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Infrared, Polarized Raman, and SERS Spectra of Borax

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Infrared and polarized Raman spectra of $Na_2B_4O_7 \cdot 10H_2O$ are recorded and analyzed. The vibrational assignments are made on the basis of vibrations due to BO_4 and BO_3 groups, water molecules, and (B)OH bonds. Three types of water molecules exist in the crystal, and the BO_4 groups are considerably distorted. Band assignments are confirmed by deuterium substitution. A SERS spectrum recorded in a silver colloid shows three enhanced bands at 800, 480, and 464 cm^{-1}.

INTRODUCTION

Borax, $Na_2B_4O_7 \cdot 10H_2O$, one of the most important compounds among borates, is extensively used as a constituent of certain kinds of glass, enamels, and glazes for metalware and pottery. It is also used to soften hard water and as an antiseptic (1–4). A systematic study of the vibrational spectra of borax has not been reported thus far. In the present investigation, the infrared, Raman, and surface enhanced raman scattering (SERS) spectra of borax have been recorded and analyzed to get information regarding the nature of different vibrating groups.

EXPERIMENTAL

Single crystals of borax were obtained by slow evaporation at room temperature of an aqueous solution of the sample. Raman spectra in the $X(YY)Z$, $X(YX)Z$, $X(ZY)Z$, and $X(ZX)Z$ polarization geometries were recorded using a Spex Ramalog 1401 double monochromator equipped with a Spectra Physics Model I65 Ar^+ laser. The excitation was performed with the 514.5-nm line with a power of about 100 mW. The IR spectrum was obtained on PE 283 (4000–200 cm^{-1}) and PE 7600 (4000–400 cm^{-1}) FTIR spectrophotometers with the sample in KBr pellets. Deuterated borax was obtained by repeated recrystallization from D_2O. Raman and IR spectra of the deuterated sample were also recorded.

A stable greenish-yellow silver colloid having a sharp absorption band at 390 nm was prepared from sodium borohydride and silver nitrate (5). Equal volumes of the colloid and 10^{-2} M aqueous solution of borax were mixed. SERS spectra were recorded on a Dilor GMBH Z24 spectrometer using a laser power of 50 mW with the sample in a capillary tube. The chemicals were procured from Sigma. Absorption spectra were recorded on a UV-240 Shimadzu UV-Visible recording spectrophotometer. When borax is adsorbed onto the colloid, the absorption band at 390 nm gets broadened and shifts to 400 nm.

CRYSTAL STRUCTURE AND FACTOR GROUP ANALYSIS

Borax crystallizes (6) in the monoclinic system with space group C_{2h}^6 ($C2/c$) having four formula units in the unit cell. The atoms lie in the positions Na(1) : 4(a), Na(2) : 4(e), and 0(1) : 4(e). All other atoms are in general positions 8(f). Factor group analysis (7) gives the distribution of irreducible representations at $k = 0$ as

$$\Gamma = 64A_g(\mathrm{R}) + 65B_g(\mathrm{R}) + 63A_u(\mathrm{IR}) + 63B_u(\mathrm{IR}),$$

where R is Raman active and IR is infrared active.

The crystal structure consists of isolated anions of the composition $B_4O_5(OH)_4$ and sodium ions octahedrally surrounded by water molecules. In the complex anion, two boron atoms are tetrahedrally surrounded by four oxygens with B–O = 1.46–1.54 Å, and the other two have three oxygen neighbors with B–O = 1.32–1.40 Å. The assignments of the observed bands could then be done on the basis of vibrations due to BO_4 and BO_3 groups, (B)O–H bonds, and water moelcules.

INFRARED AND RAMAN SPECTRA

Vibrations of the BO_4 Group

For a BO_4 tetrahedron having T_d symmetry, the normal modes of vibrations $\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(F_2)$, and $\nu_4(F_2)$ usually appear around 400, 200, 1100, and 260 cm^{-1}, respectively (8). In the crystal, the ion occupies a general site (C_1).

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TABLE 1
Correlation Scheme for the Internal Vibrations of the BO_4 Group

f^r	ν_{vib}	Free ion symmetry T_d	Site symmetry C_1	Factor group C_{2h}
4	4	$(\nu_1)A_1$ (R)		$A_g(\nu_1 + 2\nu_2 + 3\nu_3 + 3\nu_4)$
8	4	$(\nu_2)E$(R)		$B_g(\nu_1 + 2\nu_2 + 3\nu_3 + 3\nu_4)$
12	4	$(\nu_3)F_2$(R,IR)	A	$A_u(\nu_1 + 2\nu_2 + 3\nu_3 + 3\nu_4)$
12	4	$(\nu_4)F_2$(R,IR)		$B_u(\nu_1 + 2\nu_2 + 3\nu_3 + 3\nu_4)$

The correlation scheme (7) given in Table 1 shows that the maximum number of components expected in each of the polarization geometries of the Raman spectrum is one for ν_1, two for ν_2, and three for ν_3 and ν_4. However, in the IR these can split into a maximum of two for ν_1, four for ν_2 and six for ν_3 and ν_4, as it is a powder spectrum corresponding to all orientations.

The most intense band in the Raman spectrum occurs at 572 cm^{-1}. As this band is polarized, it is easily assigned to the symmetric stretching mode (ν_1) of BO_4. In the $X(ZY)Z$ and $X(ZX)Z$ polarization geometries two and three bands, respectively, are observed for this mode (Table 2). As the maximum number expected for this mode in each of the polarization geometry is one, the additional bands are possibly associated with the librational modes of water (9). In IR, this mode is split into two components at 590 and 525 cm^{-1}, as expected from correlation scheme (Table 1). The appearance of this IR-inactive mode is due to the lower site symmetry of the ion in the crystal.

The Raman bands in the region 340–390 cm^{-1} are polarized and appear as two components in most of the polarization geometries. These are, therefore, assigned to $\nu_2(E)$, the symmetric bending mode of BO_4. This IR-inactive mode appears as a very weak band at 320 cm^{-1} in the IR. The weak Raman bands in the region 1000–1100 cm^{-1} and the strong IR bands at 1003 and 1132 cm^{-1} with comparatively weak components between 1000 and 1200 cm^{-1} (Table 2) are assigned to the $\nu_3(F_2)$ asymmetric stretching mode of BO_4. The appearance of six bands is justifiable, as a maximum of six components can appear for this mode in IR spectra (Table 1). The $\nu_4(F_2)$ asymmetric bending mode appears as medium intense bands in both Raman and IR spectra (Table 2). The splitting and very large shift from free state values observed for all the internal modes of BO_4 are indicative of strong distortion from tetrahedral symmetry.

Vibrations of the BO_3 Group

The normal frequencies of a planar BO_3 group having point group D_{3h} are expected around 940, 740, 1300, and 650 cm^{-1} for $A_1'(\nu_1)$, $A_2''(\nu_2)$, $E'(\nu_3)$, and $E'(\nu_4)$, respectively (8). A correlation scheme (Table 3) shows that ν_1, ν_2, ν_3, and ν_4 could appear with a maximum of one, one, two, and two components, respectively, in Raman spectra for each of the polarization geometries and two, two, four, and four components in IR spectra.

The polarized bands between 930 and 950 cm^{-1} in the Raman spectrum are assigned to $\nu_1(A_1')$ the symmetric stretching mode of BO_3. In the IR spectrum, it appears at 947 cm^{-1}. The nondegenerate and Raman-inactive $\nu_2(A_2'')$ symmetric bending mode appears as weak bands at 758 and 756 cm^{-1} in the $X(YY)Z$ and $X(YX)Z$ spectra, respectively. This IR-active mode is observed as a strong band at 828 cm^{-1} in the IR spectrum. The weak Raman bands and the strong IR bands observed in the 1300–1500 cm^{-1} region are assigned to $\nu_3(E')$, the asymmetric stretching mode of BO_3. Four components observed (Table 2) for this mode in IR is justifiable, as the doubly degenerate species can split into a maximum of four components (Table 3). The asymmetric bending mode $\nu_4(E')$ is observed as weak bands in both Raman and IR spectra (Table 2).

Vibrations of Water Molecules and (B)O–H Bonds

As it was not possible to locate the hydrogen atoms from X-ray studies (6), the positions of hydroxyl ions and water molecules are not known. In the present study, the wide range of bands observed in the region 3000–3600 cm^{-1} is indicative of different environments for the water molecules. In the Raman spectrum of the powder sample (Fig. 1) there are six bands (Table 2) in the O–H stretching mode region, all of which show isotopic shift on deuteration. This suggests the possibility for three types of water molecules in borax. This result is further supported by the presence of three bands in the IR spectrum (Fig. 2) in the bending mode region (Table 2). These bands also show changes on deuteration. However, one cannot rule out the possibility of factor group splitting giving rise to the large number of observed components.

The Raman band at 860 cm^{-1} in the spectrum of the powder sample is completely missing on deuteration. Therefore, it is assigned to a librational mode of water (9). The bands in the region 1300–1500 cm^{-1} do not show considerable change on deuteration except for the band at 1424 cm^{-1} (IR). The slight change in its intensity may be due to the presence of the B(OH) in-plane bending mode in the same region which gets shifted on deuteration. Independent assignment of in-plane and out-of-plane bending modes of (B)OH bonds in HBO_4 and HBO_3 is difficult as the internal modes of BO_4 and BO_3 also fall in the same region. However, their presence in the 1000–1500 and 700–900 cm^{-1} regions (9,10) is identified based on isotopic shift and changes in intensities of the

TABLE 2
Vibrational Spectral Data and Band Assignments

Raman								
X(YY)Z	*X(YX)Z*	*X(ZY)Z*	*X(ZX)Z*	Polycrystalline	Deuterated	IR	IR deuterated	Assignments
3410sbr 3340wbr 3300vwbr 3189vwbr	3420sbr 3165sbr	3570wbr 3075w	3540wbr 3469wbr 3340wbr 3148w	3575s 3495s 3447s 3400s 3357s 3140s	3575wbr 3449mbr 3348wbr 2641s 2591s 2560sh 2523vs 2495s 2375s	3560sh 3503s 3357vs 3060sh	3560sh 3500s 3356vs 3060sbr 2590m 2525m 2496m 2420sh 2240sh	$\nu H_2O/D_2O/$(B)O–H/ (B)O–D
2878w						2910w 2875w		Combination with δH_2O
1650 wbr		1642wbr	1638w	1640vw		1710sh 1656m 1580w	1710sh 1656m 1580sh	δH_2O
1334w 1328w	1337wbr					1483vs 1424s 1385w 1350vs	1483vs 1429m 1385w 1348vs	ν_3BO_3, (B)OH ipb
1250w						1282m 1235m	1256m 1210m	δD_2O (B)OH, ipb
1031wbr 1027w	1030w		1068w 1038w			1175w 1140sh 1132s 1078m 1038sh 1003vs	1180sh 1150sh 1133s 1079m 1035sh 1004vs	ν_3BO_4,(B)OD,ipb (B)OH, ipb
943m	933m			957m	958w 920w	947s 890sh	946s 875w	ν_1BO_3(B)OD, ipb (B)OD, ipb
848vw 788wbr	784vwbr	848w	845w	860w		785w 710w	770m 711m	γH_2O (B)OH, opb
758wbr	756w			776mbr	782mbr	828s	826vs	ν_2BO_3
688w						660w	660w	ν_4BO_3
572vs	572s	575w 528w	573wbr 545vw 528w	590vw 530wbr	585s 572s 560sh	590w 525w	520w	ν_1BO_4, ωH_2O γD_2O(B)OD, opb
		460m	478w 461m	474m	469m	465m 430w	464s 440m	ν_4BO_4, ωD_2O ν(Na)H_2O
386m 364mbr	383m 348m	340vw	386w 350w	390w 361m	396w 349s	320vvbr	325mbr	ν_2BO_4 ν(Na)D_2O
287wbr 190wbr 173mbr 163mbr 127w 107mbr 81m 68w	278w 234w 189wbr 167w 128wbr 108m 80w 67vw	318w 138mbr 78mbr 68w	315wbr 187wbr 165w 140m 77s 66m	 160w 120m 90m 78w	 197m 167m 121m 92w	235s 220s	235m 220w	External modes

Note. r, rocking; w, wagging; ν, stretching; δ, bending, ipb, in-plane bending; opb, out-of-plane bending; vs, very strong; s, strong; m, medium; w, weak; vw, very weak; br, broad; sh, shoulder.

TABLE 3
Correlation Scheme for the Internal Vibrations of the BO_3 Group

f^r	ν_{vib}	Free ion symmetry D_{3h}	Site symmetry C_1	Factor group C_{2h}
4	4	$(\nu_1)A_1'$ (R)	A	$A_g(\nu_1 + \nu_2 + 2\nu_3 + 2\nu_4)$
4	4	$(\nu_2)A_2''$(IR)		$B_g(\nu_1 + \nu_2 + 2\nu_3 + 2\nu_4)$
8	4	$(\nu_3)E'$(R,IR)		$A_u(\nu_1 + \nu_2 + 2\nu_3 + 2\nu_4)$
8	4	$(\nu_4)E'$(R,IR)		$B_u(\nu_1 + \nu_2 + 2\nu_3 + 2\nu_4)$

bands in deuteration. The complete assignment is given in Table 2.

SERS SPECTRUM

When added to the colloid, the aqueous solution of borax does not show colloid aggregation even at high concentrations. In most cases, colloid aggregation is a prerequisite for surface enhancement (11–13). Further, no low-frequency Raman band is observed in the SERS spectrum (Fig. 3) corresponding to a metal-molecule chemisorbed system (14–18). Similar cases have been reported earlier (18, 19).

The bands enhanced in the SERS spectrum are those at 800, 480, and 464 cm^{-1}. The most intense Raman band at 590 cm^{-1} in the normal Raman spectrum of the powder sample is missing in the SERS. This is justifiable, as the selection rules for SERS are different from those of normal Raman spectroscopy [20] and the enhancement depends on factors like the orientation of the molecule on the silver surface, size and shape of the colloidal particle, and concentration of the sample. In the normal Raman spectrum, the symmetric BO_3 bending mode (ν_2BO_3) is observed as a medium broadband around 776 cm^{-1}, and the asymmetric BO_4 bending mode (ν_4BO_4) as a medium intense band at 474 cm^{-1}. Therefore, the enhanced band at 800 cm^{-1} is assigned to ν_2BO_3 and the bands at 480 and 464 cm^{-1} to ν_4BO_4. The splitting of the triply degenerate ν_4BO_4 mode into two components indicates a lowered local symmetry of the ion on adsorption (18).

CONCLUSIONS

(i) BO_4 groups are considerably distorted in the crystal.
(ii) There are three types of water molecules in borax.
(iii) The symmetric bending mode of BO_3 and the asymmetric bending mode of BO_4 are enhanced in the SERS spectrum.

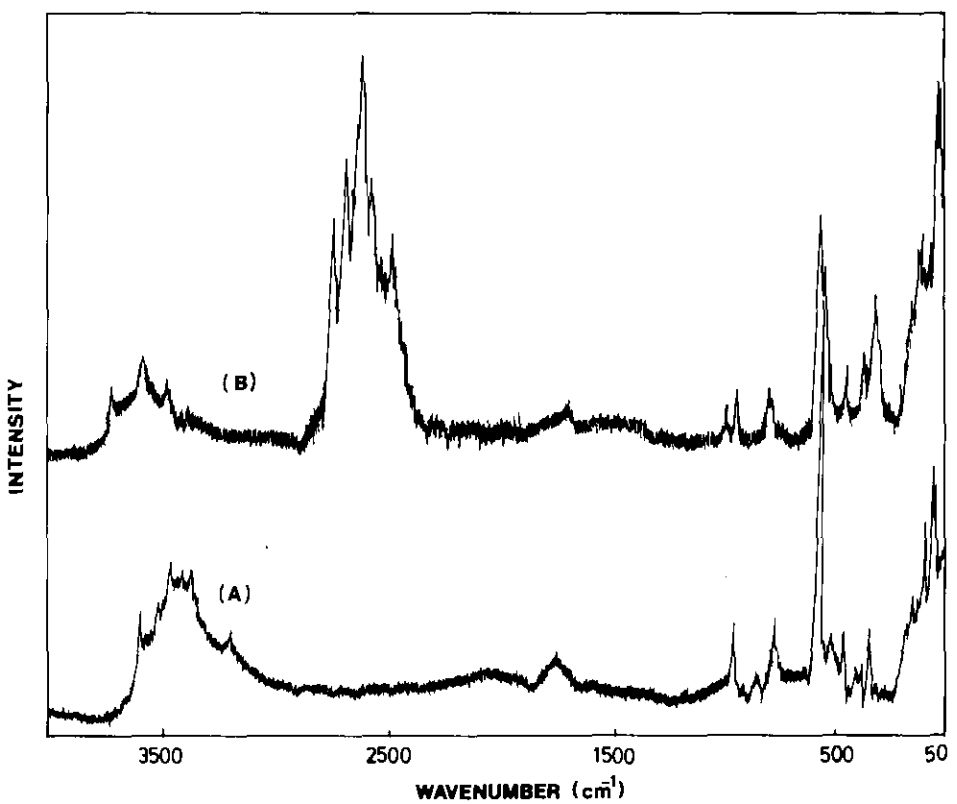

FIG. 1. Raman spectrum of (A) borax and (B) deuterated borax.

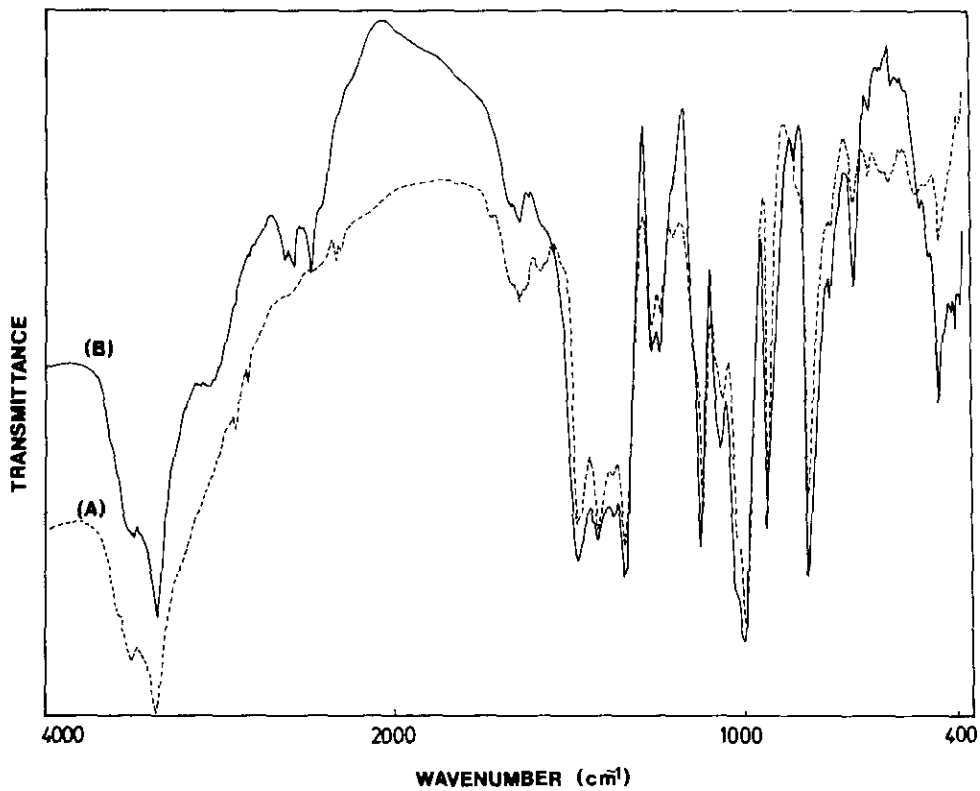

FIG. 2. IR spectrum of (A) borax and (B) deuterated borax.

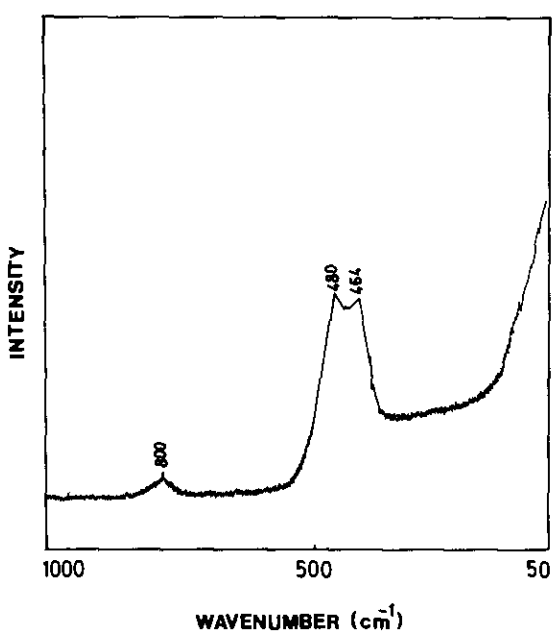

FIG. 3. SERS spectrum of borax.

(iv) The symmetry of the BO_4 group is lowered on adsorption onto the silver surface.

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