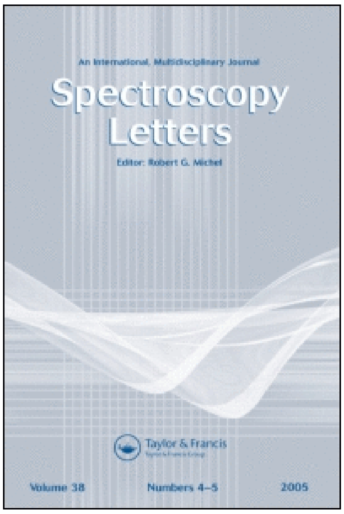

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# Effect of Deuteration on Order-Disorder in Hydrogen Disulfate Compounds, $M_3H(SO_4)_2$ (M = Na, K, Rb, Cs, $NH_4$)

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# EFFECT OF DEUTERATION ON ORDER-DISORDER IN HYDROGEN DISULFATE COMPOUNDS, $M_3H(SO_4)_2$ ($M$ = Na, K, Rb, Cs, $NH_4$)

Key words: hydrogen disulfate, deuteration,
order-disorder, infrared, Raman

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## ABSTRACT

All the hydrogen disulfates $M_3H(SO_4)_2$ (M = Na, K, Rb, Cs and $NH_4$) display broad infrared spectra characteristic of very strong O-H••••O hydrogen bonds overlapped by $SO_4$ group vibrations. Raman spectra (for compounds with M = Na, K, Rb) display the characteristic $SO_4$ modes more clearly. An ordered solid state at room temperature is suggested for M = Na and partially for K, while disorder is present when M = $NH_4$, Cs and Rb. Deuteration brings about ordering for M = K, $NH_4$ and in part when M = Rb, Cs. Order is also facilitated by lowering the temperature.

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## INTRODUCTION

The compounds $M_3H(SO_4)_2$ (where M = Na, K, Rb, Cs and $NH_4$) are very interesting since they appear to contain very strong and unusual O-H••••O hydrogen bonds[1]. When M = $NH_4$, the salt undergoes five phase transitions at atmospheric pressure[2] and ferroelectric phases may also be stabilized by application of pressure to the solid[3]. In addition, phase transitions have been observed for the salt with M = Rb and also when the solids M = K, Rb have been deuterated[4,5]. Some vibrational spectra have been published for these compounds[1] but structural data exist only for the sodium[6] and ammonium (phase II)[7] salts.

The infrared spectra published so far show very broad, low wavenumber features typical of strongly hydrogen bonded O-H••••O systems[8-10] with "internal" vibrations of the more or less distorted $SO_4$ groups superimposed. Interactions between the various vibrations give rise to a number of negative transmission windows (Evans holes) which yield spectra of rather unusual appearance[1,11]. The broad features arise from the stretching mode, $\nu$(O-H) and the in-plane and out-of-plane bending frequencies, $\delta$(O-H) and $\gamma$(O-H), respectively. The $SO_4$ group vibrations are the symmetric stretch ($A_1$,$\nu_1$) the bending frequency (E,$\nu_2$) and the stretching and bending modes (F,$\nu_3$ and $\nu_4$) respectively and are better studied in the Raman spectra where the O-H vibrations are not observed.

Spectra have been employed to gain insight into three main areas. First, splitting of the sulfate $\nu_1$ Raman band is a spectroscopic criterion for an asymmetric hydrogen bond, arising because the two $SO_4^{2-}$ groups become differentiated as the bridging proton moves closer to one of them. Secondly, the frequencies of the various O-H modes have been correlated with the O•••O distance[10]. Finally, the presence (or absence) of substructure in the $\nu_3$ and $\nu_4$ bands may be employed as an indication of order (disorder) in the crystalline solid[12].

This letter presents some results from a deuteration study on $M_3H(SO_4)_2$ compounds and discusses those items listed above wherever possible.

## EXPERIMENTAL

Crystalline samples of $M_3H(SO_4)_2$ with M = Na, K were prepared from supersaturated solutions of the respective $MHSO_4$ salts. The ammonium derivative crystallized from an aqueous solution containing 40% $(NH_4)_2SO_4$ and 24% $H_2SO_4$ after slow evaporation. The salts with M = Rb, Cs were also obtained by slow evaporation at ca. 313K of aqueous solutions containing $MHSO_4$ and $M_2SO_4$. All deuterated samples were prepared by several recrystallizations from $D_2O$.

Infrared spectra were obtained using a Perkin-Elmer Model 580 spectrophotometer and a conventional variable temperature cell was employed for spectra at lower temperatures. Raman spectra were obtained on polycrystalline samples with a JEOL-IRS-S1B spectrophotometer in Skopje or with a Spex Ramalog instrument at the University of Melbourne.

## RESULTS AND DISCUSSION

The spectra are given in Figures 1-8 and some assignments are presented in Tables 1 and 2. Assignments of spectral features as due to hydrogen motion are confirmed by their marked intensity decrease on deuteration.

### 1. $Na_3H(SO_4)_2$

The infrared spectrum (Fig. 1) agrees with that presented earlier[1]. The broad band envelope with submaxima near 940, 860, 790, 700 and 570 $cm^{-1}$ which intensifies on cooling is assigned to the O-H stretching and those near 1610 and 1400 $cm^{-1}$ to the $\delta$(O-H) and $\gamma$(O-H) modes respectively. The crossover of the stretching and bending modes is a general effect

## TABLE 1

### Infrared and Raman Assignments: $Na_3H(SO_4)_2$

| Raman | $Na_3H(SO_4)_2$ | | $Na_3D(SO_4)_2$ |
|---|---|---|---|
| | 1610 | $\delta$(O-H) | |
| | 1530 | | |
| | 1400 | $\gamma$(O-H/D) | 1060 |
| | 1240 | $\nu_3(SO_4)$ | 1240 |
| 1198 | 1212 | | 1212 |
| 1160 | 1178 | | 1180 |
| 1110 | 1100 | | 1100 |
| 1000 | | $\nu_1(SO_4)$ | |
| | 940 | $\nu$(O-H/D) | 950 |
| | 860 | | 880 |
| | 790 | | 790 |
| | | | 660 |
| | 570 | | 580 |
| | | | 480 |
| 635 | 640 | $\nu_4(SO_4)$ | 640 |
| 610 | 620 | | 620 |
| | 603 | | 603 |
| 490 | | $\nu_2(SO_4)$ | |
| 440 | | | |

## TABLE 2

### $(NH_4)_3H(SO_4)_2$: O-H Modes in IR Spectra, 100K

| $(NH_4)_3H(SO_4)_2$ | | $(NH_4)_3D(SO_4)_2$ |
|---|---|---|
| 1560 | $\delta$(O-H/D) | 1060 |
| 1350 | $\gamma$(O-H) | 960 |
| 875 | $\nu$(O-H/D) | 875 |
| 800 | | |
| 740 | | |
| 685 | | 690 |
| 470 | | 470 |
| | | 430 |

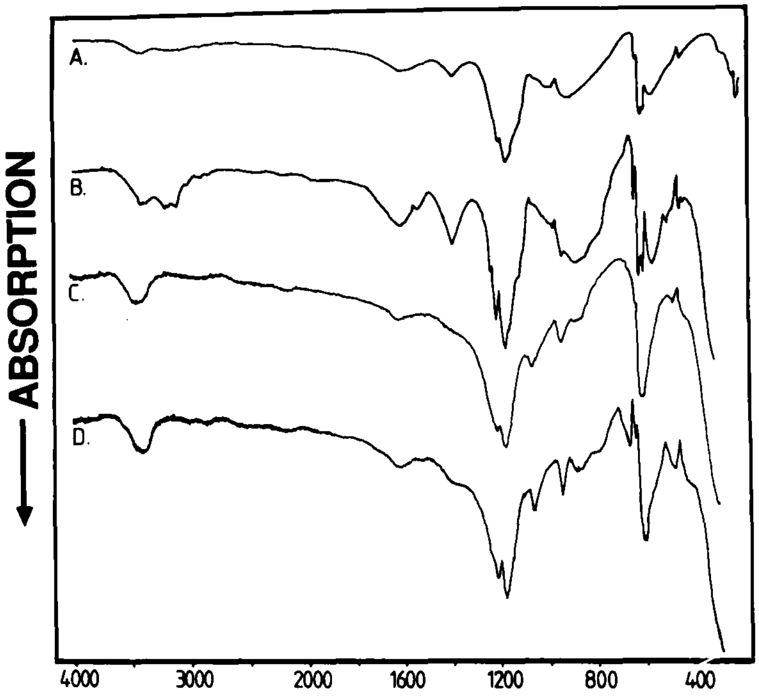

FIG. 1 Infrared spectra of sodium salt

A. $Na_3H(SO_4)_2$ at 300K B. Same at 100K
C. $Na_3D(SO_4)_2$ at 300K D. Same at 100K

for compounds with very strong hydrogen bonds[8,13] and is observed in the spectra of all compounds in the series. The mean positions of the $\nu(O\text{-}H)$ and $\gamma(O\text{-}H)$ vibrations correlate very well with the O····O distance (2.432 Å) in the crystal[10].

The Raman spectrum is given in Fig. 2A. The modes of the $SO_4$ group are quite intense and the substructure which is evident at both 100K and 300K in the $\nu_3$ and $\nu_4$ infrared bands is further emphasized. This is a clear indication of an ordered state in the $Na_3H(SO_4)_2$ crystalline solid.

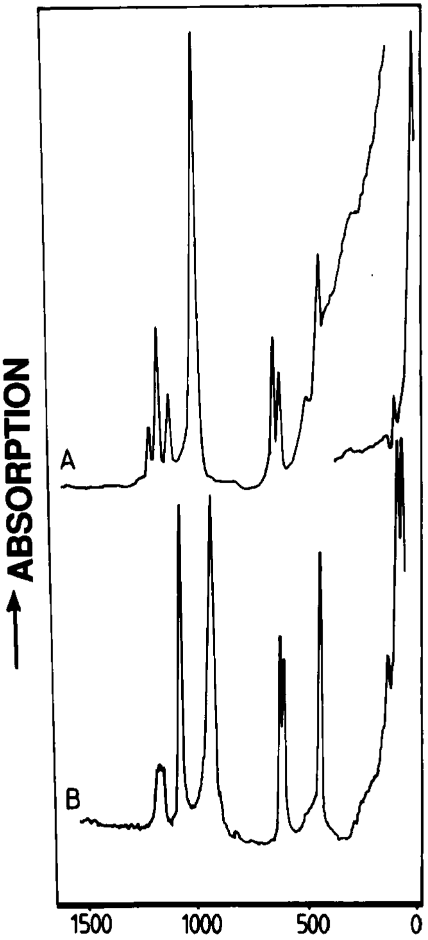

FIG. 2 Raman spectra (polycrystalline, 300K)

A. $Na_3H(SO_4)_2$
B. $K_3H(SO_4)_2$

The effect of deuteration has not been established unambiguously, but if the deuterated analogs of $\delta$(O-H) and $\gamma$(O-H) are assigned to features ca. 1200 $cm^{-1}$ and at 1060 $cm^{-1}$ respectively, a positive isotope effect is observed with $\nu_H/\nu_D$ frequency ratios of 1.34 [for $\delta$(O-H)] and 1.32 [$\gamma$(O-H)]. There are candidates for the deuterated analogs of the 940 and 700 $cm^{-1}$ $\nu$(O-H) bands arising at 660 ($\nu_H/\nu_D$ = 1.42) and 480 $cm^{-1}$ ($\nu_H/\nu_D$ = 1.45) respectively. (See also Table 1). In any event, it is clear that ordering in the solid is not affected by deuteration.

## 2. $(NH_4)_3H(SO_4)_2$

The broad pattern of absorbances due to both the N-H and O-H vibrations together with the several Evans holes give the infrared spectrum of this compound a most unusual aspect. Furthermore, this changes markedly on deuteration (Figure 3). The O-H vibrations change with temperature in the same manner as those for the sodium salt. The relatively large difference between their respective O····O distances (2.54 Å when M = $NH_4$) does not markedly affect the spectra. The 470 $cm^{-1}$ band which sharply increases in intensity as the temperature decreases has been assigned to the $\nu$(O-H) mode[1], while likely assignments for $\delta$(O-H) and $\gamma$(O-H) are the broad features at 1560 $cm^{-1}$ and 1350 $cm^{-1}$ respectively.

The $\nu_3$ (ca. 1200 $cm^{-1}$) and $\nu_4$ (ca. 600 $cm^{-1}$) sulfate "internal" modes do not show any splitting or substructure and this can be taken to indicate a disordered crystalline state at room temperature. After deuteration and temperature lowering, however, bands due to both $NH_4^+$ and $SO_4^{2-}$ groups show a substructure consistent with progressive ordering in the solid. This may be the spectroscopic equivalent of the observation that deuteration promotes a paraelectric-ferroelectric tran-

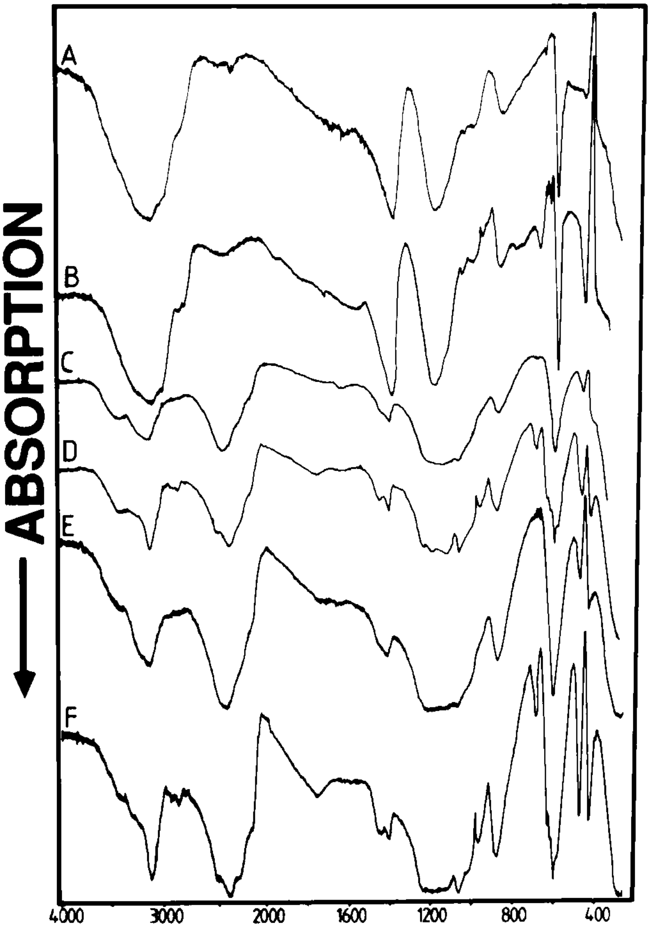

FIG. 3 Infrared spectra of ammonium salt

A. $(NH_4)_3H(SO_4)_2$ at 300K
B. Same at 100K
C. ca. 50% deuterated sample at 300K
D. Same at 100K
E. ca. 70% deuterated sample at 300K
F. Same at 100K

*sition and stabilizes the ferroelectric state in this compound*[14]. It is evident that motion of the $NH_4^+$ ion also contributes to the room temperature disorder.

The new bands which arise after deuteration at ca. 1060 and ca. 960 $cm^{-1}$ may be assigned to the $\delta$(O-D) and $\gamma$(O-D) modes respectively. For these, the $\nu_H/\nu_D$ ratios are 1.47 and 1.406 respectively, but there is no clear isotope effect on the $\nu$(O-H) band. (See also Table 2.)

## 3. $K_3H(SO_4)_2$

The crystal structure of this compound is not known, but while it appears to be isomorphous with the ammonium salt[7], it does not display any of the dielectric anomalies associated with the latter as the temperature is reduced[5]. The Raman spectrum in Fig. 2 is entirely in agreement with that published earlier[1] and shows six "internal" modes as would be expected for a $HSO_4$ unit with $C_{3v}$ symmetry. The splitting in the $\nu_1$ band may be considered as a spectroscopic indication of an asymmetric hydrogen bond and the separation (143 $cm^{-1}$) between the two components which leads to the lower $\nu_1$ frequency (937 $cm^{-1}$) suggests that the hydrogen bonded O····O distance will be longer than that in the sodium and ammonium salts[1].

The broad bands near 700 $cm^{-1}$ and 1560 $cm^{-1}$ in the infrared spectrum were previously assigned to $\nu$(O-H) and $\delta$(O-H) respectively[1]. A low intensity peak at 1360 $cm^{-1}$ which intensifies only slightly on cooling (but which is removed by deuteration) is a likely candidate for the $\gamma$(O-H) mode. The low intensity possibly arises because the thermal motion of the H atom is along the bond instead of being normal to it (as is the usual case)[15].

After deuteration, the band which appears at 892 $cm^{-1}$ (Figure 4) may be assigned to $\gamma$(O-D) although the $\nu_H/\nu_D$

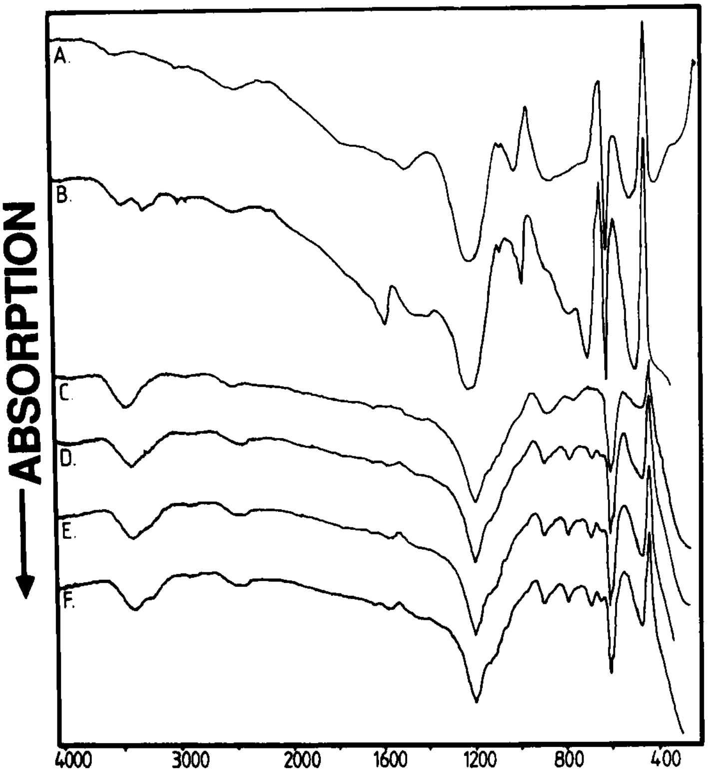

FIG. 4 Infrared spectra of potassium salt

| | | | |
|---|---|---|---|
| A. | $K_3H(SO_4)_2$ at 300K | B. | Same at 100K |
| C. | $K_3D(SO_4)_2$ at 300K | D. | Deuteride, ca. 200K |
| E. | Same, ca. 150K | F. | Same at 100K |

ratio is rather large (1.52). It is known that for systems with crystallographically symmetrical hydrogen bonds, this ratio is $<$ 1.40 for stretching modes but $>$ 1.40 for bending modes[9]. The $\delta$(O-D) vibration may lie in the region of the $SO_4$ $\nu_3$ mode.

The most interesting behavior is exhibited by the bands in the 1000-600 $cm^{-1}$ region, characteristic of the $\nu$(O-H)

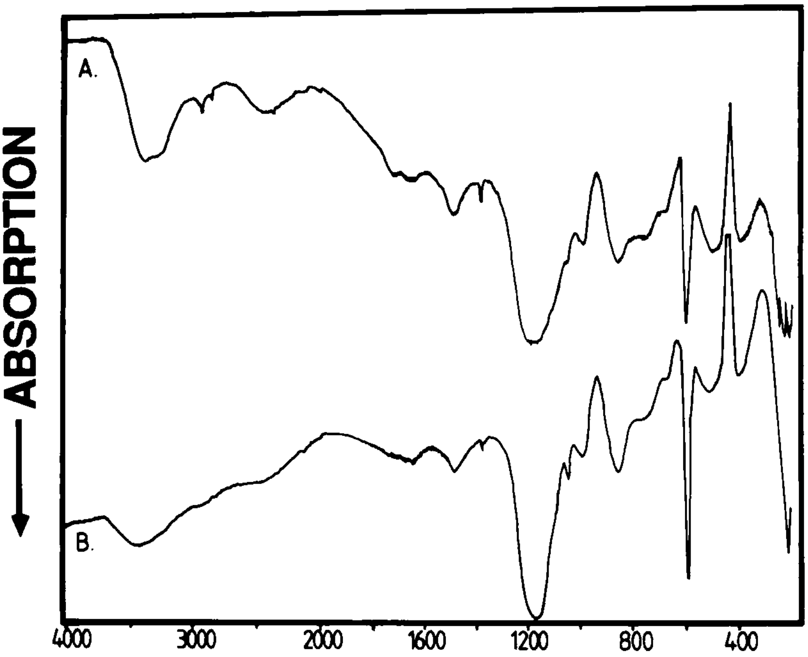

FIG. 5 Infrared spectra at 300K

A. $Rb_3H(SO_4)_2$ B. $Cs_3H(SO_4)_2$

vibration. The ν(O-H) pattern may be affected by lengthening of the O····O distance on deuteration, but it is not clear how the modes are correlated. Also, the interactions between modes and the effect of temperature lowering in this region are drastically reduced (Figure 4C-F). The broad band around 800 $cm^{-1}$ appears to be the most temperature-sensitive and gives rise to a triplet (860, 760, 680 $cm^{-1}$) as the temperature is lowered. The higher intensity (cf. Na salt) of the 860 $cm^{-1}$ band indicates stronger coupling with the O····O modes. It is possible that this coupling obscures any effects of ordering at ambient temperature

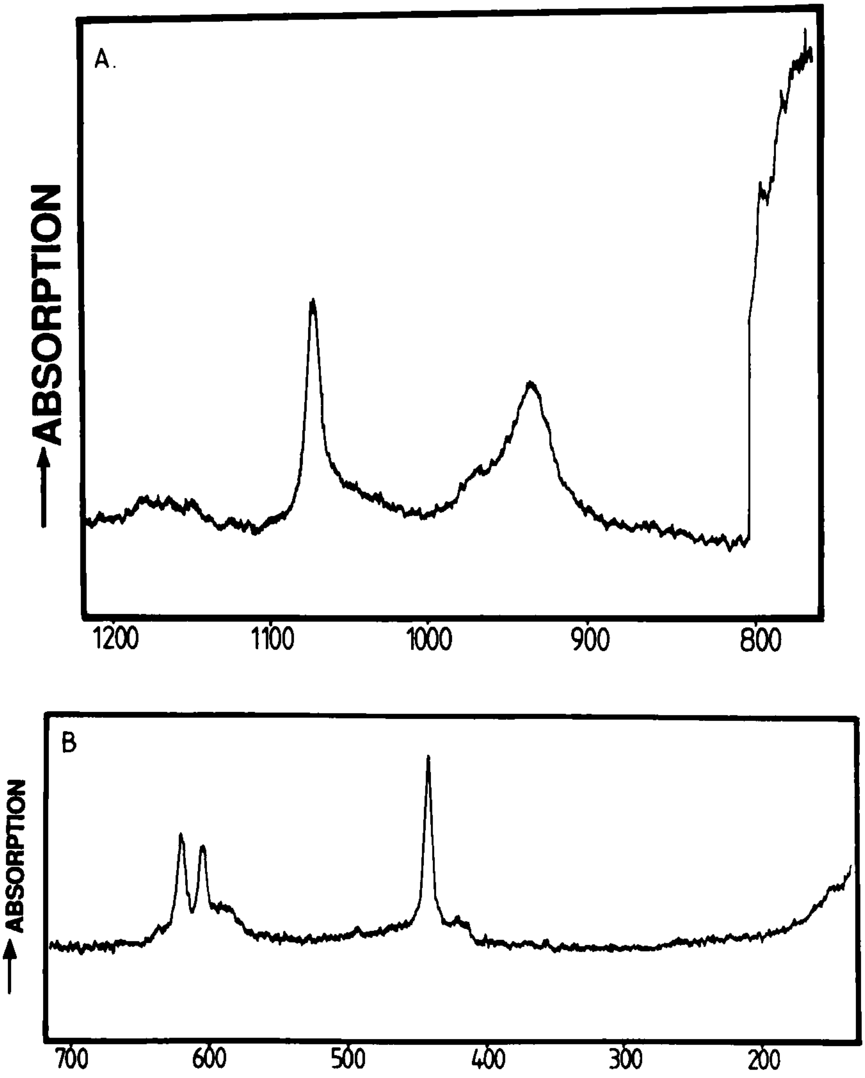

FIG. 6 Raman spectrum of $Rb_3H(SO_4)_2$, 300K

A. 1200-800 $cm^{-1}$ region

B. 700-200 $cm^{-1}$ region

The discontinuity at 800 $cm^{-1}$ is a sensitivity change on the instrument.

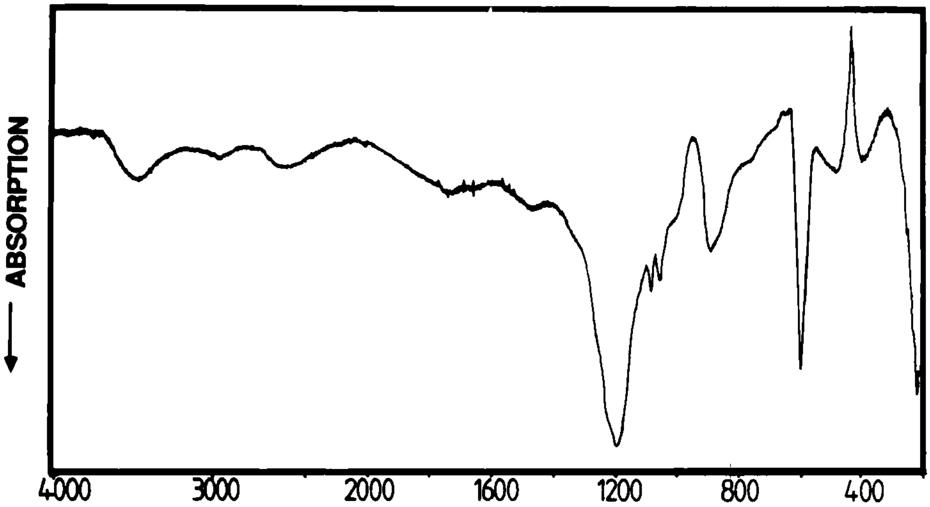

FIG. 7 Infrared spectrum of $Rb_3D(SO_4)_2$, 300K

since the $\nu_3$ and $\nu_4$ modes of the $SO_4$ group clearly display substructure once the compound is deuterated.

## 4. $Rb_3H(SO_4)_2$ and $Cs_3H(SO_4)_2$

Initial, ambient temperature results are presented for these two compounds, neither of which has been investigated structurally. In both cases, a fairly prominent, broad $\nu$(O-H) feature occurs near 860 $cm^{-1}$, but the usual Evans holes indicate that there are other components of this mode, as expected. The bands characteristic of $\delta$(O-H) and $\gamma$(O-H) vibrations are clearly at higher frequencies in the infrared spectra (Figure 5) than those in the potassium and ammonium salts, and this indicates stronger hydrogen bonding (and shorter O••••O distances). Features which may be assigned from the Raman spectrum of $Rb_3H(SO_4)_2$ (Figures 6A,

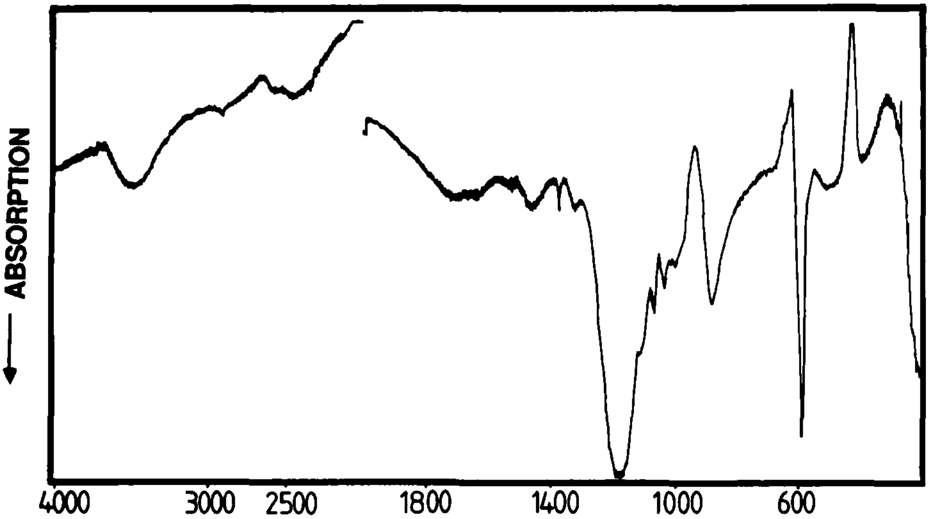

FIG. 8 Infrared spectrum of $Cs_3D(SO_4)_2$, 300K

B) are: $\nu_2$(442 cm$^{-1}$), $\nu_4$(604,620 cm$^{-1}$) and $\nu_3$(ca. 1200 cm$^{-1}$). The slightly smaller separation (136 cm$^{-1}$) in $\nu_1$(1072 and 936 cm$^{-1}$) is also in agreement with a shorter O····O distance.

Although the $\nu_3$ bands are broad in the infrared spectra (Figure 5) there is evidence of some ordering in $Rb_3H(SO_4)_2$ from the Raman spectrum which shows a small splitting in $\nu_4$ and some degree of fine structure in $\nu_3$.

After a single interaction with $D_2O$, no large isotope is apparent in the infrared spectra (Figures 7,8). The original bending modes decrease in intensity and new bands appear near 1330, 1080 and 1050 cm$^{-1}$, but it is not clear whether these arise as a result of the deuteration or from impurities (such as $RbHSO_4$). The shift of the $\nu$(O-H) band from 860 cm$^{-1}$ to 890 cm$^{-1}$ on deuteration and the concomitant shift of $\gamma$(O-H) from 1490 cm$^{-1}$ to 1470 cm$^{-1}$ can be taken as an indication of an increase in the O····O distance. While the $\nu_3$ peaks become somewhat narrower and show signs of fine structure after deuteration, the $\nu_4$ modes near 600 $cm^{-1}$ remain intense singlets. Evidently these species are subtly different from the potassium salt in which $\nu_4$ splitting is clearly present, even at room temperature.

Such subtle differences in ordering may have profound influences on other solid state properties. Consequently, a systematic study of these types of materials is currently continuing.

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