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Infrared and Raman Spectra of $K_4H_2(S_2I_2O_{14})$

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The infrared and Raman spectra of $K_4H_2(S_2I_2O_{14})$ were recorded and analyzed. Band assignments were made on the basis of the characteristic vibrations of SO_4^{2-} and IO_3^- ions and OH group frequencies. Bands indicate that the symmetry of the SO_4^{2-} ion in the crystal is less than its free ion symmetry. The trio bands, characteristic of strong hydrogen bonded systems, are observed in the infrared spectrum. The IO_3^- ions exist almost independently in the crystal.

INTRODUCTION

The iodatosulfate $K_4H_2(S_2I_2O_{14})$ is of considerable interest because of the existence of a finite heteropolyanion $(S_2I_2O_{14})^{-6}$ (1). It crystallizes in the monoclinic system $P2_1/n$ with two formula units per unit cell (1). The centrosymmetric anion $(S_2I_2O_{14})^{-6}$ having six oxygen atoms in common is constituted of two sulfate tetrahedra and two octahedra of much distorted IO_6 which share each of the apices with the two sulfate tetrahedra. In this work, infrared and Raman spectroscopic techniques have been used as a probe to determine the nature of the sulfate and iodate ions and the role of hydrogen in the crystal.

EXPERIMENTAL

Samples were prepared by dissolving stoichiometric amounts of $KHSO_4$ and KIO_3 in minimum water and allowing the solution to evaporate at room temperature for some days (1). Infrared spectrum was recorded on a Perkin–Elmer 577 spectrophotometer with samples as KBr pellets. The crystallographic axes were found using a polarizing microscope. The crystal unique axis is b. A well polished crystal with sides parallel to the a, b, and c was used for the polarized Raman study. Raman spectra were recorded on a Spex Ramalog 1401 double monochromator equipped with a Spectra Physics model 165 Ar^+ (λ = 514.5 nm) laser. The spectra were obtained for the orientations $a(ba)c[A_g]$, $a(bb)c[A_g]$, $a(cb)c[B_g]$, and $a(ca)c[B_g]$ with a spectral resolution of 2 cm^{-1} and a laser power of 40 mW. Unfortunately, the results of these polarization measurements were inconclusive, since most of the bands appear at the same wave number in the A_g and B_g symmetries. Attempts to repeat the experiment with another single crystal have not been successful due to the nonavailability of good quality crystals of sufficient size after repeated trials of growth procedure. Therefore the polarization data are not taken into consideration in the analysis of this spectra.

DISCUSSION

The factor group analysis of $K_4H_2(S_2I_2O_{14})$ predicts 141 modes and they are distributed as

$$\Gamma_{141} = 36A_g + 36B_g + 35A_u + 34B_u.$$

Band assignments (Table 1) have been carried out on the basis of the characteristic vibrations of SO_4^{2-} and IO_3^- ions and OH group frequencies.

Internal Modes of the Sulfate Ion

The free SO_4^{2-} ion has T_d symmetry with four fundamentals at the following frequencies: ν_1 = 981 cm^{-1} (A_1), ν_2 = 451 cm^{-1} (E), ν_3 = 1104 cm^{-1} (F_2) and ν_4 = 613 cm^{-1} (F_2). All the modes are Raman active while ν_1 and ν_2 are infrared inactive. The Raman bands observed for the four orientations and the infrared bands are given in Figs. 1 and 2.

There are four SO_4 units in the Bravais cell of this iodatosulfate and they occupy C_1 sites. Table 2 gives the relationship between various symmetry species of T_d, C_1, and C_{2h} groups.

The band observed at 968 cm^{-1} in the Raman spectrum is assigned to the symmetric stretching mode ν_1. This infrared inactive mode (under T_d symmetry) appears in the infrared spectrum with medium intensity. The asymmetric stretching mode ν_3 splits into five bands in the IR spectrum. Degeneracy of this mode is lifted in the Raman spectra also. With the lifting of the degeneracies of ν_2 (in one orientation), ν_3 and ν_4 modes, additional bands are observed in the IR spectrum for the ν_3 mode and the

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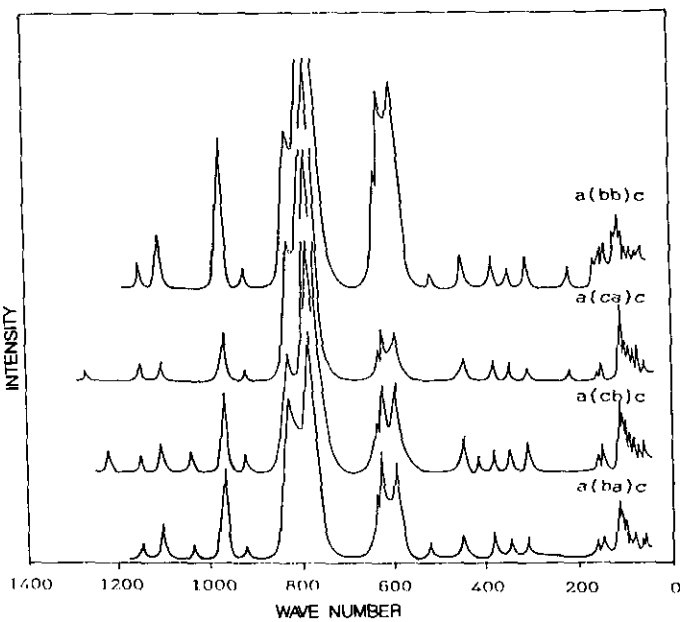

FIG. 1. Raman spectra of $K_4H_2(S_2I_2O_{14})$.

appearance of the IR inactive ν_1 and ν_2 modes in the IR spectrum suggest that both the site symmetry effect and correlation field effect are strong in the crystal.

The symmetric stretching band ν_1 splits into two (968 and 920 cm^{-1}) and this can be considered as a spectroscopic indication of hydrogen bonding (2) and the SO_4^{2-} and HSO_4^- entities can thus be distinguished. The lowest frequency 920 cm^{-1} is assigned to the vibrations of HSO_4^- ion by analogy with the spectra of hydrogen sulfates $MHSO_4$ (2). Due to the hydrogen atom being attached to the oxygen atom of the SO_4 group, one of the S–O bonds is expected to be elongated, normally up to 1.6 Å (3). In the present case, the maximum value of the S–O bond length is 1.499 Å and this is in correlation with the high value of the lowest Raman ν_1 band. The S–(OH) bond appears to be shortened with increase in the hydrogen bond strength as has been observed in $Na_3H(SO_4)_2$ (2). The Raman spectra of $K_4H_2(S_2I_2O_{14})$ show no bands equivalent of OH stretching modes. But the trio bands, characteristic of strong hydrogen bonded systems (4) appear at ~2780 cm^{-1}, ~2380 cm^{-1}, and ~1600 cm^{-1} in the infrared spectrum. The γ OH vibrations are observed at ~740 cm^{-1} in the IR. The in-plane δ OH bending vibrations of hydrogen bonds are expected in the region 1200–1300 cm^{-1}. This band is identified in the infrared spectrum and in two orientations in the Raman spectra.

IO_3^- Vibrations

The structure of $K_4H_2(S_2I_2O_{14})$ shows two kinds of I–O bonds, three short ones of 1.837 Å and the three long ones of 2.704 Å forming a distorted IO_6 ion (1). The free ion symmetry of IO_3^- ion is C_{3v}. In this crystal, all the iodate ions are at general positions. The correlation of C_{3v} with C_{2h} factor group through C_1 site group is shown in Table 3.

The high frequency band near 820 cm^{-1} in the Raman

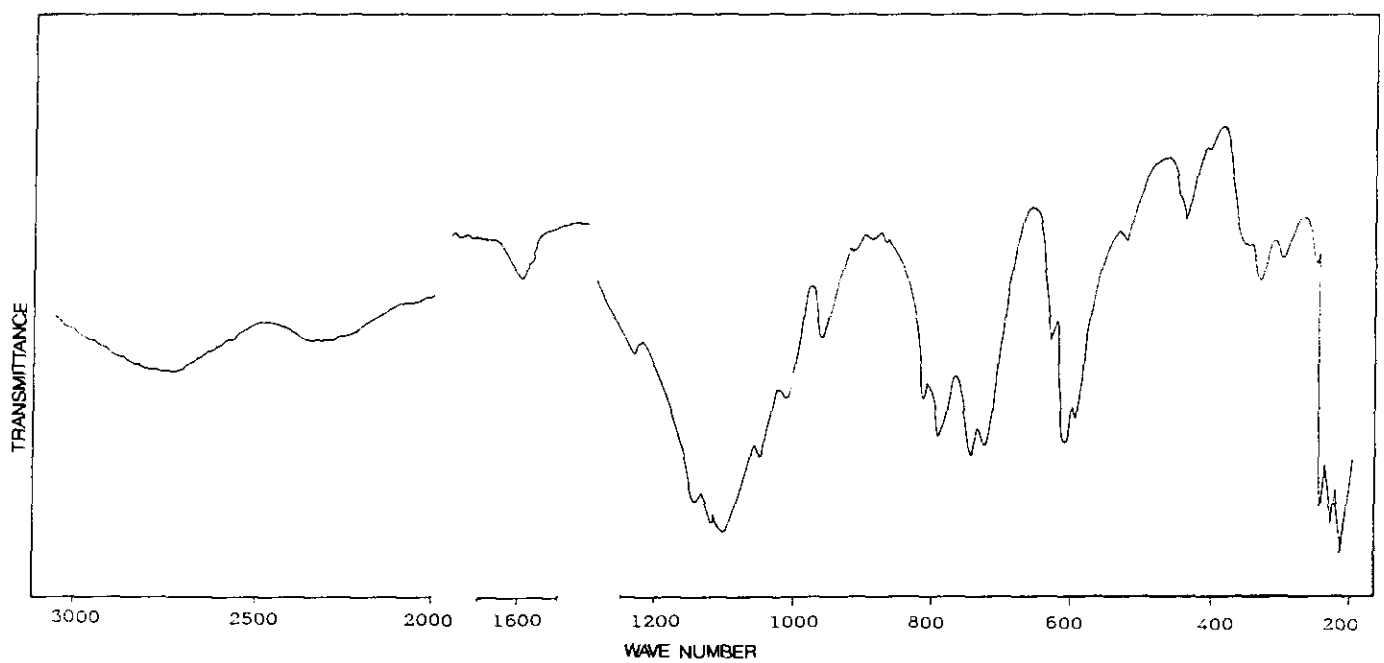

FIG. 2. IR Spectrum of $K_4H_2(S_2I_2O_{14})$.

TABLE 1
Vibrational Spectral Data and Band Assignments (cm^{-1}) of $K_4H_2(S_2I_2O_{14})$

Raman					
$a(ba)c$ A_g	$a(bb)c$ A_g	$a(cb)c$ B_g	$a(ca)c$ B_g	IR	Assignments
55	55	55	55		
60	65	—	—		
—	70	70	70		
76	78	80	78		
90	90	90	87		
97	97	95	95		
105	103	105	105		external modes
108	108	108	—		
—	133	—	—		
145	145	145	145		
158	158	155	155		
—	215	—	215	210	
—	—	—	—	230	
—	—	—	—	240	
306	306	306	306	305	
345	345	348	348	340	$\nu_4(IO_3)$
380	380	380	380	355	$\nu_2(IO_3)$
—	—	413	—	—	
449	449	445	445	445	$\nu_2(SO_4)$
520	520	—	—	525	
595	595	595	595	590	
623	623	623	623	610	$\nu_4(SO_4)$
632	632	632	630	630	
—	—	—	—	730	
—	—	—	—	740	2 $\nu_2(IO_3)$, γ_{OH}
786	786	786	786	795	$\nu_1(IO_3)$
823	823	823	823	820	$\nu_3(IO_3)$
920	920	920	920	—	ν_{S-OH}
968	968	968	968	968	$\nu_1(SO_4)$
1033	—	1035	—	1020	
—	—	—	—	1060	
1100	1100	1100	1100	1105	$\nu_3(SO_4)$
—	—	—	—	1120	
1145	1145	1145	1145	1145	
—	—	1220	1270	1230	δ_{OH} in plane bending
				1600	
				2380	trio bands
				2780	

TABLE 2
Correlation of the Internal Vibrational Modes of SO_4^{2-} Ion in $K_4H_2(S_2I_2O_{14})$

	Free ion symmetry T_d	Site symmetry C_1	Factor group symmetry C_{2h}
$[\nu_1 : (x^2 + y^2 + z^2)]$	A_1	$9A$	$9A_g(x^2, y^2, z^2, xy)$
$[\nu_1 : (x^2 + y^2 - 2z^2, x^2 - y^2)]$	E		$9B_g(xz, yz)$
$[\nu_3, \nu_4)\ (xy, xz, yz)]$	$2F_2$		$9A_u$
			$9B_u$

TABLE 3
Correlation of the Internal Vibrational Modes of IO_3^- Ion in $K_4H_2(S_2I_2O_{14})$

	Free ion symmetry C_{3v}	Site symmetry C_1	Factor group symmetry C_{2h}
$[(\nu_1, \nu_2) : (x^2 + y^2, z^2)]$	$2A_1$	$6A$	$6A_g(x^2, y^2, z^2, xy)$
			$6B_g(xz, yz)$
			$6A_u$
$[(\nu_3, \nu_4) (x^2 - y^2, xy, xz, yz)$	$2E$		$6B_u$

and IR spectra is assigned to ν_3. The unambiguous assignment of ν_1 mode is difficult due to the possible occurrence of the overtone $2\nu_2$ (5). However, the band at 786 cm^{-1} in the Raman spectrum is assigned to ν_1 since only one band is observed in the region 700–800 cm^{-1} and it is the most intense band in the Raman spectrum. The Raman band at 750 cm^{-1}, typical of octahedrally coordinated I, (6), is absent in the Raman spectra. So it can be inferred that the iodine atoms are not octahedrally coordinated in this compound. The X-ray structural investigations also report that the long I–O bonds are weak. The stretching and bending frequencies of the iodate ion in this crystal are close to that of a free IO_3^- ion (5), except for the lifting of the degeneracy of the ν_4 mode. This indicates that IO_3^- ions exist almost independently in $K_4H_2(S_2I_2O_{14})$.

It is difficult to assign the external modes of SO_4^{-2} and IO_3^- ions and the metal–oxygen stretching modes which fall below 400 cm^{-1}, as there can be interactions between these ions, even though they are weak, which can modify the translational and librational modes.

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