

INFRARED SPECTRA OF THE DIHYDRATES OF CALCIUM SELENATE AND YTTORIUM PHOSPHATE - COMPARISON WITH THE SPECTRUM OF GYPSUM

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ABSTRACT

The infrared spectra of protiated and deuterated $\text{CaSeO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{YPO}_4 \cdot 2\text{H}_2\text{O}$ were compared with the spectrum of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) with which the two investigated compounds are almost certainly isostructural. From the position of the bands in the OD stretching region of the spectra of partly deuterated compounds having low deuterium content, one may conclude that the strength of the hydrogen bonds which water molecules form with the anions increases in the order sulfate, selenate, phosphate. While studying the spectra of mixed crystals, particular attention was paid to the bands originating from the stretching vibrations of the tetrahedral anions.

INTRODUCTION

As a part of our systematic studies of the spectral properties of, and the spectra-structure correlations in various classes of isostructural inorganic compounds (e.g. alums, Tutton's salts, struvite and its analogues etc.), some of the results of the investigation of calcium selenate dihydrate and yttrium phosphate dihydrate are presently reported and compared with those of gypsum for which detailed structural data are available [1]. The stress is put on those spectral regions from which information about the hydrogen bonding and the geometry of the water molecules and the tetrahedral anions can be derived. The task was facilitated by the fact that for gypsum the results of a number of spectroscopic studies are available (see refs. 2-4 and references therein).

EXPERIMENTAL

The investigated compounds were prepared using standard laboratory methods. Samples deuterated to various degrees were obtained similarly, using appropriate mixtures of H_2O and D_2O . The infrared spectra were recorded on a Perkin-Elmer 580 infrared spectrophotometer, a VLT-2 (RIIC) variable-temperature cell being used for low temperature measurements.

RESULTS AND DISCUSSION

The comparison of the infrared spectra of $\text{CaSeO}_4 \cdot 2\text{H}_2\text{O}$, $\text{YPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ reveals a striking similarity, especially as far as the regions of absorption by the water molecules are concerned.

Thus, in the region of the HOH bending vibrations, a doublet of bands exists in the spectrum of each of the three studied compounds,

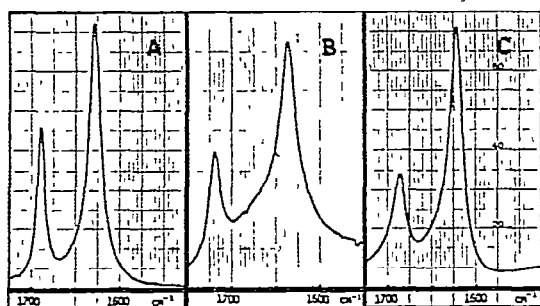


Fig. 1. The HOH bending region in the spectra of $\text{CaSeO}_4 \cdot 2\text{H}_2\text{O}$ (A), $\text{YPO}_4 \cdot 2\text{H}_2\text{O}$ (B) and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (C)

the low-frequency component exceeding in intensity the high-frequency one (Fig. 1). The situation is analogous in the DOD bending region of the spectra of the fully deuterated compounds, a doublet of bands being again present.

That these doublets in the spectra of calcium selenate dihydrate and yttrium phosphate dihydrate appear, as in gypsum, as a result of the existence of a strong correlation field

is clearly demonstrated by the analysis of the DOD bending region in the spectra of the partially deuterated compounds. At low deuterium content, when the possibility of correlation-field interaction is negligible (all the neighbours of the few existing D_2O molecules are different from them), namely, a single band is found

in the corresponding region (see the uppermost curves in Fig. 2), the components of the D_2O doublet appearing and gaining in intensity when the deuterium content is increased. Such a behaviour closely resembles that in gypsum [3] and is additional evidence that the three compounds are indeed isostructural.

From the relative intensities of the two bands in the HOH bending region (Fig. 1), the angle between the bisectors

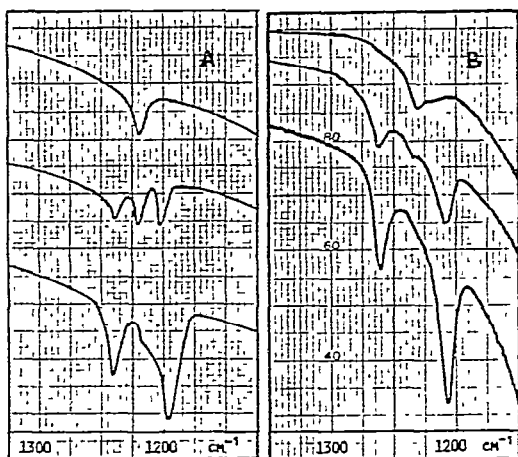


Fig. 2. The DOD bending region in the spectra of $\text{CaSeO}_4 \cdot 2\text{H}_2\text{O}$ (A) and $\text{YPO}_4 \cdot 2\text{H}_2\text{O}$ (B).

of the water molecules coordinated to the same metal cation was estimated [2] and it was found that this angle increases in the order calcium selenate, yttrium phosphate, calcium sulfate. On the other hand, the fact that the splitting of the components of the doublets is largest for the yttrium compound indicates that, as expected, the water molecules are coordinated more strongly to the metal cation in this case than in the two calcium compounds.

Structural information can be extracted also from the analysis of the OD stretching region of isotopically isolated HDO molecules

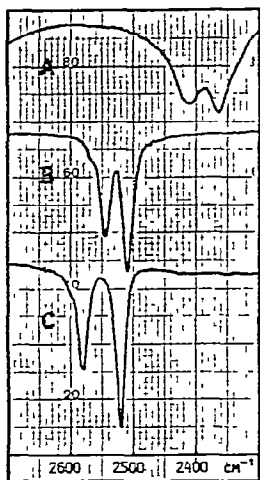


Fig. 3. The OD stretching region of isotopically diluted HDO molecules in the dihydrates of yttrium phosphate (A), calcium selenate (B) and calcium sulfate (C).

(see Fig. 3). It can be seen, simply by inspection, that the situation in this region too is analogous in all three of the investigated compounds, the strength of both existing hydrogen bonds being appreciably greater in the case of yttrium phosphate dihydrate, whereas of the two calcium compounds the hydrogen bonds are stronger in the selenate than in the sulfate. This is in agreement with our earlier findings that in cases of isomorphous sulfate-selenate pairs of hydrates stronger hydrogen bonds are formed with the selenate [5]. We believe that this is no mere coincidence but, rather, a natural consequence of the differences in the electronegativities of the central atom in the XO_4 ions. Selenium is, namely, less electronegative than sulfur, the electron density in the regions of the oxygen lone pairs is expected to be greater and so the conditions for hydrogen bonding should be more favorable. On the other hand, the reason for the significantly stronger H-bonds formed in $YPO_4 \cdot 2H_2O$ probably lies more in the higher over-all charge of the

trivalent phosphate (as compared with the divalent selenate and sulfate) than in the fact that phosphorus is less electronegative than either selenium or sulfur.

In order to study the degree of distortion of the XO_4 anions from their ideal tetrahedral geometry, spectra of mixed sulfate-

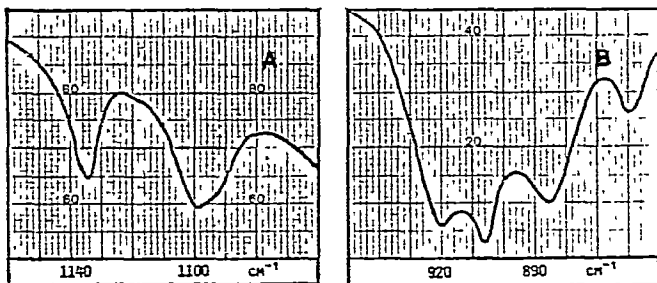


Fig. 4. The region of the SO_4 (A) and SeO_4 (B) stretching vibrations in mixed $\text{Ca}(\text{S},\text{Se})\text{O}_4 \cdot 2\text{H}_2\text{O}$ crystals with low guest-ion content.

selenate crystals with low guest-ion content were recorded and the regions of the sulfate stretching vibrations in a predominantly selenate crystal and vice versa are reproduced in Fig. 4. As in the case of isotopic dilution, in crystals such as these the correlation-field interactions

are negligible for the guest-ions and the spectra reflect solely or predominantly the effective symmetry of the guest anions. From the appearance of the spectra given in Fig. 4 it can easily be seen that the selenate ions are more distorted than the sulfate ones.

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