

STRONG HYDROGEN BONDING. ASSIGNMENTS IN THE VIBRATIONAL SPECTRA OF THE ISOMORPHOUS SALTS : KHSO_4 AND KHSeO_4 .

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ABSTRACT

Despite the fact that KHSO_4 and KHSeO_4 are isomorphous, the infrared spectra of these compounds are remarkably different. The characteristic 'A,B,C' trio is present in the spectrum of KHSeO_4 whereas multiplet structure of the O-H stretching band is found in KHSO_4 . On lowering the temperature, the bands in the 3000-2000 cm^{-1} region become more structured and new bands appear in the 2000-1500 cm^{-1} interval. Deuteration causes marked changes in the infrared spectra, as expected for strongly hydrogen bonded systems, although the Raman spectra are largely unaffected. Assignments in terms of separate R-O(H) and RO_3 units are presented.

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INTRODUCTION

The vibrational spectra of various hydrogensulfates and hydrogenselenates have been extensively studied by both infrared¹⁻⁶ and Raman^{3,4,7,8} methods. Thus the infrared spectra of powders of the title compounds,^{1,2} the Raman spectra of KHSO_4 single crystals⁴ and the polarized infrared spectra of KHSeO_4 single crystals⁶ have been reported. Some details, however, are still open for discussion even after the recent communication by Baran⁹ has been taken into account. Among the questions still warranting discussion are the interpretation of the bands in the regions where the in-plane bendings of the OH groups and the out-of-plane bendings of the OD groups are expected to appear and the exact origin of the strong IR absorption of the OH stretching vibrations.

The crystal structures of KHSO_4 and KHSeO_4 have also been closely examined. The structure of the sulfate compound was first solved by Loopastra and MacGillavry¹⁰ and has been refined several times since then¹¹⁻¹³. The compound crystallizes in the orthorhombic space group $Pbca$ with 16 formula units per unit cell. The hydrogensulfate ions are of two types: half of them form dimers, hydrogen bonded across an inversion center whereas the rest build chains of ions hydrogen bonded along a glide plane. All atoms are in general positions. The structure of KHSeO_4 is almost identical¹⁴, the only remarkable difference being the strength of the hydrogen bonds which are appreciably stronger in the selenate than in the sulfate analogue.

In an effort to shed some more light on the unsolved problems concerning the vibrational spectra of these two compounds, we present here the results of our IR spectroscopic investigations of the powdered (protiated and deuterated) materials at room temperature (RT) and at liquid-nitrogen temperature (LNT), together with the Raman spectra.

EXPERIMENTAL

The compounds were prepared by action of dilute, H_2SO_4 or H_2SeO_4 on K_2CO_3 . Deuterated samples were obtained by recrystallization from D_2O (the deuteration was not complete, however, due to rapid H/D exchange which occurs when the deuterates are exposed to air). The IR spectra were recorded on a Perkin-Elmer 580 grating infrared spectrophotometer. The spectra obtained with KBr pellets were essentially identical with those recorded using mulls in Nujol. The low-temperature spectra were recorded using a VLT-2 low-temperature cell cooled with liquid nitrogen. Raman spectra were obtained using a JEOL-IRS-SIB spectrophotometer operating with the green 514.42 nm exciting line.

RESULTS AND DISCUSSION

The IR spectra of powdered KHSeO_4 and KHSO_4 are shown on Fig. 1 and Fig. 2, respectively. Although the compounds are strictly isomorphous, the spectra, as can be seen, are remarkably different. The broad features of the spectra reflect hydrogen bonding interactions and are affected by deuteration (Fig. 3 and Fig. 4) whereas the Raman spectra display the "internal" R-O vibrations (R=S, Se) with manifestations of hydrogen bonding scarcely being evident (Fig. 5 and Fig. 6). Thus, the Raman spectra are largely unaffected by deuteration.

An interpretation and assignment of the spectral features for KHSeO_4 was proposed earlier by Baran⁶. In that paper, it was proposed that the vibrational modes were localized in individual R-O bonds with various couplings between the stretching vibrations. If the R-O oscillators were indeed localized in this manner, eight Raman bands of comparable intensity would be expected (in the absence of correlation field splitting) originating from the R-O stretching vibrations of the two crystallographically-different HRO_4^- ions. In fact, the Raman

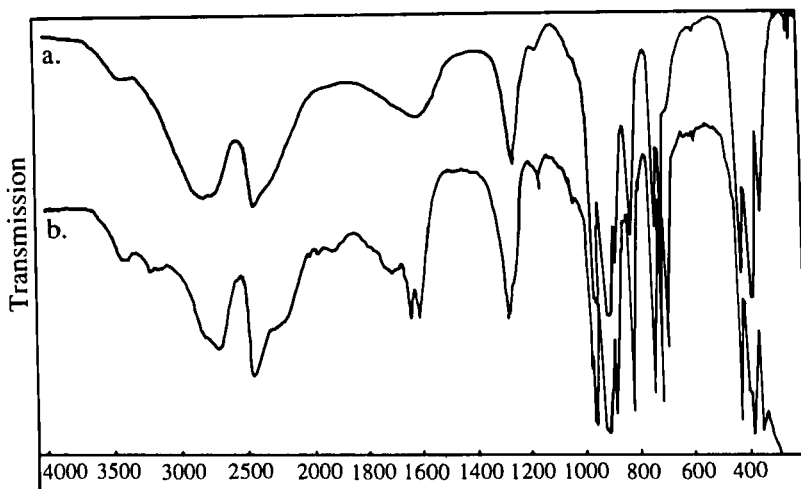


FIG. 1. Infrared Spectra of KHSeO_4
(a) ambient temperature (b) at 77K.

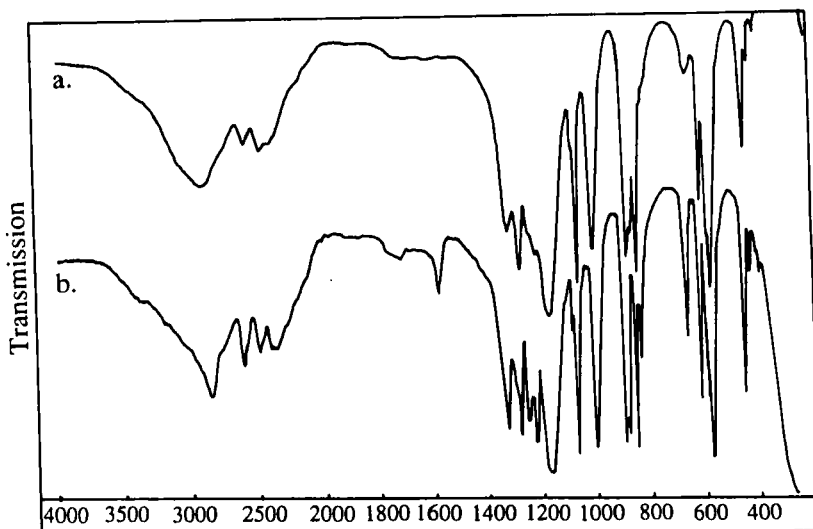


FIG. 2. Infrared Spectra of KHSO_4
(a) ambient temperature (b) at 77K.

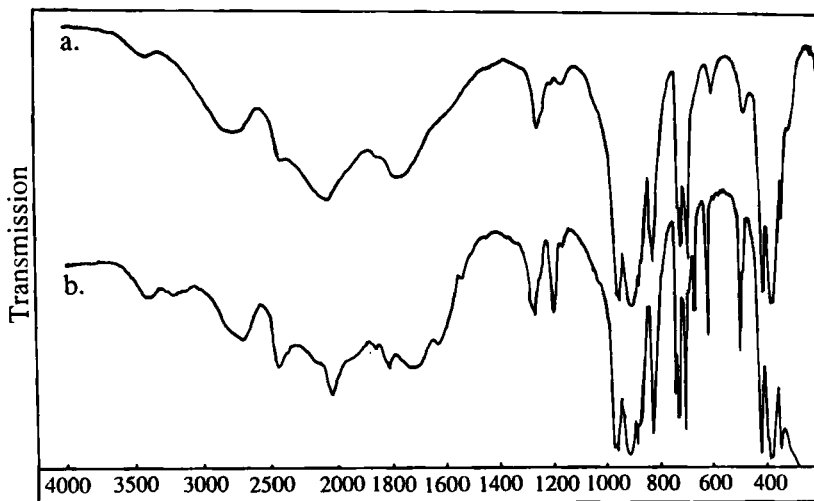


FIG. 3. Infrared Spectra of $K(D,H)SeO_4$
(a) ambient temperature (b) at 77K.

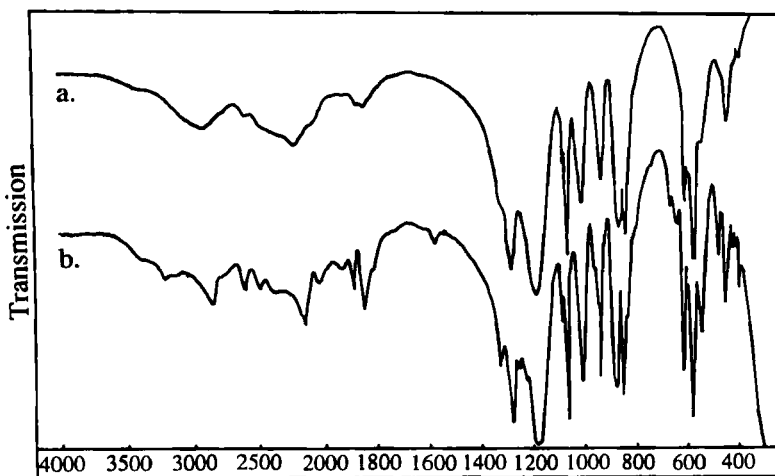


FIG. 4. Infrared Spectra of $K(D,H)SO_4$
(a) ambient temperature (b) at 77K.

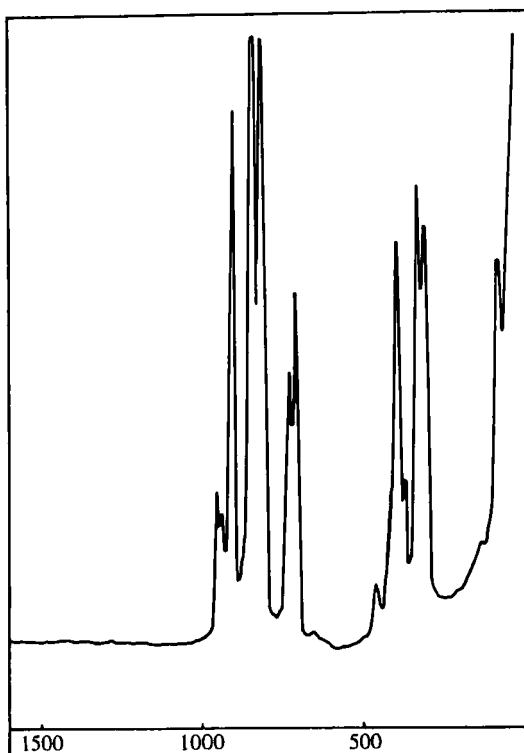


FIG. 5. Raman spectrum of KHSeO_4 (ambient temperature, polycrystalline).

spectra of both solids are dominated by the doublets (ca. 845/820 cm^{-1} for KHSeO_4 ; 1030/1005 cm^{-1} for KHSO_4) which are by far the most intense peaks (Figures 5 and 6). Such a band pattern is clearly more in line with the existence of separate R-O(H) and RO_2 modes than with ones localized in the R-O band and is the interpretation we prefer. This difference has been incorporated into the assignments given in the Table. In other cases, our assignments do not differ from those of Baran.

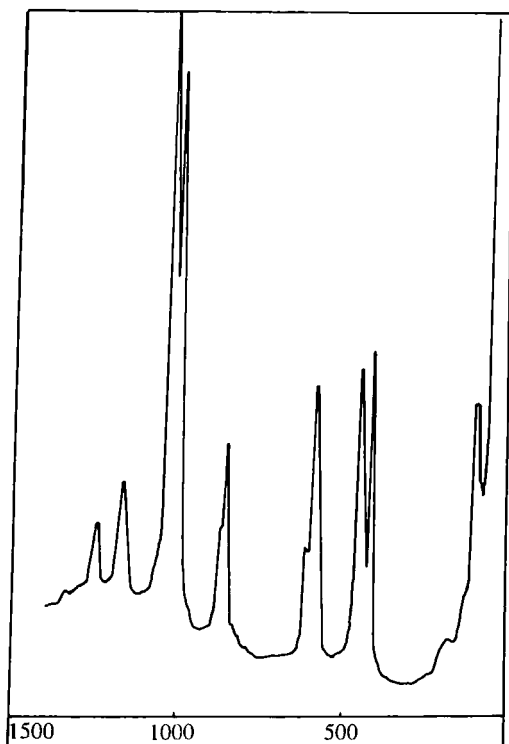


FIG. 6. Raman spectrum of KHSO_4 (ambient temperature, polycrystalline).

It should be pointed out that as a consequence of the low site symmetry of the structural units, quartets (with components of A_{1g} , B_{1g} , B_{2g} and B_{3g} symmetry) should appear in the Raman spectra, whereas triplets (with components of B_{1u} , B_{2u} and B_{3u} symmetry) should be characteristic for the infrared ones. Furthermore, the $u-g$ correlation field splitting should be larger than the $u-u$ (or $g-g$) one for the ions forming dimers, while the opposite should be true for chain ions (this latter expectation was found to be borne out in the spectra of the KHSO_4 salt⁴).

Contrary to the expectations, however, the majority of the bands in our IR spectra show no evidence of correlation field splitting, probably as a result of overlapping of bands which belong to vibrations of different symmetry species. Among the exceptions, the presence of doublets around 970/955 and 750/740 cm^{-1} in the IR spectra of KHSeO_4 , and around 1080/1070 and 900/880 cm^{-1} in KHSO_4 , can be mentioned. The former two doublets are assigned respectively to the νSeO_3 and $\nu\text{Se-O(H)}$ vibrations of the chain-forming HSeO_4^- ions, and the latter to the corresponding vibrations of the hydrogensulfate chains. Thus, our assignment of the bands below 1500 cm^{-1} in the spectra of KHSeO_4 and K(D,H)SeO_4 (Fig. 3) is in agreement with that made by Baran⁶, but not always with the assignment of previous investigators².

As far as the KHSO_4 IR spectrum is concerned, attention should be paid to the region below 1400 cm^{-1} . Here, the band at around 1330 cm^{-1} at room temperature sharpens appreciably when the temperature is lowered and disappears on deuteration (Fig. 4). Since this behaviour is characteristic for vibrations which involve proton motions, the 1330 cm^{-1} band is assigned to the in-plane OH bending vibration and not to sulfate stretching as was made by Goypiro *et al.*⁴. The very low intensity of the corresponding Raman band supports this assignment (it is generally believed that the in-plane and out-of-plane OH bending vibrations give rise to only weak Raman bands). The bands at around 1255 and 1225 cm^{-1} also sharpen on lowering the temperature and disappear on deuteration, so that they too must be due to in-plane OH bendings. The position of all three above-mentioned bands is independent of the degree of deuteration and so none of them can be a component of a correlation-field split mode. The existence of three such bands in a situation when only two types of OH groups are present in the structure is in good agreement with the suggested possibility of proton disorder in the chain HSO_4^- ions¹³.

TABLE

Infrared and Raman Assignments : KHSO_4 and KHSeO_4
(Powder samples. Frequencies in cm^{-1})

KHSO_4		KHSeO_4		Assignment
R	IR	R	IR	
	2865		2815	} $\nu(\text{OH})$
	2615		2700	
	2500		2450	
	2380		2350	
	1560		1640 1608	
1340	1330	1278	1275	} $\delta(\text{OH})$
	1255 1225		1255	
1250	1280	960	970	} $\nu(\text{R-O}_3)$ def.
1170	1190	945 915	955 910	
1005	1005	850	880	} $\nu(\text{R-O}_3)$
1030	1070	820	820	
875	900	740	750	} $\nu(\text{R-OH})$
860	880	720	740	
	855		730 715	
	835			} $\gamma(\text{OH})$
	820		690	
	670			
640	620			} $\nu(\text{R-O}_3)$ def.
615	590	460	425	
	575	405	410	
				} O-R-OH def.
450	455	335	400	
415	430			
	415 400	320	380 350	
180				Translation. Libration.
90		90		

At least two other bands (at around 835 and 670 cm^{-1}) in the LNT spectrum of KHSO_4 (cf. Fig. 2) are strongly temperature sensitive and disappear on deuteration, so that they are assigned to the γOH vibrations of chain-forming ions and dimers respectively. In a previous assignment⁴, only the latter of the two bands was assigned to the out-of-plane OH bending, whereas the former was attributed to one of the S-O(H) stretching modes. The appearance of three new bands below 700 cm^{-1} (at around 640, 550 and 480 cm^{-1}) in the LNT spectrum of K(D,H)SO_4 (the γOD vibrations are expected in this region) not only further confirms this assignment but also supports the notion of proton-disorder (as mentioned, three bands are again found for two vibrations only).

The OH stretching vibrations in KHSeO_4 show the characteristic 'A,B,C' trio of bands, whereas a multiple structure of the bands above 2000 cm^{-1} is found for KHSO_4 . At LNT, a band (an analogue of the 'C' band) grows around 1580 cm^{-1} in the spectrum of KHSO_4 . In the LNT spectrum of deuterated KHSeO_4 the corresponding band, most probably, appears at around 1200 cm^{-1} with an intensity which is about an order of magnitude smaller than the intensity of 'C' band in the spectrum of the protiated compound (compare Fig. 1 with Fig. 3).

Several explanations¹⁵⁻¹⁹ have been offered in an attempt to clarify the origin of the bands in the OH stretching region of systems with strong hydrogen bonds. It has been argued, for example, that the bands and their structure (especially when 'A,B,C' trio is present) may be due to an Evans-type Fermi resonance interaction between the strong continuous absorption due to the OH stretching fundamental, on one hand, and the overtones of the in-plane and out-of-plane bending OH vibrations, on the other¹⁷. Another mechanism, proposed by Fisher, Hofacker

and Ratner (FHR)¹⁸, is based on a model of a polaron-like quasiparticle. It predicts that the intensity of bands 'A' and 'B' should depend on the square root of the temperature, whereas band 'C' should be strongly temperature dependent and should exhibit fine structure. The latter band, furthermore, is predicted to lose intensity when it is shifted downwards on deuteration. It should perhaps be mentioned that the FHR model was originally developed for an ionic defect in crystals but the authors were of the opinion that "...suitable modifications should allow it to be applied also to many other associated systems, such as chromous and cobaltic acids, ferroelectrics, and perhaps solutions containing hydrogen-bonded substances"¹⁸.

If the former of the two outlined explanations is accepted as the correct one, then the pronounced structure of the bands ('A' and 'B') in the KHSO_4 spectrum could be understood in terms of multiple resonance interactions of the two νOH vibrations with various second-order transitions involving bending OH and stretching SO_3 vibrations. Even so, the importance of the FHR mechanism should not be neglected. As predicted in this model, namely, all bands in the OH stretching region are temperature dependent (quantitative measurements on the integrated intensities have not been performed, however). Furthermore, again in agreement with the predictions of the FHR model, there is the existence of fine structure of band 'C' in the spectrum of KHSeO_4 and the grossly diminished intensity of its probable OD analogue. In this context it should be mentioned that Baran has reported that the 'C' band shows polarization which is different from the polarization of the other two bands of the trio⁶. This is something that had been found earlier by Hadzi and coworkers²⁰. On the basis of these findings it seems to us that perhaps the three bands have different origin, which would again be in line with the FHR model.

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