional mode ν_6 as $\nu_2SeO_4^{2-}$ also occurs in the same region. On deuteration, the band at 350 cm^{-1} and the combination bands around 2050 cm^{-1} disappear (Table 6). Therefore, the band at 350 cm^{-1} in IR is due to ν_6 of NH_4^+. The presence of the ν_6 and its combination with ν_2 indicates that the ion is in a locked in position in the lattice.

SERS SPECTRA

The first step in identifying a metal-molecule complex formation is to look for low frequency bands in the SERS spectrum. For molecules forming an Ag–N bond, a band in the 170 cm^{-1} region is commonly seen whereas for Ag–O bond one appears around 250 cm^{-1} (22–25). The SERS spectrum of MASS in colloid 1 shows a band at 160 cm^{-1} (Fig. 3) indicating a Ag–N chemisorbed system. The most intense band observed at 840 cm^{-1} in the spectrum of saturated solution is replaced by two medium intense bands at 860 and 880 cm^{-1}. An additional weak broad band appears around 1400 cm^{-1} which could be due to δNH_3^+ or δCH_3. Appearance of this band supports the inference that chemisorption has taken place through the N atom. In other words, the CH_3NH_3 group is close to the metal surface. The splitting and shifting observed for the stretching mode of SeO_4^{2-} are due to the reduced local symmetry of the ion on chemisorption.

MASS in colloid 2 shows two strong sharp bands (Fig. 3) at 128 and 262 cm^{-1}. These are respectively the Ag–N and Ag–O stretching modes. The value 128 cm^{-1} is unusually low. In other words, in colloid 2, there are two adsorption sites and hence bands due to both $CH_3NH_3^+$ and SeO_4^{2-} will be affected. The two bands at 791 and 965 cm^{-1} are assigned to the stretching modes of SeO_4^{2-}. This large shift from free state values is due to the lowering of the free ion symmetry of SeO_4^{2-} on adsorption through its oxygen atom. A similar shift is also observed for the bending mode (Table 7).

The metal-molecule stretching band at 244 cm^{-1} observed (Fig. 3) for SAS in colloid 2 shows that adsorption occurs through the oxygen atom of SeO_4^{2-}. The enhanced band at 1010 cm^{-1} may be due to a combination mode. This assignment is justifiable as combination bands can appear in SERS spectra (26).

CONCLUSIONS

(i) In both the crystals the symmetry of the SeO_4^{2-} is lower than T_d.

(ii) The symmetry of $CH_3NH_3^+$ is lower than C_{3v} and hydrogen bonding is strong in MASS.

(iii) NH_4^+ is not rotating freely in the crystal lattice of SAS.

(iv) Bands due to SeO_4^{2-} are enhanced in the SERS spectra of both compounds.

TABLE 7
SERS Spectral Data (cm^{-1}) and Band Assignments

MASS solution	MASS in colloid 1	MASS in colloid 2	SAS in colloid 2	Assignment
		1520		δNH_3^+, δCH_3
	1400	1401		
			1595	δNH_4^+
			1400	
			1010	combination
1000				νC–N
	880	965		νSeO_4^{2-}
840	860	791		
404 349		450	450	δSeO_4^{2-}
		262	244	νAg–O
	160	128		νAg–N

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