Short Communication

Vibrational spectra of ScAsO₄·H₂O

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The powder Fourier-transform (FT) infrared and Raman spectra of ScAsO₄· H₂O were recorded and are discussed with a factor-group analysis based on of its known structural characteristics. Copyright © 2006 John Wiley & Sons, Ltd.

INTRODUCTION

The recently prepared[1] $ScAsO_4 \cdot H_2O$ constitutes the first example of an orthoarsenate monohydrate belonging to the $MnMoO_4 \cdot H_2O$ structural type.[2] As only a very limited number of oxoanions adopting this structure are known,[1] it seems interesting to investigate its vibrational behavior. The present IR and Raman study will extend our knowledge on the vibrational peculiarities of the AsO_4^{3-} groups in different crystalline environments.

EXPERIMENTAL

The compound was prepared by hydrothermal synthesis at 493 K using a Teflon-lined stainless steel bomb, reacting a mixture of Sc_2O_3, hydrated arsenic acid, Li_2CO_3 and distilled water for 7 days, and subsequent slow furnace cooling. $ScAsO_4 \cdot H_2O$ was obtained in the form of indistinct, tiny, colorless plates.[1]

IR spectra in the range 4000–400 cm⁻¹ were recorded with a Bruker IF66 Fourier-transform (FT) IR instrument using the KBr pellet technique. A total of 80 scans were accumulated at a nominal resolution of ±4 cm⁻¹. Raman spectra in the range 4000–100 cm⁻¹ were measured on powdered samples using the FRA 106 Raman accessory of the same FT-IR instrument (500 scans, nominal resolution ±4 cm⁻¹). Radiation from a Nd : YAG solid-state laser (1064 nm) was used for excitation.

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RESULTS AND DISCUSSION

$ScAsO_4 \cdot H_2O$ crystallizes in the triclinic space group $P\bar{1}$ (no. 2) with two formula units ($Z = 2$) in the unit cell, and all atoms are located in general positions. It is built up by $Sc_2O_8(H_2O)_2$ dimers formed by the edge-sharing of two relatively distorted $ScO_5(H_2O)$ octahedra. These dimers are corner-linked to slightly distorted AsO_4 tetrahedra.[1]

In order to perform the spectral analysis, it appears adequate to use the factor-group approximation to consider the coupling effects within the two AsO_4^{3-} moieties present in the unit cell.[3,4] The correlation between the symmetry of the 'free' ion (T_d), its site-symmetry (C_1) and the factor-group (C_i) is presented in Table 1. As it can be seen, the so-called *mutual exclusion rule* is operative, in agreement with the existence of an inversion center in the crystal structure. Therefore, the *g*-modes are only Raman active whereas the *u*-modes show only IR activity.

For the fundamental vibrations of an 'isolated' tetra-hedral AsO_4^{3-} anion, the following wavenumbers have

Table 1. Factor-group analysis of the AsO_4^{3-} vibrations in the investigated lattice ($P\bar{1}$ (C_i^1) and $Z = 2$)[a]

Vibrational mode	'Free' ion/T_d	Site symm./C_1	Factor group/C_i
Symm. stretching	A_1	A	$A_g + A_u$
Symm. bending	E	$2A$	$2A_g + 2A_u$
Antisymm. stretching	F_2	$3A$	$3A_g + 3A_u$
Antisymm. bending	F_2	$3A$	$3A_g + 3A_u$

[a] Activity under factor-group symmetry: A_g, Raman active; A_u, IR active.

been determined[5] in aqueous solution: ν_1 (A_1) (symmetric stretching) = 818 cm^{-1}, ν_2 (E) (symmetric bending) = 350 cm^{-1}, ν_3 (F_2) (antisymmetric stretching) = 791 cm^{-1} and ν_4 (F_2) (antisymmetric bending) = 405 cm^{-1}. It is interesting to note that $AsO_4{}^{3-}$ is the only tetrahedral oxoanion of a main group element for which $\nu_1 > \nu_3$ (Ref. 6), although in crystalline orthoarsenates the symmetric stretching mode is often intercalated between the ν_3 components.[7–10]

The IR spectrum of ScAsO$_4$·H$_2$O in the range between 4000 and 400 cm^{-1} is shown in Fig. 1, whereas the corresponding Raman spectrum in the spectral range 1200–100 cm^{-1} is presented in Fig. 2. The proposed assignment is shown in Table 2.

The stretching vibrations of H$_2$O are seen as a very strong and well-defined IR doublet. Its position suggests the participation of these molecules in hydrogen bonds of medium length,[11] in agreement with the structural analysis.[1] The bending vibration of the water molecule, located at 1641 cm^{-1} in the IR spectrum, presents an unusually high intensity and is seen as a very weak feature in the Raman spectrum at 1638 cm^{-1}. The stretching motions are absent

Table 2. Wavenumbers and assignment of the vibrational spectra of ScAsO$_4$·H$_2$O^a

IR, ν (cm^{-1})	Raman, ν (cm^{-1})	Assignment
3300 vs, 3203 vs	–	$\nu(H_2O)$
1641 vs	1638 vw	$\delta(H_2O)$
978 vs	935 vs	$\nu_s(AsO_4{}^{3-})$
899 s, 849 vs, 793 s	866 vs, 832 s, 805 m	$\nu_{as}(AsO_4{}^{3-})$
746 w	744 vw	$\rho(H_2O)$
540 vs, 486 vs	484 w	$\delta_{as}(AsO_4{}^{3-})$
–	385 m, 347 s	$\delta_s(AsO_4{}^{3-})$
–	323 vw, 287 w, 244 vw, 188 vw, 167 w, 138 w	See text

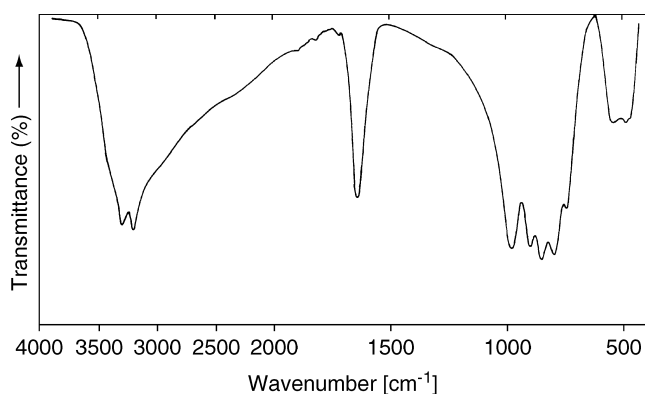^{a} vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

Figure 1. FT-IR spectrum of ScAsO$_4$·H$_2$O in the spectral range 4000–400 cm^{-1}.
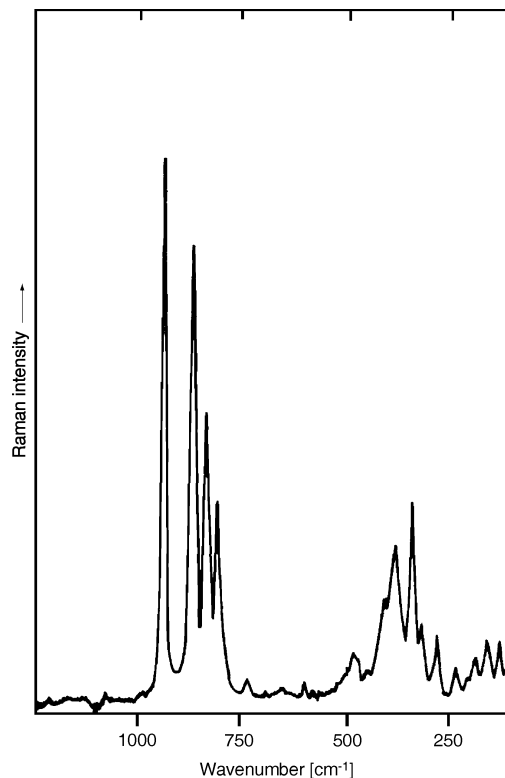
Figure 2. FT-Raman spectrum of ScAsO$_4$·H$_2$O in the spectral range 1200–100 cm^{-1}.

in the Raman spectrum. A weak IR band found at 746 cm^{-1} and its Raman counterpart at 744 cm^{-1} can be assigned to a librational mode of the water molecule.[12,13]

A comparison of the IR and Raman spectra in the $AsO_4{}^{3-}$ stretching region shows that the factor-group predictions are clearly fulfilled in both cases. The strongest Raman line can confidently be assigned to the symmetric stretching vibration.[4,14] Consequently, in the present case the solution behavior ($\nu_1 > \nu_3$) is maintained in the solid state.[5] Besides, in both spectra the three expected ν_3 components are also found.

Regarding the bending vibrations, the antisymmetric deformation is seen as a relatively strong, broad IR doublet that probably overlaps the third, factor-group predicted, and missing component. In the Raman spectrum, only one relatively weak feature can be assigned to this vibration. This behavior is in agreement with the well-known intensity criteria that predict that for tetroxoanions the antisymmetric bending must be stronger in the IR than in the Raman spectra, whereas the inverse behavior is expected for the corresponding symmetric mode.[4,14,15] This symmetric deformation (measured here only in the Raman spectrum) shows again the two expected factor-group components.

The last Raman lines, below 347 cm^{-1} and not assigned in Table 2, are surely related to the Sc–O vibrations and to the external (lattice) vibrations of the crystal.[3]

Finally, it is interesting to note that the corresponding IR and Raman components (*cf* Table 2) present clearly different wavenumbers, pursuant to the different phononic origins of the respective vibrational modes. These energy differences are usually considered as a valuable criterion for the evaluation of the strength of the coupling effects in the unit cell,[16,17] and in the present case show that these effects are relatively important.

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