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K. Ben Mabrouk, T.H. Kauffmann, H. Aroui, M.D. Fontana. Raman study of cation effect on sulfate vibration modes in solid state and in aqueous solutions. *Journal of Raman Spectroscopy*, 2013, 44 (11), pp.1603-1608. 10.1002/jrs.4374 . hal-00863209

**HAL Id: hal-00863209**

**<https://hal.science/hal-00863209>**

Submitted on 27 Nov 2018

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# Raman study of cation effect on sulfate vibration modes in solid state and in aqueous solutions

Kawther Ben Mabrouk,<sup>a,b,c</sup> Thomas H. Kauffmann,<sup>a,b</sup> Hassen Aroui<sup>c</sup> and Marc D. Fontana<sup>a,b</sup>

<sup>a</sup>Université de Lorraine Laboratoire Matériaux Optiques, Photonique et Systèmes EA 4423 2, rue Edouard Belin, 57070 Metz, France

<sup>b</sup>Supélec Laboratoire Matériaux Optiques, Photonique et Systèmes EA 4423 2, rue Edouard Belin, 57070 Metz, France

<sup>c</sup>Université de Tunis Laboratoire Dynamique Moléculaire et Matériaux Photoniques, Ecole Supérieure des Sciences et Techniques de Tunis 5 av. Taha Hussein, 1008 Tunis, Tunisia

## Abstract

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Raman spectra of potassium, sodium, and ammonium sulfates ( $K_2SO_4$ ,  $Na_2SO_4$ , and  $(NH_4)_2SO_4$ ) are reported and analyzed. These sulfates have been investigated under two states: solid (anhydrous and hydrated) salts and aqueous solutions. The effects of monovalent ions ( $K^+$ ,  $Na^+$ , and  $NH_4^+$ ) and hydration on the position of Raman lines assigned to internal vibrations of sulfate anion  $SO_4^{2-}$  are discussed. In solid salts, the line position of each Raman peak is shown to decrease with increasing radius of the cation. The main  $\nu_1$  mode of sulfate molecule is particularly affected. It is emphasized that this sensitivity in solid sulfates vanishes in aqueous solutions. As a consequence, this mode can be probed by Raman spectroscopy as the main signature of  $SO_4^{2-}$  to determine its concentration within a single calibration.

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**Keywords:** sulfates; cation dependence; calibration; Raman study.

## Introduction

Sulfates correspond to a wide family of salts, which are present under different states and compositions in ground, air, and water on Earth and on Mars as well. Sodium sulfate is used for manufacture of paper and glass and is employed as food additive and detergent while potassium sulfate is a fertilizer. They can be found as anhydrous or hydrated minerals or dissolved in solutions. Their detection and identification are very important in the environment to reveal the source of pollution<sup>[1]</sup> and in geology to study the origin of various physical and chemical transformations. In addition, a variety of sulfates have been identified on Mars through different missions,<sup>[2]</sup> and the hydration states of Mg, Ca, and Fe sulfates are of prime importance for the knowledge of the hydrologic history of Mars. Moreover, Raman spectroscopy measurements are motivated by structural studies, and this technique was shown to be powerful for these investigations,<sup>[3]</sup> in particular for the comparison between ligated and unligated sulfates. In the first family such as  $MgSO_4$  and  $Al_2(SO_4)_3$ ,<sup>[4–7]</sup> metal-ligand vibrations were detected in the Raman spectrum, whereas in other sulfates such as  $Na_2SO_4$ ,  $K_2SO_4$ , and  $(NH_4)_2SO_4$ , solely modes corresponding to the ‘free’ molecule  $SO_4^{2-}$  were observed in the spectrum. In the second family, it was therefore assumed that the cation has only an indirect effect on vibration modes. In this work, we are interested to analyze this influence in solids and in aqueous solutions.

Numerous Raman studies of sulfates have been undertaken. Recently, Maubec et al.<sup>[8]</sup> have studied the molecular structure of different minerals of the alunite supergroup. They have reported on the effect of ionic substitutions on the Raman band positions of different vibrations. They showed that the sulfate environment is barely affected by the nature of the cations.

Frost et al.<sup>[9]</sup> have reported that the peak position of the sulfate band varies with the mineral and that the  $SO_4^{2-}$  symmetric stretching band position increases with increasing hydrogen bond strength.

In the present work, we are interested to  $Na_2SO_4$ ,  $K_2SO_4$ , and  $(NH_4)_2SO_4$ , under usual conditions (i.e., at room temperature and atmospheric pressure). The influences of cation and water molecule on Raman spectra have been studied, and we successively investigated measurements in unhydrated

anhydrous solids, and then solutions of the same compounds. We report and analyze the shift of any band assigned to sulfate anion. It is pointed out that all lines are sensitive to the nature of the cation, but the main line position ( $\nu_1$  mode) of  $\text{SO}_4^{2-}$  becomes independent of the cation in aqueous solutions, so that this mode can be used to detect the presence of sulfate salts in water and to determine their concentrations, within only one calibration.

## Vibration modes of $\text{SO}_4^{2-}$

According to the  $T_d$  symmetry of the free anion  $\text{SO}_4^{2-}$ , nine modes of internal vibrations of the molecule corresponding to the irreducible representations as  $A_1 + E + 2F_2$  are expected. All modes are Raman active, but only the  $F_2$  modes are infrared active. The  $\nu_1$  ( $A_1$ ) is the symmetric stretching mode,  $\nu_2$  ( $E$ ) and  $\nu_4$  ( $F_2$ ) modes correspond to the bending vibration, and  $\nu_3$  ( $F_2$ ) is an anti-symmetric stretching mode. Figure S1 illustrates the Raman normal modes of this anion.

Line positions depend on the nature of cation as well as environment conditions such as temperature or pressure. The number of lines is defined by the structure of the peculiar sulfate and its state. Then, a symmetry lowering and thus the degeneracy lifting are expected when going from the free molecule corresponding to the sulfate dissolved in water or to the lattice of the solid salt.

For solid sodium sulfate, we give in Table S1 the correlation between the symmetry of the free molecule, its site symmetry in the lattice and the crystal symmetry group. It should be underlined that in the context of our paper, Raman data of various sulfates are compared regardless the substance symmetry. We will refer hereafter to the labels  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ ,  $\nu_4$  of the vibration modes of the ‘free’ molecule, even in the case of degeneracy lifting of the corresponding lines due to symmetry lowering.

## Results and discussion

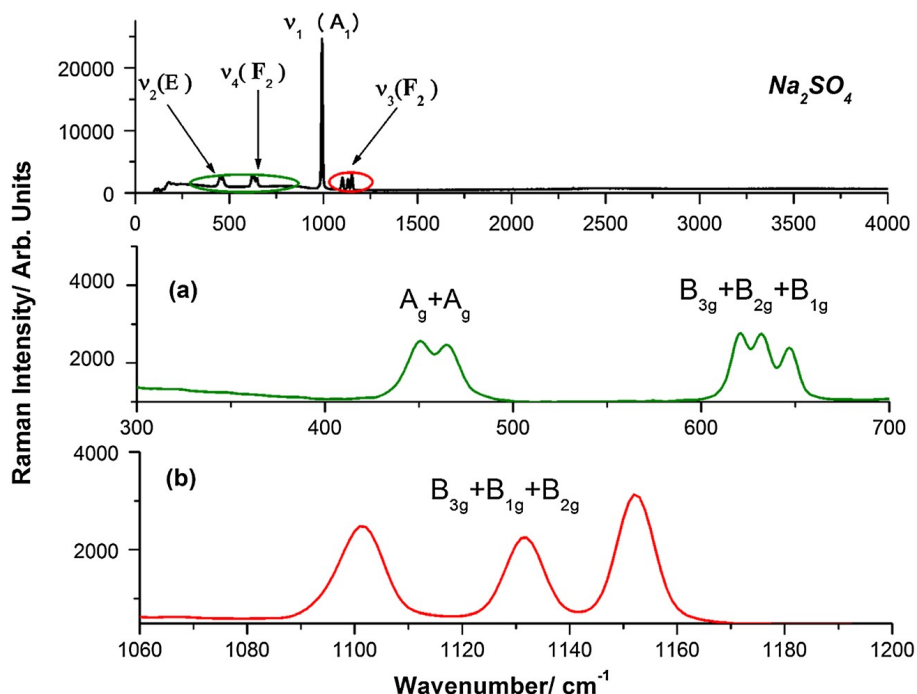
### Experimental conditions

Potassium, sodium, and ammonium sulfate samples used in this work are commercially obtained from *Roth* with purity higher than 99.9%. Aqueous solutions were prepared by weight.

Spectra were recorded at room temperature (25°C) using a Raman spectrometer RXN-1 from *Kaiser Optical System*. The spectrometer is equipped with a visible 532 nm laser (*Invictus*) configured as standard for fiber coupling with FC connectors. The laser beam was brought to the sample through a specific probe with an excitation fiber of 62.5  $\mu\text{m}$ . The laser light is focused on the sample contained in a quartz cell using a 50 $\times$  long working-distance objective (*Olympus*) at about 8 mm with a laser power of 71 mW. The Raman light was collected by the same objective in backscattering configuration filtered by a Notch filter and brought through a 100  $\mu\text{m}$  core fiber to the double holographic grating. The scattered light was detected by a charge-coupled device camera of 1024  $\times$  256 pixels cooled using a Peltier device to 40°C. Spectra were recorded over the 150–4300  $\text{cm}^{-1}$  wavenumber range with a spectral resolution of 1  $\text{cm}^{-1}$ .

### Spectra analysis of anhydrous sulfates

In Fig. 1 is shown the Raman spectrum of solid sodium sulfate ( $\text{Na}_2\text{SO}_4$ ). The main peak corresponds to the  $\nu_1$  ( $A_1$ ) mode centered at 992  $\text{cm}^{-1}$ . The  $\nu_2$ ,  $\nu_4$ , and  $\nu_3$  modes are detected in the low-wavenumber and in the high-wavenumber sides, respectively. The lifting of triply and doubly degenerate modes of the  $\text{SO}_4^{2-}$  ion is clearly seen in the spectrum, as expected by the symmetry lowering according to Table S1.

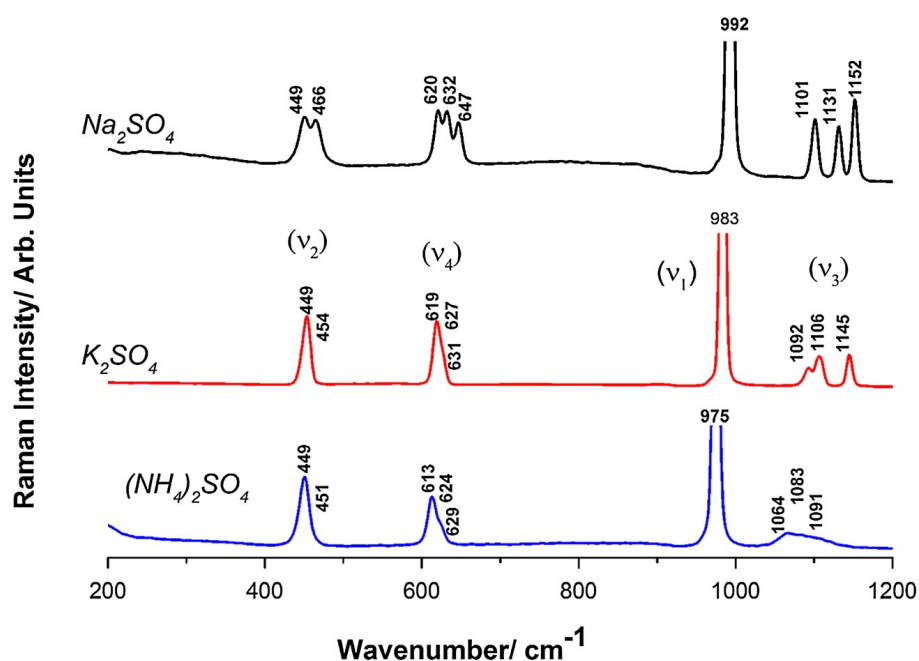


**Figure 1.** The Raman spectrum of solid  $\text{Na}_2\text{SO}_4$ : (a) 300–700  $\text{cm}^{-1}$  range showing  $\nu_2$  and  $\nu_4$  modes and (b) 1060–1200  $\text{cm}^{-1}$  range including  $\nu_3$  mode.

**Table S1.** Correlation between molecular symmetry, site symmetry and factor group symmetry for  $\text{SO}_4^{2-}$  vibrations.

Molecular symmetry	Site symmetry	Group symmetry
$T_d$	$D_2$	$D_{2h}$
$A_1$	$A$	$A_g$
$E$	$A$	$A_g$
	$A$	$A_g$
$F_2$	$B_1$	$B_{1g}$
		$B_{1u}$
	$B_2$	$B_{2g}$
		$B_{2u}$
	$B_3$	$B_{3g}$
		$B_{3u}$

Raman spectra recorded in solid ammonium, sodium, and potassium sulfates are compared in Fig. 2. The spectra show some similarities, regardless of the nature of the cation. The  $\nu_2$  mode is centered at about 449  $\text{cm}^{-1}$ , the  $\nu_4$  mode is between 610–650  $\text{cm}^{-1}$ , then the very intense peak  $\nu_1$  is lying in the wavenumber range 970–995  $\text{cm}^{-1}$ , and finally, the triplet  $\nu_3$  occurs between 1100 and 1160  $\text{cm}^{-1}$ . Wavenumbers and assignments of lines corresponding to internal vibrations of  $\text{SO}_4^{2-}$  are listed in Table 1 and are in good agreement with previous works.<sup>[10–14]</sup> In this table, we have listed for each sulfate the assignment modes and the measured wavenumbers.

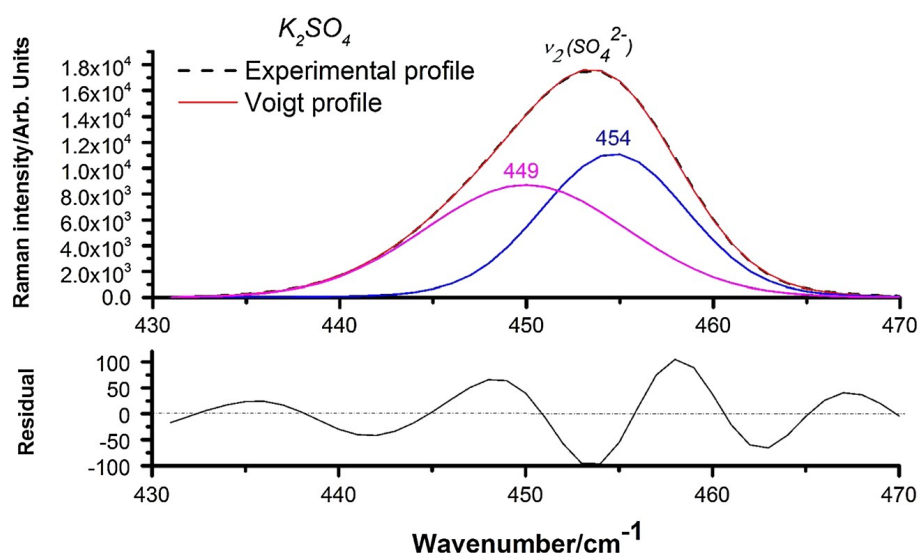


**Figure 2.** Raman spectra of solid sodium, potassium, and ammonium sulfates within the 200–1200  $\text{cm}^{-1}$  range.

**Table 1.** Raman bands of various solid sulfates and their assignments to the internal vibrations of  $\text{SO}_4^{2-}$ .

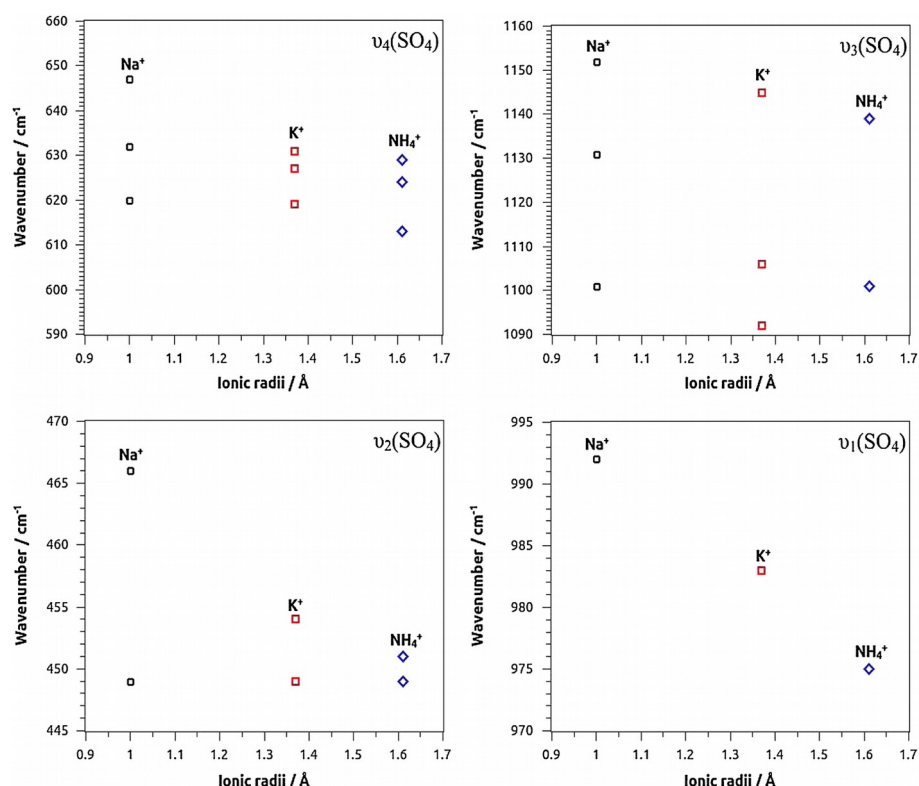
Band position ( $\text{cm}^{-1}$ )				Assignments
$\text{Na}_2\text{SO}_4$	$\text{K}_2\text{SO}_4$	$(\text{NH}_4)_2\text{SO}_4$	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	
449	449	449	439	$\nu_2(E)$
466	454	451	451	
620	619	613	613	$\nu_4(F_2)$
632	627	624	619	
647	631	629	642	
992	983	975	988	$\nu_1(A_1)$
1101	1092	1064	1083	$\nu_3(F_2)$
1131	1106	1083	1113	
1152	1145	1091	1131	

The Raman lines are more resolved in the Na sulfate and are more broadened and shifted to lower wavenumber when going to the K-compound and then to  $\text{NH}_4$ -compound. The doublet  $\nu_2$  and triplet  $\nu_4$  appear less resolved in potassium and ammonium sulfates than in sodium compound. Then, deconvolution using ‘fityk’ software and a Voigt profile of these peaks is necessary to extract the different components of these bands. Figure 3 shows the deconvolution of the  $\nu_2$  mode into two component bands.



**Figure 3.** Deconvolution of the  $\nu_2$  mode of  $\text{SO}_4^{2-}$  into two component bands for the potassium sulfate.

As seen in Table 1 and Fig. 4, the wavenumber of each  $\text{SO}_4^{2-}$  vibration exhibits a remarkable decrease when passing from the sodium sulfate to the potassium sulfate and then to the ammonium compound. According to Maubec *et al.*,<sup>[8]</sup> this shift can be related to the differences of the polarizing power of cations. Because the polarizing power is defined as  $Z/r^2$ , where  $Z$  is the ion charge and  $r$  the radius, the wavenumber decreases as the polarizing power decreases.

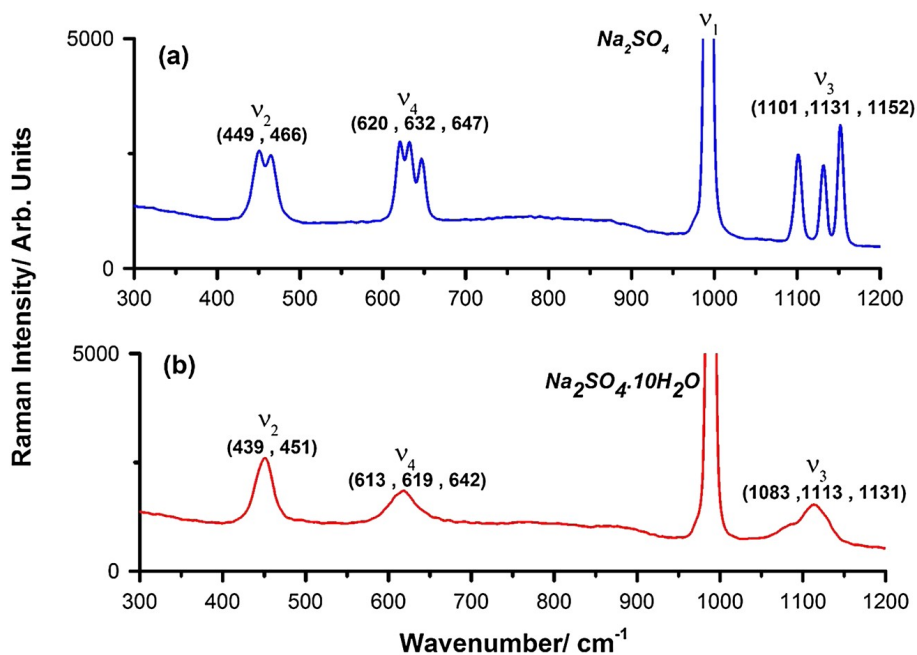


**Figure 4.** Correlation between Raman band positions of  $\text{SO}_4^{2-}$  measured in solid sulfates and the radius of cation.<sup>[14]</sup>

### Sodium sulfate in solid state and in aqueous solution

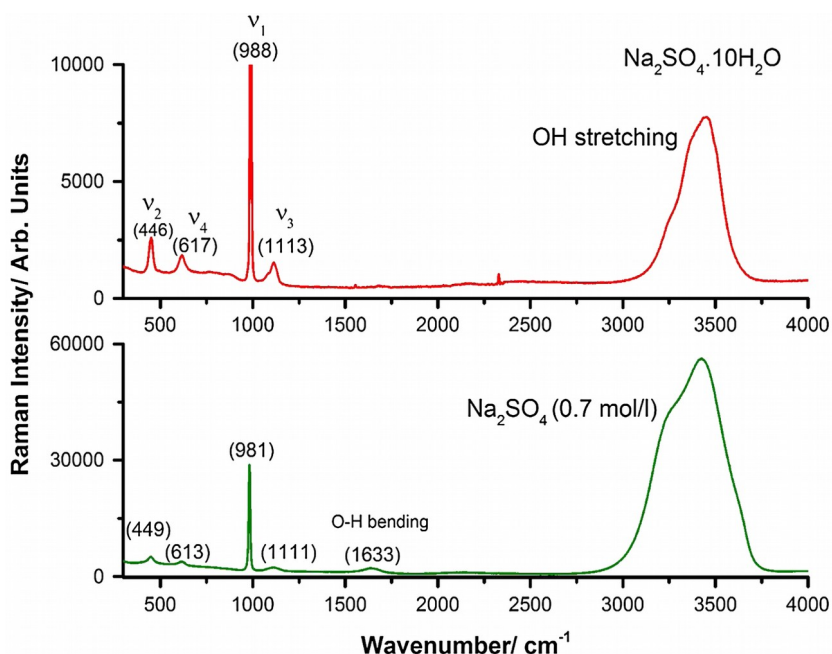
In Fig. 5, we compare the Raman spectra of hydrated and anhydrous sulfate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4$ ). The incorporation of  $\text{H}_2\text{O}$  leads to the broadening and to the downshift of all  $\text{SO}_4^{2-}$  lines. In Fig. 5(a), the components of the doubly and triply degenerate  $\nu_2$ ,  $\nu_3$ , and  $\nu_4$  vibration modes are clearly discernible in the Raman spectrum of the dry  $\text{Na}_2\text{SO}_4$ . As seen in Fig. 5(b), for hydrated sulfate, these modes are not resolved. A Voigt deconvolution model has been achieved to extract the

wavenumber components of these modes (listed in Table 1 and this figure). The decrease of the wavenumber of each  $\text{SO}_4^{2-}$  mode when the sodium sulfate is hydrated (Table 1) is probably related to the increase of interatomic distances due to the presence of OH groups. As a result, the polarizing power of the cation decreases to induce the decrease of sulfate wavenumbers.



**Figure 5.** Raman spectra of (a) anhydrous and (b) hydrated sodium sulfate at 300–1200  $\text{cm}^{-1}$  range.

In Fig. 6 are compared the Raman spectra recorded for hydrated and aqueous solution of sodium sulfate. The characteristic OH vibrations, as the bending mode at about  $1633 \text{ cm}^{-1}$  and the stretching mode from  $2800$  to  $3800 \text{ cm}^{-1}$ , are obviously more resolved in the solution. When compared with results obtained for solid sulfates (Table 1 and Fig. 2), the broadening and the downshift of all lines are still enhanced when going from the hydrated crystal to the solution of the same compound. In addition, it should be mentioned that in aqueous solutions, the bands correspond to the free  $\text{SO}_4^{2-}$  (symmetry  $T_d$ ) and degenerate modes ( $v_2$ ,  $v_3$ , and  $v_4$ ), contrary to the situation of anhydrous and hydrated solids, in which the degeneracy is lifted by symmetry (according to Table S1).

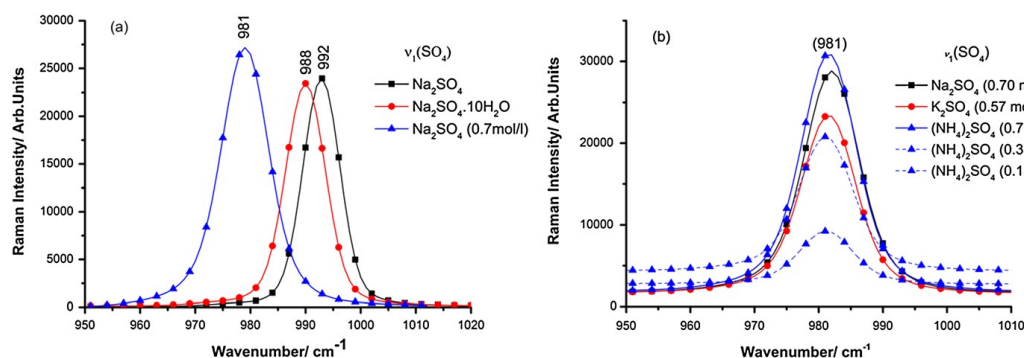


**Figure 6.** Raman spectra of hydrated sodium sulfate and aqueous solution ( $0.7 \text{ mol.l}^{-1}$ ) showing the OH bands. The bending band at  $1633 \text{ cm}^{-1}$  and the stretching band in the region  $2800\text{--}3800 \text{ cm}^{-1}$ .

## Behavior of the $\nu_1$ mode in solid and liquid sulfates

In this part, we focus our attention to the  $\nu_1$  Raman line of sulfate anion and its sensitivity to the cation type and the presence of water. This mode is well resolved and is very intense in all Raman sulfate spectra. Figure 7(a) shows the relative change according to the state (anhydrous, hydrated, and aqueous solution) of sodium sulfate. In addition to the downshift mentioned previously, the  $\nu_1$  mode exhibits a linewidth increasing from the solid to the liquid state ( $7.6$  to  $10.4\text{ cm}^{-1}$ ), which can be attributed to structure disordering, which increases from solid to liquid state.

In Fig. 7(b) is plotted the  $\nu_1$  peak recorded in various aqueous solutions of Na, K, and  $\text{NH}_4$  sulfates. Ammonium spectra recorded at a series of three molarities ( $0.15$ ,  $0.37$ , and  $0.57\text{ mol.l}^{-1}$ ) illustrate a clear increase of linewidth and integrated intensity with increasing molarity. As seen by this figure, this peak has remarkably the same position in all solutions regardless of the nature of the cation and the  $\text{SO}_4^{2-}$  concentration. Compared to solid sulfates, this cation invariance is in contrast with the line position dependences reported in Figs 2 and 7(a).



**Figure 7.** (a) The  $\nu_1$  mode for anhydrous, hydrated, and the aqueous solution of  $\text{Na}_2\text{SO}_4$ . (b) The  $\nu_1$  mode for ammonium, potassium, and sodium sulfate aqueous solutions. For the three sulfates, the three largest peaks correspond to the same weight content of salt in water ( $100\text{ g.l}^{-1}$ ) but to notably different molarities.

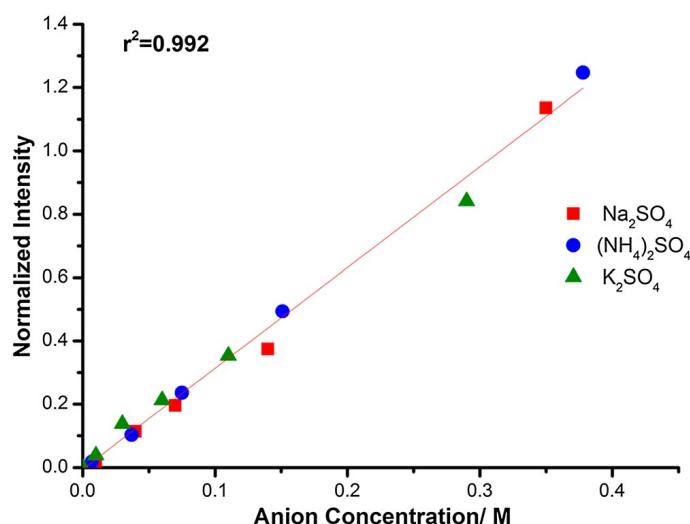
Using the same experimental technique, Rull et al.<sup>[15]</sup> reported the changes at room temperature of the main Raman internal mode  $\nu_1$  of  $\text{SO}_4^{2-}$  as function of concentration in several alkali sulfate aqueous solutions. The  $\nu_1$  mode position was shown to shift weakly within  $2\text{ cm}^{-1}$  when different dissolved salts are considered. More recently, Matsumoto et al.<sup>[16]</sup> have performed a similar study in alkali and ammonium sulfate solutions, as function of the temperature, under a pressure of 25 MPa. The cation effect on the main Raman  $\nu_1$  mode clearly appeared at high temperature ( $350^\circ\text{C}$ ). Nevertheless, their data are consistent with our results, when considering the room temperature and the same molarities range.

## Sulfate calibration

As it is proportional to the concentration,<sup>[17]</sup> Raman intensity is sometimes used to determine the concentration of a substance. This requires at first a suitable calibration of the substance content. Here, thanks to the remarkable property of  $\nu_1$  mode in aqueous solutions, a single calibration for all sulfates under study can be achieved. This calibration is illustrated by Fig. 8 for different sulfate solutions with varying dilution. The Raman intensities determined here are in fact integrated over the whole wavenumber range  $960\text{--}1000\text{ cm}^{-1}$  covered by the  $\nu_1$  mode, and after their normalization by the corresponding intensity of the OH-bending band. This normalization insures that the quantity used in the Raman spectrum – here the integrated intensity – is unaffected by any change in experimental conditions. The integrated intensity is obtained within a precision of 6% estimated as the standard deviation from six samples with the same concentration.

The regression coefficient  $r^2$  of the calibration curve (Fig. 8), equal to 0.992, demonstrates that the same calibration is valid for the three substances  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ , and  $(\text{NH}_4)_2\text{SO}_4$ . Within these conditions our results can be used to probe dissolved sulfates and to determine their concentration

in water using Raman sensor. In addition, using the cation dependence of  $\nu_1$  mode, one can distinguish between sulfates after drying.



**Figure 8.** Calibration of peak area (intergrated intensity) of the Raman line  $\nu_1$  of  $\text{SO}_4^{2-}$  with the concentration in  $\text{mol.l}^{-1}$ .

## Conclusion

Raman spectra of anhydrous and hydrated sodium, potassium, and ammonium sulfates were reported and compared. The positions of Raman lines attributed to different internal  $\text{SO}_4^{2-}$  vibrations in solid sulfates are tabulated, and their shift is attributed to the indirect effect related to the size of cation radius. The hydration gives rise to a similar shift of Raman lines. The cation dependence vanishes when the sulfate is dissolved in water. Then, the Raman spectrum has the same profile in different sulfates regardless of the nature of the cation. Different promising applications in geochemistry and environment can be derived from this study. A Raman sensor could be used to unambiguously identify different sulfate minerals and to distinguish between hydrated and anhydrous states of the same sulfate. Moreover, the intensity of the main Raman peak can be exploited to determine the concentration of sulfate in aqueous solution via a single calibration.

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