Vibrational Spectra of Copper Sulfate Hydrates Investigated with Low-Temperature Raman Spectroscopy and Terahertz Time Domain Spectroscopy

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ABSTRACT: In this paper, the vibrational spectra of copper sulfate hydrates (CuSO₄·*x*H₂O, *x* = 5, 3, 1, 0) have been investigated with lowtemperature Raman spectroscopy and terahertz time domain spectroscopy (THz-TDS). It is found that the four groups of Raman bands between 90 and 4000 cm⁻¹ can be assigned to lattice vibration as well as intramolecular vibrations of a copper complex, sulfate group, and water molecules. The variation of vibrational spectra during the dehydrated process are discussed in detail considering the transformation of the crystal structure, especially the bands between 3000 and 3500 cm⁻¹, which are attributed to the ν_1 and ν_3 modes of water molecules. In addition, as a complement of Raman spectra, the THz spectra at 0.1–3



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THz indicate the absorption due to the low-frequency lattice vibration and hydrogen bond.

INTRODUCTION

Copper sulfate pentahydrate, commonly called chalcanthite or blue vitriol, is a naturally occurring mineral. When heating CuSO₄·5H₂O, it will dehydrate in three steps, losing two water molecules at 50 °C, then another two at 90 °C, and the last one at 230 °C.^{1,2} In the hydrates, water molecules either coordinate with copper ions or form hydrogen bonds, both of which have important impacts on the structure and chemical properties of the hydrates. Therefore, the chemical environment of water molecules has been intensively investigated by X-ray diffraction and vibrational spectroscopy in copper sulfate hydrates and sulfates with similar structure.^{3,4} Structure tests show that different hydrates have different crystal symmetry and coordination.^{5–9} Thermo-Raman and IR spectroscopy have been exploited to study the dehydrated process and the change of vibrational models due to phase transition.^{2,10,11} However, the resolution of Raman spectra is lowered at high temperature, especially for the detection of water molecules whose vibrational modes have weak Raman response. In addition, the hydrogen bond is a kind of weak interaction, whose response frequency is usually lower than 100 cm⁻¹. In such a frequency range, Raman and IR spectra are of poor frequency resolution.

Recently, with the development of the generation and detection technologies of terahertz rays, terahertz time domain spectra have been applied in many fields, such as materials analysis, medical diagnosis, and security inspection.^{12,13} THz measurements are highly sensitive to water molecules, and therefore, it is an effective method to study the rotational modes of water vapor and the hydrogen bonds in condensed water and hydrates.¹⁴ Hydrogen bonds in some organic molecules have been reported in the literature;^{15,16} however,

related research on inorganic hydrates is rarely reported, to our knowledge.

In this paper, we present the study of Raman and THz spectra of copper sulfate hydrates and analyze the vibrational modes and hydrogen bonds in these compounds in detail. Compared to previous research, our Raman spectra were collected at low temperature (-175 °C) with a high frequency resolution, and the assignment of the bands that belong to water molecules is clarified. Furthermore, with THz spectra, we studied the response of the hydrogen bond and lattice vibration in the low-frequency region (<100 cm⁻¹), which has not been reported in these hydrates.

EXPERIMENTAL PROCEDURES

Sample Preparation. Powder of copper sulfate pentahydrate with high purity was used as the raw material in our experiments. In order to get the trihydrate, monohydrate, and anhydrate, the pentahydrate was heated to 50, 90, and 230 $^{\circ}$ C, respectively, and kept for 30 min to complete the phase transition.

Raman Experiments. Raman spectra were obtained on a LabRAM HR800 Raman spectrometer (HORIBA Jobin-Yvon Ltd.) with a temperature control accessory (Dlink). The Raman scattering was excited by the 632.8 nm line of a He–Ne laser and detected with a CCD camera in frequency ranges of 90–1500 and 2500–4000 cm⁻¹. The spectra at 25 and -175 °C were collected for comparison.

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Terahertz Spectra Experiments. Terahertz time domain spectra were measured with Z3 THz time domain spectrometer system (Zomega Terahertz Corp., U.S.A.), which is equipped with a photoconductive antenna for the generation of THz radiation and an electro-optical crystal for detection. The pump laser is a mode-locked Ti:sapphire laser (Spectra Physics, U.S.A.) with the center wavelength of 800 nm and a pulse duration of 100 fs. The equipment was filled with high-purity (99.999%) nitrogen when collecting the time domain signal. Corresponding frequency domain spectra in the range of 0.1-3THz were obtained through Fourier transform. We repeated the measurements three times, and the average values were adopted.

RESULTS AND DISCUSSION

The Raman spectra of hydrates and anhydrates of copper sulfate between 90 and 1500 cm^{-1} are shown in Figure 1. It is



Figure 1. Raman spectra of $CuSO_4$ ·xH₂O below 1500 cm⁻¹. For all four kinds of hydrates, the Raman spectra at temperatures of 25 and -175 °C are collected.

found that the spectra are well-resolved at low temperature and that the Raman bands can be divided into three groups. The modes below 400 cm⁻¹ are related to the external modes of the ions (lattice phonons) and internal modes of the copper complex, while the modes above 400 cm⁻¹ are associated with the intramolecular vibration of sulfate.¹⁷ The frequencies of Raman bands are listed in Tables 2 and 3. According to the spectra of pentahydrate, the broad band located at 125 cm⁻¹ consists of three modes, 122, 131, and 140 cm⁻¹, which are

 Table 1. Crystal Structure Information of Copper Sulfate

 and Its Hydrates

formula	crystal structure	lattice parameters	coordination of Cu ²⁺
CuSO ₄ ·5H ₂ O ¹⁸	triclinic	$ a = 6.141, b = 10.736, c = 5.986(Å), \alpha = 82°16', \beta = 107°26', \gamma = 102°40' $	4H ₂ O + 2O[SO ₄ ²⁻]
$CuSO_4 \cdot 3H_2O^7$	monoclinic	$ a = 5.592, b = 13.029, c = 7.341(Å), \beta = 97^{\circ}3' $	3H ₂ O + 3O[SO ₄ ²⁻]
$CuSO_4{\cdot}H_2O^8$	pseudomonoclinic	$ \begin{aligned} &a = 5.037, b = 5.170, c = \\ &7.578, \alpha = 108^\circ 37', \beta \\ &= 108^\circ 23', \gamma = 90^\circ 56', \end{aligned} $	2H ₂ O + 4O[SO ₄ ²⁻]
CuSO ₄ ¹⁹	orthorhombic	$a = 8.409, b = 6.709, c = 4.839(\text{\AA})$	60[S0 ₄ ²⁻]

attributed to intermolecular vibration of copper and sulfate ions (external modes). The 280 cm⁻¹ band splits into three, 248, 268, and 283 cm⁻¹, which can be assigned to the internal modes of the complex. In CuSO₄·SH₂O copper ion is six-coordinate, in which four of ligands are water molecules and the other two are oxygen atoms from two sulfate groups. The bands lying in 400–1500 cm⁻¹ are generated by the internal vibration of sulfate ions. The peaks at 425, 441, and 468 cm⁻¹ are related to the symmetric bending vibration of SO₄²⁻ (ν_2 modes). In addition, the peaks at 611, 984, and 1148 cm⁻¹ correspond to ν_4 (antisymmetric bending), ν_1 (symmetric stretching), and ν_3 modes (antisymmetric stretching), respectively. The results are in good agreement with the ones in ref 17, except for several weak bands.

During the heating process, CuSO₄·5H₂O transforms into CuSO₄·3H₂O first, and the corresponding changes in the Raman spectrum are observed. The peak of ν_1 shows a blue shift, from 984 to 1010 cm⁻¹, and the ν_3 mode shows a red shift, from 1148 to 1127 cm⁻¹. The band of the ν_4 mode splits to two, 586.5 and 618 cm⁻¹, and the bands below 400 cm⁻¹ also differ a lot (see Table 2). It can be explained by the change in crystal structure. The trihydrate has a monoclinic structure, and the six ligands of copper are three water molecules and three oxygen atoms. Therefore, both internal modes of the sulfate group and the lattice modes vary. At higher temperature, another two water molecules are lost to form monohydrate, which has pseudomonoclinic symmetry, and the ligands are made up of two water molecules and four oxygen atoms. Because sulfate ions have two kinds of crystal environments, obvious splitting appears in the Raman spectrum. For instance, the ν_1 mode at 1010 cm⁻¹ splits into two at 1011.5 and 1045 cm⁻¹, and the ν_3 mode at 1127 cm⁻¹ splits into the doublet at 1100 and 1209 cm⁻¹. The bands of the ν_2 and ν_4 modes also exhibit remarkable changes; the former (423, 435, and 482) combine into two, 420.5 and 510 cm^{-1} , while the latter (586.5, 618) split into three, 607, 620, and 665.5 cm⁻¹. Moreover, the modes below 400 cm⁻¹ become more intense in the monohydrate. A typical example is that the band at 387 cm⁻¹ shifts to 345.5 cm⁻¹ and becomes much stronger. From the monohydrate to the anhydrous one, the new phase possesses orthorhombic symmetry and different lattice parameters. As a result, the two bands of the ν_1 mode merge into one band at 1059.5 cm⁻¹, and the peaks of the ν_2 , ν_3 , and ν_4 modes also show some shift.

Figure 2 presents the vibrational spectra of H₂O molecules in hydrates. According to symmetry analysis, free water molecules have three nondegenerate normal modes, the symmetric stretch mode ν_1 (3825 cm⁻¹), the bend mode ν_2 (1654 cm⁻¹), as well

x	= 5	x	= 3	<i>x</i> = 1		x = 0		
25 °C	−175 °C	25 °C	−175 °C	25 °C	−175 °C	25 °C	−175 °C	mode
125	122	123	127	105	109.5	110	116	lattice vibration
	131	160	145	130	137	164	170	
	140		153			186	192	
			164					
280	248		193.5	207.5	213	268	273	internal modes of complex
	268	250	250	244	247.5			
	283		276	268	273			
		386	387	345	347.5			

Table 2. Raman Bands of CuSO₄·xH₂O below 400 cm⁻¹

Table 3. Raman Bands of CuSO₄·xH₂O between 400 and 1500 cm⁻¹

x	= 5	x = 3		x = 1		x = 0		
25 °C	−175 °C	25 °C	−175 °C	25 °C	−175 °C	25 °C	−175 °C	mode
455	425	429	423	419	420.5	458.5	459	$\nu_2[{\rm SO_4}^{2-}]$
	441		435	515	510	497	482.5	
	468	481	482				500	
611	611	586.5	586.5	607	607	583	579	$\nu_4[SO_4^{2-}]$
		620	618	620.5	620	605	587	
				669	665.5		607	
						932	930.5	
984	984	1009	1010	1014	1011.5	1057	1059.5	$\nu_1[SO_4^{2-}]$
				1043.5	1045			
1146	1148	1126	1127	1097	1100	1162.5	1154	$\nu_3[SO_4^{2-}]$
				1204	1209	1174	1173	
						1197	1203	



Figure 2. Raman spectra of $CuSO_4$:xH₂O between 2500 and 4000 cm⁻¹.

as the asymmetric stretch mode ν_3 (3936 cm⁻¹).²⁰ However, in the condensed state, such as in inorganic hydrates, the H₂O molecules coordinate with a cation. Thus, the vibrational frequencies may be different from the ones in free H₂O molecules due to the interaction with the center cation.

In the previous research, the vibrational spectrum of H_2O in $CuSO_4$ · SH_2O has been reported, and the observed bands are assigned to corresponding modes.¹⁷ In the present paper, we show the Raman spectra of water molecules in the other copper sulfate hydrates, which are listed in Table 4. As mentioned above, in $CuSO_4$ · SH_2O , the copper ion is coordinated by four H_2O molecules and two oxygen atoms (from the sulfate group) to form an octahedron, whereas another H_2O molecule connects the adjacent octahedral through a hydrogen bond to

Table 4. Raman Bands of CuSO₄·xH₂O above 3000 cm⁻¹ at -175 °C

x = 5	x = 3	x = 1
3110	3100	3105
3190	3155	
3355	3360	3370
3475	3410	
5775	5410	

keep the structure stable. The aforementioned five H₂O molecules can be divided into three groups; two of them weakly bond to Cu^{2+} (denoted by I-H₂O), the other two have stronger bond strength (marked as II-H₂O), and the last one is denoted by III-H₂O. As shown in Figure 2, the resolution of the spectra is poor due to noise and spectral broadening at room temperature, whereas the results at -175 °C are much better. The pentahydrate is detected with four bands, and their center frequencies are 3110, 3190, 3355, and 3475 cm⁻¹. After losing two I-H₂O molecules, the trihydrate is formed, in which all three H_2O molecules coordinate to Cu^{2+} , but they are still divided into two groups because of different bonding strengths. Figure 2 and Table 4 indicate that CuSO₄·3H₂O possesses four Raman bands above 3000 cm⁻¹, whose frequencies are 3100, 3155, 3360, and 3410 cm⁻¹. When monohydrate is obtained at about 90 °C, only two bands are investigated at 3105 and 3370 cm⁻¹. Anhydrous copper sulfate has no Raman peak above 3000 cm⁻¹; therefore, its spectrum is not given. According to ref 17, in the pentahydrate, the peaks around 3110 and 3190 cm^{-1} can be assigned to the ν_1 mode of I-H₂O and II-H₂O, respectively, and the bands at 3355 and 3475 $\rm cm^{-1}$ can be ascribed to the ν_1 and ν_3 modes of III-H₂O₂ respectively. However, through comparing three types of hydrates, we may draw some different results. The monohydrates have only one

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type of H_2O ; thus, the two bands at 3105 and 3370 cm⁻¹ should be assigned to its ν_1 and ν_3 modes. We also find that the frequency difference between the two modes reaches up to 265 cm^{-1} , which may be common in the other two hydrates. Then, in the pentahydrate, the bands located at 3110 and 3355 cm⁻¹ are more likely generated by the ν_1 and ν_3 modes of the water molecules coordinated with copper ions (including I- and II-H₂O, whose Raman frequency may be too close to be distinguished), respectively, while bands at 3190 and 3475 cm⁻¹ can be ascribed to the ν_1 and ν_3 modes of III-H₂O, respectively. Similarly, in the trihydrate, peaks at 3100 and 3360 cm⁻¹ are attributed to the ν_1 and ν_3 modes of two H₂O molecules with the same environment, and those at 3155 and 3410 cm⁻¹ are generated by corresponding modes of another H₂O. From the preceding discussion, we may conclude that the water molecules coordinated to Cu2+ have approximate vibrational frequency in all three hydrates despite the fact that all six ligands are not the same (see Table 1). Additionally, the water molecule bridging the coordination octahedron through a hydrogen bond has very different Raman bands.

A hydrogen bond is a kind of weak interaction whose frequency occurs below 100 cm⁻¹ in some compounds. Research shows that the Raman frequency of a hydrogen bond in liquid water is about 75 cm⁻¹ and shifts suddenly to 220 cm^{-1} when ice is formed and that in some organic hydrates, their frequencies are usually below 100 cm^{-1.16,21} In such a frequency range, compared with the limited application of Raman spectroscopy and IR spectroscopy, terahertz time domain spectroscopy exhibits its advantages with highfrequency resolution. Apart from the hydrogen bond, lowfrequency lattice phonons also respond to THz waves and cause obvious absorptions. In this work, the THz time domain spectra of copper sulfate hydrates have been measured, and corresponding frequency domain spectra (FDS) are also obtained though fast Fourier transformation (FFT). As an example, we show the transmission spectra of the reference (without any sample) and the pentahydrate in Figure 3. Compared to the reference spectrum, many absorption lines are observed in the sample spectra. In order to decrease the interference of scattering and other noises, we repeat the measurements three times, and the average values are utilized. For four kinds of compounds, the absorption peaks in FDS have been extracted and are listed in Table 5. The frequency



Figure 3. THz spectra of the reference (without any sample) and copper sulfate pentahydrate.

Table 5. Absorption Bands of $CuSO_4$ · xH_2O between 0.1 and 3 THz

x = 5		x = 3		x = 1		x = 0	
THz	cm^{-1}	THz	cm^{-1}	THz	cm^{-1}	THz	cm^{-1}
1.34	44.5	1.60	53.4	1.76	58.6	1.87	62.3
1.46	48.7	1.88	62.7	1.90	63.4	2.35	78.3
1.61	53.7	2.18	72.5	2.24	74.5	2.76	92.0
1.76	58.7	2.34	78.0	2.39	79.7	2.86	95.3
1.93	64.3	2.50	83.3	2.80	93.2		
2.00	66.7	2.86	95.4				
2.13	71.1						
2.26	75.3						
2.41	80.4						
2.55	84.9						
2.82	94.0						

range is between 0.1 and 3 THz (about $3-100 \text{ cm}^{-1}$); therefore, the absorption mainly originates from lattice vibration and the hydrogen bond. As shown in Table 5, the number of absorption bands decreases with the decrease of water molecule number. For x = 0, there are four peaks that are generated by low-frequency lattice phonons because there is no H_2O in it. For x = 5, 3, and 1, the hydrogen bond will contribute to the absorption of the THz wave, and their peaks may lie in the relatively lower frequency region. However, it is not easy to assign the bands to a certain mode because lowfrequency vibrations are usually intermolecular modes and many atoms or atomic groups may be involved. Moreover, the hydrogen bond is a kind of many-body interaction. Nevertheless, the study of lattice vibration and the hydrogen bond with THz-TDS reveals more information about the crystal structure and chemical properties of hydrates. Some theoretical calculation based on structural chemistry may help to distinguish and assign the absorption peaks.

CONCLUSIONS

In this work, we utilize low-temperature Raman spectra and THz-TDS to study the vibrational modes of copper sulfate hydrates. It is found that some broadened Raman bands are well-resolved at low temperature, and fine spectral structure is obtained. On the basis of crystal structure and previous work in this field, we analyze the variation in Raman bands of these four components, especially the bands corresponding to water molecules, which have been rarely concerned about. What is more, the terahertz spectra show that there are some absorption bands at $3-100 \text{ cm}^{-1}$ that can be attributed to lattice vibration and a hydrogen bond. In conclusion, with Raman and THz spectroscopies, we can investigate effectively the intramolecular modes, lattice vibration, and hydrogen bond in condensed-state matters.

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Notes

The authors declare no competing financial interest.

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