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Vibrational Spectra of $M_2Cu(SO_4)_2 \cdot 6H_2O/D_2O$ (M = NH_4 or K)

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The IR and polarized Raman spectra of $M_2Cu(SO_4)_2 \cdot 6H_2O$ (M = NH_4 or K) and their deuterated analogs have been recorded and analyzed. The site locations for the SO_4^{2-} ions in these crystals are found to be identical. These SO_4^{2-} tetrahedra are angularly distorted. The vibrational bands of the metal aquo complex for $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$ are shifted considerably from those for other Tutton salts. One can infer from the spectral data that the NH_4^+ ion is not rotating freely in the lattice. Separate bands have been identified for three different types of water molecules in both samples. This interpretation is confirmed by analysis of the spectral changes due to the replacement of hydrogen by deuterium in the H_2O units.

Introduction

Among the monoclinic double salts of the type $M_2^IM^{II}(SO_4)_2 \cdot 6H_2O$ (M^I and M^{II} are monovalent and divalent cations, respectively), the copper-containing Tutton salts are not exactly isostructural because the coordination numbers of some of the oxygen atoms bonding to NH_4^+ and K^+ ions are different (*1*). Also, an earlier investigation reported that the arrangement of water molecules about the central copper ion in $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$ differs from the general pattern for this series (*2*). IR and single-crystal Raman studies have been conducted for these compounds in order to understand the difference between the vibrational modes of $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$, $K_2Cu(SO_4)_2 \cdot 6H_2O$, and other Tutton salts.

Experimental

Single crystals used for the present investigation are grown by slow evaporation of equimolar aqueous solutions of A.R. grade $CuSO_4 \cdot 5H_2O$ and M_2SO_4 (M = NH_4 or K) at room temperature. Partially deuterated samples are obtained by repeated crystallization of solutions of the corresponding samples in pure D_2O. A Spex Ramalog 1401 double monochromator equipped with a Spectra Physics Model 165 Ar^+ laser has been employed to obtain the Raman spectra in the Stokes region of the green line (514.5 nm). The IR spectra have been recorded with a PE 580 spectrophotometer using a Nujol technique.

$(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$ and $K_2Cu(SO_4)_2 \cdot 6H_2O$ belong to the monoclinic system with space group $P2_1/a$ (C_{2h}^5) ($Z = 2$) (*2, 3*). Group theoretical analysis predicts 234 and

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TABLE I

VIBRATIONAL SPECTRA DATA (cm^{-1}) BAND ASSIGNMENTS

$(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O/D_2O$					$K_2Cu(SO_4)_2 \cdot 6H_2O/D_2O$					
Raman			IR		Raman			IR		
H_2O					H_2O					
A_g $a(cc)b$	B_g $a(cb)c$	D_2O	H_2O	D_2O	A_g $a(cc)b$	B_g $a(cb)c$	D_2O	H_2O	D_2O	Assignments[a]
57 w					63 w	63 w				t^{s}
62 m	64 m	64 m			71 m	70 m	70 m			
81 s	81 s	81 s								l^{s}
96 m	96 m	96 m			95 m	89 s				
106 wbr					104 mbr					$\nu_{\text{O-H...O}}$
120 s	120 s	120 m			114 w	114 m	114 w			l^{s}
					118 s	118 s	118 s			
142 m	146 m				142 m	142 m				l^{n} or ν_6^{c}
176 w	164 wbr				169 w	169 w				
193 m	175 m	175 m	210 s	210 w	193 s	192 s	192 s	210 s	210 vw	ν_5^{c}
223 m	233 w	235 m	230 m	245 vw	232 m	230 s	232 m	235 m	250 vw	
238 m			245 w		258 s	258 m	258 m	250 w		ν_4^{c}
270 w	264 w				289 m	287 w				ν_2^{c}
					307 w	307 w	307 w			
						320 w	320 w			$\nu^{K^+...O}$
342 w	339 w		355 vw	270 w	363 w	369 w		365 vw	270 w	ν_3^{c}
373 wbr	370 wbr									ν_6^{n}
					384 w					$2\nu_5^{c}$
403 wbr	393 wbr				406 m	409 w				ν_1^{c}
438 w	437 w	438 w	425 wbr	425 br	442 m	442 s	442 s	440 m	440 m	ν_2^{s}
458 s	458 s	458 s			463 s	463 s	463 s	470 w	470 w	
	485 vw	350 wbr	540 wbr			559 mbr	424 mbr	550 wbr	410 vw	l^{w}
608 w	604 sh	604 w	610 vs	610 vs	613 s	610 s	610 w	615 vs	615 vs	
617 s	618 s	617 s	640 w	640 m	622 m	626 m	625 m	660 m	655 w	ν_4^{s}
632 m	633 m				636 s	636 m	636 vw			
	676 wbr			500 vw	691 w	683 vw	500 w			
756 wbr	748 w	548 w	680–800 br			740 wbr	553 w	775 br		l^{w}

773 w	784 wbr	575 w		570 w	798 wbr	802 w	584 wbr		630 vw	
810 wbr	830 vw		860 wbr	710 wbr	848 vw			860 wbr		
922 w	914 w	914 w			926 w	921 w				$2\nu_2^s$
962 w	964 w	986 vs	975 m	975 m	970 w	972 w	988 vs	965 s	965 s	
986 vs	986 vs				988 vs	988 vs		995 w	995 vw	ν_1^s
1052 w	1052 w				1046 w	1046 w				$\nu_1^s + l^s$
1079 m	1071 m	1071 s			1081 m	1074 m	1074 s			
1105 m	1106 m	1105 w	1080 vs	1080 s	1110 m	1110 m	1110 m	1095 vs	1095 vs	ν_3^s
1126 m	1127 s	1127 m	1130 m	1130 m	1136 s	1136 s	1136 s	1135 s	1135 s	
1153 m	1154 m				1161 s	1161 m	1161 m			
1392 w	1408 w		1390 vs 1425 br	1400 vw						
1441 wbr	1436 mbr									ν_4^n
1486 m	1474 mbr									
1626 mbr	1624 mbr	1200 mbr			1638 mbr	1642 w	1200 mbr			W I
1640 mbr	1643 wbr	1218 m	1500–1650 br	1190 w	1686 mbr	1706 wbr	1223 m	1530–1670 br		ν_2W II
1685 w	1673 mbr	1254 w			1715 w	1727 wbr	1238 mbr			W III
	1691 w									ν_2^n
1713 mbr	1712 wbr									
1752 w	1764 w									$\nu_4^n + \nu_6^n$
	2037 w		2030 w							$\nu_2^n + \nu_6^n$
	2061 w		2200 br							
		2640 w					2662 w			νHDO
		2709 w					2725 w			
3025 wbr	3029 w									ν_1^n
	3096 w									$\nu_2^n + \nu_4^n$
3125 wbr	3135 wbr	2276 w		2300 w						
3195 wbr	3181 w		3140–3200 br	3150 wbr						ν_3^n
3215 w	3213 w									
3257 mbr	3258 w	2366 w			3250 mbr	3260 mbr	2329 mbr			W III
3288 w		2389 w			3287 mbr		2352 mbr			ν_1W II
3301 w	3301 vw	2392 vw	3300–3480 br	2400 br	3295 wbr	3318 w	2415 mbr	3000–3500 br	2400 br	W I
3353 wbr	3356 wbr	2414 w		2550 wbr	3355 w	3357 w	2431 w		3400 wbr	W III
3398 wbr	3397 wbr	2433 wbr			3380 w	3382 wbr	2470 m			ν_3W II
3432 w	3438 w	2470 mbr			3424 wbr		2562 w			W I

Note. Relative intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad. ν_6^n, torsional oscillation of NH_4^+.

[a] Superscripts n, s, c, and w refer to modes of NH_4^+, SO_4^{2-}, $[Cu(H_2O)_6]^{2+}$, and H_2O, respectively. The l and t represent the librational and translational modes, respectively.

186 normal modes (including three acoustic modes) for NH_4Cu and KCu, respectively. They are distributed as

$$\Gamma_{234}^{NH_4Cu} = 57A_g(R) + 57B_g(R) + 60A_u(IR) + 60B_u(IR)$$

and

$$\Gamma_{186}^{KCu} = 45A_g(R) + 45B_g(R) + 48A_u(IR) + 48B_u(IR).$$

Internal Modes of SO_4^{2-}

The ion occupies a lower site symmetry C_1 in both $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$ and $K_2Cu(SO_4)_2 \cdot 6H_2O$ crystals. As a result, the IR-inactive ν_1 and ν_2 modes may become active, and the degeneracies of ν_2, ν_3, and ν_4 modes may be removed. For both crystals, $\nu_1(A_1)$ modes are found to split into two components in their Raman spectra. However, in the IR spectra, only one band is observed at 975 cm^{-1} for $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$ whereas $K_2Cu(SO_4)_2 \cdot 6H_2O$ possesses two bands in this region. As the correlation field splitting is usually large for hydrogen bonded systems (*4*), the observed splittings rule out the possibility of the existence of two types of SO_4^{2-} ions in $K_2Cu(SO_4)_2 \cdot 6H_2O$ crystal as suggested earlier by Gupta *et al.* (*5*). The splittings for both crystals are due to a correlation field effect. The partial or complete lifting of the degeneracy of $\nu_2(E)$, $\nu_3(F_2)$, and $\nu_4(F_2)$ modes in the IR and Raman spectra is due to a crystalline field. The removal of the degeneracy of the bending modes in the Raman spectra suggests that the angular distortion of SO_4^{2-} is greater than the linear distortion. From the order of splittings in the IR spectra it is evident that the distortion is greater for the $K_2Cu(SO_4)_2 \cdot 6H_2O$ crystal.

Internal Modes of $[Cu(H_2O)_6]^{2+}$

The vibrational assignments of this complex (see Table I) are based on the earlier normal coordinate analysis by Brown and Ross (*6*) and the observation of metal aquo complex bands for other Tutton salts (*7, 8*). Appearance of multiple bands for ν_4 (IR, Raman) and ν_5 (Raman) is due to the reduction of the site symmetry of the complex from O_h to C_i. As a consequence of the strain produced by the crystalline field (*9*), ν_3 and ν_4 modes are found to be active in the Raman spectra. Comparing the spectra of $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$ and $K_2Cu(SO_4)_2 \cdot 6H_2O$, one observes that all of the bands of the complex are shifted to low wave numbers for $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$. This shift is due to larger $Cu–H_2O$ bond lengths (*2*). Because the bands due to the vibrational modes of the complex are weak and fall in the low wave number region, it is difficult to observe all of the corresponding bands for the deuterated samples.

Internal Modes of Water

The internal modes of water are identified on the basis of H_2O units involving three different hydrogen bond lengths [2.826 Å (w_1), 2.727 Å (w_2), and 2.683 Å (w_3)] in $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$ crystal. In $K_2Cu(SO_4)_2 \cdot 6H_2O$, the bond lengths are close to these values. In the Raman spectra, separate weak broadbands with frequencies shifted from their free state values have been observed for all of the modes for the three different types of water molecules. Due to the lower site symmetries of H_2O and NH_4^+ ions in the crystal, vibrational interaction between the groups is possible in the high-frequency (3120–3440 cm^{-1}) region. However, assignments of water bands are proposed with help from the spectrum of a deuterated sample (see Table I). The considerable shifting of the bending modes that is observed in both the Raman and IR spectra for $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$ indicates strong hydrogen bonding for water, probably stronger than that for ammonium ions, consistent with the crystal data (*10*).

Internal Modes of NH_4^+

Internal modes of ammonium group are identified on the basis of their free state values (*11*), their hydrogen bond strength, and their deuterium substitution. The appearance of ν_2 around 1400 cm^{-1} in IR indicates moderate (probably weak) hydrogen bonding for this ion (*12*). It is the low polarizability and anharmonic force fields of NH_4^+ that cause the bands to be weaker and broader than the corresponding modes of SO_4^{2-} ions even though they occupy similar types of sites (C_1) in the crystal. From the presence of combination bands in the region 1750–2070 cm^{-1} in the Raman spectra and at 2030 cm^{-1} in the IR spectra, one can infer that NH_4^+ is not freely rotating in the lattice (*13*).

External Modes

It is difficult to observe the translational modes of the complex as they are strongly mass dependent. Also, the translational modes of NH_4^+ overlap with the internal modes of the complex in the region 150–225 cm^{-1}. Hence only the assignments of external modes of SO_4^{2-} ion have been proposed (see Table I), taking into account the fact that the translatory modes are generally weak in the Raman spectra whereas the libratory modes will appear with appreciable intensity.

Tutton Salts: A Comparison

Comparison of IR and polarized Raman data of $K_2Mg(SO_4)_2 \cdot 6H_2O$ (*7*), $(NH_4)_2M(SO_4)_2 \cdot 6H_2O$ (M = Zn, Mn) (*14*), $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$ (*8*), and $M_2Cu(SO_4)_2 \cdot 6H_2O$ (M = NH_4, K) (see Table 1) shows that the SO_4^{2-} tetrahedron is more angularly distorted in all of the compounds except $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$. From the splittings of the bending modes, one can infer that this distortion in different compounds is in the order $K_2Cu(SO_4)_2 \cdot 6H_2O > (NH_4)_2Cu(SO_4)_2 \cdot 6H_2O > (NH_4)_2Mn(SO_4)_2 \cdot 6H_2O > (NH_4)_2Zn(SO_4)_2 \cdot 6H_2O > K_2Mg(SO_4)_2 \cdot 6H_2O$. The distortion in $K_2Cu(SO_4)_2 \cdot 6H_2O$ is to such an extent that the degeneracy of the ν_2 mode is completely removed in the IR spectrum. Combination bands indicate that the NH_4^+ ions are not rotating freely in the lattice of all four compounds. Bands of the metal aquo complex in $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$ considerably shift from those of other compounds, indicating a difference in the nature of the Cu–H_2O bonds.

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