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Infrared Spectra of $KNaSO_4$ and $K_3Na(SO_4)_2$

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The infrared spectra, transmittance and polarized reflectance, of $KNaSO_4$ and $K_3Na(SO_4)_2$ are reported. Group theoretical analysis was carried out and a vibrational assignment proposed on basis of C_{3v} and D_{3d} symmetries. Factor group and site effects are discussed.

Introduction

Potassium sodium sulfate and tripotassium sodium sulfate crystallize in trigonal structures, space groups $P3m1$ and $P\bar{3}m1$, respectively (*1*). Both structures are built up of SO_4 tetrahedra and MO_6, MO_{10}, and MO_{12} polyhedra. The SO_4 units in $KNaSO_4$ are distorted with S–O distances ranging from 1.368 to 1.496 Å and the O–S–O angles vary between 105 and 113.5°. On the other hand, the SO_4 tetrahedra in $K_3Na(SO_4)_2$ approach true T_d symmetry with S–O distances between 1.470 and 1.477 Å and O–S–O angles of 109.2 to 109.8°. There are two formula units in the $KNaSO_4$ unit cell but ony one formula unit in the $K_3Na(SO_4)_2$ unit cell; that is, there are two SO_4 units in each primitive cell. The relative simplicity and similarity of the two structures prompted us to record the infrared spectra, transmittance and reflectance, of $KNaSO_4$ and $K_3Na(SO_4)_2$, polycrystalline and single crystal, and to analyze the spectra using factor group analysis.

Experimental

$KNaSO_4$ and $K_3Na(SO_4)_2$ were prepared according to the method described elsewhere (*1*) using stock reagents supplied by Alfa Ventron Corp. and British Drug Houses (BDH) of stated purity ≥99.9%. Crystals were also obtained by slow evaporation of aqueous solutions using distilled water. Some large single crystals of $KNaSO_4$ were successfully grown in solution whereas $K_3Na(SO_4)_2$ invariably formed overgrowth crystals. Both compounds were confirmed by X-ray diffraction.

The infrared transmittance spectra were recorded with a Perkin–Elmer 180 spectrophotometer using the standard KBr disc technique in the 250–2500 cm^{-1} region. Far infrared spectra, 50–250 cm^{-1} region, were obtained on samples in Nujol mull between polyethylene windows. Reflectance spectra of single crystals were recorded with AgBr polarizer on the reflectance accessory.

Factor Group Analysis

In $KNaSO_4$, [C_{3v} – $P3m1$, $Z = 2$], the SO_4 groups are on sites b and c, K atoms are on

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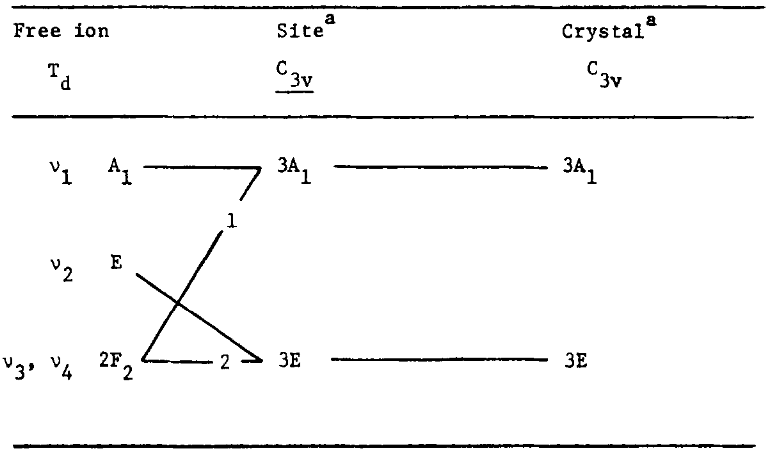
TABLE I

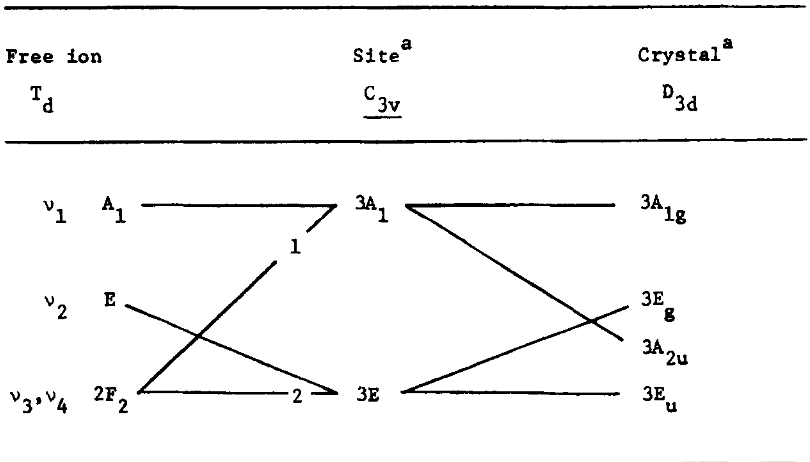


[a] A_2 mode and its derivatives not included.

sites *a* and *b*, and Na atoms occupy sites *a* and *c*. Using standard correlation mapping procedures (*2*) it is found that the internal modes of the SO_4 group consists of $3A_1$ and $3E$ species as illustrated in Table I; therefore, two SO_4 groups will have $6A_1$ and $6E$ internal modes. The external modes obtained in a similar manner are subdivided into $2A_2$ and $2E$ for SO_4 rotations along with $6A_1$ and $6E$ for translations of SO_4, Na, and K. Since A_1 and E modes are infrared active then $6A_1$ and $6E$ internal modes are expected to be observed.

In $K_3Na(SO_4)_2$, $[D^3_{3d} - P\bar{3}m1, Z = 1]$, the SO_4 groups are on the *d* site. K atoms occupy sites *a* and *d*, and Na occupies site *b*. The 18 internal modes of the SO_4 groups obtained by correlation mapping are illustrated in Table II, of which 9 modes are infrared active, viz. $3A_{2u}$ and $3E_u$. The ex-

TABLE II



[a] A_2 mode and its derivatives not included.

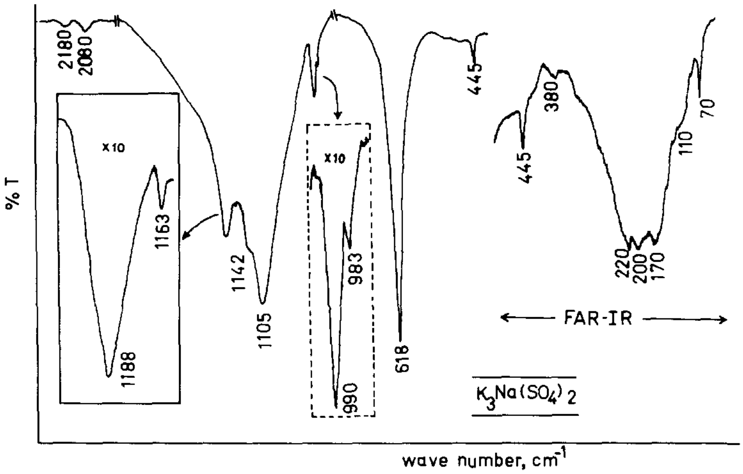


FIGURE 1

ternal modes are subdivided into A_{2g}, E_g, A_{2u}, E_u for SO_4 rotations and $2A_{1g}$, $2E_g$, $4A_{2u}$, $4E_u$ for translations of SO_4, Na, and K.

Results and Discussion

The fundamental vibration frequencies for SO_4^{2-} of T_d symmetry have been reported (*3*) as 981 (A_1), 451 (E), 1104 (F_2), and 613 (F_2) where only the F_2 modes are infrared active. Since the selection rules are relaxed in the crystal (*4*) it is possible to observe all four fundamentals in the infrared spectrum.

The infrared transmittance spectrum recorded for polycrystalline $K_3Na(SO_4)_2$ and the reflectance spectrum recorded for $KNaSO_4$ single crystal are given in Figs. 1 and 2, respectively. The vibrational frequencies of $KNaSO_4$ and $K_3Na(SO_4)_2$ from transmittance and reflectance spectra along with assignments are tabulated in Table III. The peak intensities shown in Fig. 1 for $K_3Na(SO_4)_2$ are the same for $KNaSO_4$ transmittance spectrum.

The observed weak 993 (A_1) and 450 (E) peaks in $KNaSO_4$, although sharp, show no splitting as might be expected; on the other hand, the two F_2 peaks are very strong. Although the 613 (F_2) peaks shows no splitting in the transmittance spectrum there is evidence of weak splitting, ~4 cm^{-1}, in the polarized reflectance spectrum. The 1104 (F_2) fundamental undergoes site group splitting, A_1 and E modes, as observed in Fig. 2 and identified in Table III. A more detailed examination by polarized reflectance revealed crystal field splittings of 60 cm^{-1} in 1190 (A_1) mode and 20 cm^{-1} in 1112 (E) mode. These observed crystal field splittings are consistent with splittings reported for gypsum (*3*) and K_2SO_4 (*5*).

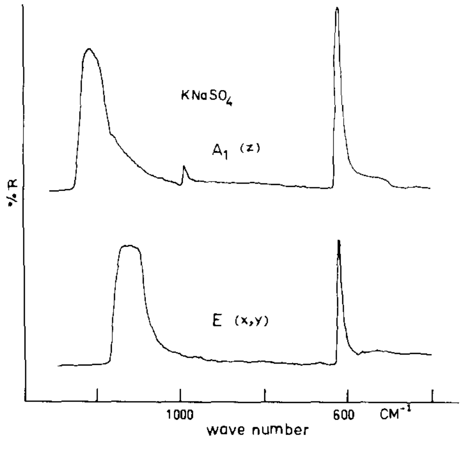


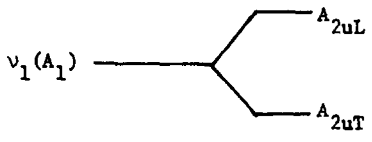
FIGURE 2

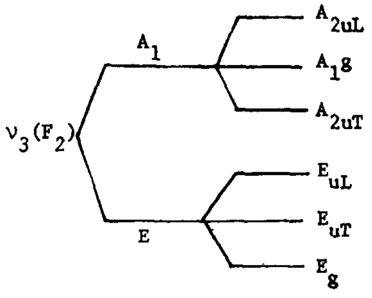
TABLE III

Infrared Vibrational Frequencies and Assignments of $KNaSO_4$ and $K_3Na(SO_4)_2$

Frequencies of free SO_4^{2-} ion (cm^{-1})	$K_3Na(SO_4)_2$ Transmittance frequency (cm^{-1})	$KNaSO_4$ Transmittance frequency (cm^{-1})	$KNaSO_4$ Reflectance frequency (cm^{-1})	Assignment
ν_1, 981(A_1)	990, 983	993	988	Symmetric stretching
ν_2, 451(E)	445	450		Symmetric bending
ν_3, 1104(F_2)	1188, 1163	1190	1210, 1150	Asymmetric stretching
	1142, 1105	1112	1100, 1080	
ν_4, 613(F_2)	618	615	620, 624	Asymmetric bending
	2180, 2080 380(?)	2188, 2080		Combination
	220, 200	220, 200		External and lattice modes
	170, 110	170, 110		
	70	70		Polyethylene reference

The infrared spectrum of $K_3Na(SO_4)_2$ resembles the $KNaSO_4$ spectrum with some variation in crystal field splitting features. The splitting of the $\nu_1(A_1)$ mode and the extra components in addition to the predicted site splitting of the $\nu_3(F_2)$ mode most likely originate with the separation of the transverse (T) and the longitudinal (L) optic modes represented in Scheme 1. The transverse and longitudinal assignments are consistent with the analysis based on dipolar coupling factors for vibrational multiplet of internal optic modes in crystals (*6*, *7*).





The weak peaks at 2180 (2188) and 2080 are assigned to a combination and overtone, viz. $A_1 + E$ and $2E$. The absorption peaks in the 250–100 cm^{-1} region originate with the external and lattice modes of the sulfate ion. The sharp polyethylene peak at 70 cm^{-1} serves as an internal reference.

The weak peak at 380 cm^{-1} in $K_3Na(SO_4)_2$ is tentatively assigned to a combination of external and lattice modes.

In summary, most of the internal modes predicted by factor group analysis for SO_4^{2-} in $KNaSO_4$ and $K_3Na(SO_4)_2$ are observed; a multiplet structure arising from internal optic modes is also evident in $K_3Na(SO_4)_2$.

Acknowledgments

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