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INFRARED SPECTRA OF $Li_2SeO_4.H_2O$, $Li_2SO_4.H_2O$ AND $Li_2(S,Se)O_4 \cdot H_2O$

B. ŠOPTRAJANOV and V. PETRUŠEVSKI

Hemiski institut, PMF, Univerzitet "Kiril i Metodij", Skopje, Yugoslavia

ABSTRACT

One of the hydrogen bonds formed by water molecules in lithium selenate monohydrate is evidently stronger than in the corresponding sulfate, whereas the other one is weaker. The temperature dependence of the stretching and bending modes of water is similar in both compounds, their frequencies decreasing on lowering the temperature. The study of mixed sulfate-selenate compounds made it possible to clearly show that the effective symmetry of the tetrahedral ions is higher than their local crystallographic one.

INTRODUCTION

Contrary to the case with lithium sulfate monohydrate which has been extensively studied both by crystallographic [1] and vibrational spectroscopic methods [2-11], little is known about the selenate analogue. It was only briefly reported that it is isomorphous with the sulfate of the analogous composition [12] and some data on the infrared spectra have been given [3]. Our interest in the study of isomorphous pairs of sufate-selenate compounds [13,14] led us to study more closely the infrared spectra of the selenate member of the pair. For purposes of comparison, the infrared spectra of the sulfate were reinvestigated. Also studied were the spectra of partially deuterated analogues and of mixed sulfate-selenate salts containing a small ammount of the guest component in the host lattice so that the guest XO_4 units could be considered to be isomorphously isolated.

EXPERIMENTAL

The studied compounds were prepared by standard methods, the doped crystals being obtained from suitable sulfate-selenate mixtures. Partially deuterated compounds were obtained starting with H_2O/D_2O mixtures with appropriate composition. The infrared spectra were recorded, at room and liquid-nitrogen temperature (RT and LNT), on a Perkin-Elmer Model 580 infrared spectrophotometer.

RESULTS AND DISCUSSION

The infrared spectra of lithium selenate monohydrate and of the corresponding sulfate analogue are compared in Fig. 1. As seen, the similarities between the two spec-

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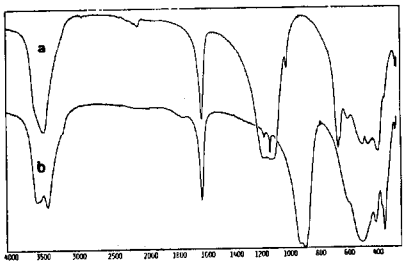

Fig. 1. Infrared RT spectra of lithium sulfate monohydrate (a) and lithium selenate monohydrate (b)

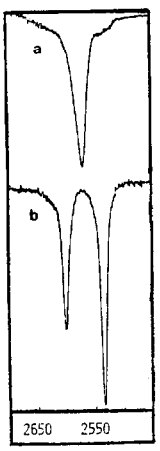

Fig. 2. The OD stretching region in the sulfate (a) and selenate (b) containing isotopically isolated HDO molecules

tra are considerable, in agreement with the reported isomorphism [12]. Some differences are also easy to notice, especially in the OH stretching region where a clearly resolved doublet is found in the case of the selenate (additional bands are observed at LNT) as compared with the single asymmetric peak present in the sulfate spectrum. The differences persist (and are even more convincing) in the OD stretching region of samples containing isotopically isolated HDO molecules. As seen in Fig. 2, one of the bands in this region of the lithium selenate monohydrate spectrum lies higher and the other one lower than in the sulfate where even at LNT we observe only a single band (at 20 K splitting of some 7 cm^{-1} was reported [8]). In any case, the vibrational spectroscopic data seem to show that the differences in the hydrogen bond strength in the sulfate are less than it could have been concluded on the basis of the differences in the Ow...O lengths (at RT the two such distances are 289.2 and 297.2 pm, and at LNT the corresponding values are 285.6 and 288.3 pm for the bonds in which the proton-acceptors are a sulfate and a water oxygen respectively). In fact, this may not even be surprising, but the practice of correlating the hydrogen-bond strength with the donor-acceptor distance is so widespread that a word of caution seems appropriate.

If one assumes that in the selenate as in the sulfate the stronger H-bond is formed with one of the XO_4 oxygens, it is easy to explain its greater strength in terms of the higher negative charge on the selenate than on the sulfate oxygens [3,13,14]. The opposite trend for the other hydrogen bond then becomes also easy to understand.

Probably the most interesting finding is the observed shift towards lower frequencies of both the stretching and the bending water vibrations when the temperature is lowered from RT (the uppermost curves in Fig. 3) to LNT, although opposite signs of the temperature coefficients would be expected (and are usually encountered). The shifts are small but significant. In fact, this finding lends additional support to the previously suggested [15] explanation for the origin of the very low HOH bending frequencies found in some crystallohydrates [16].

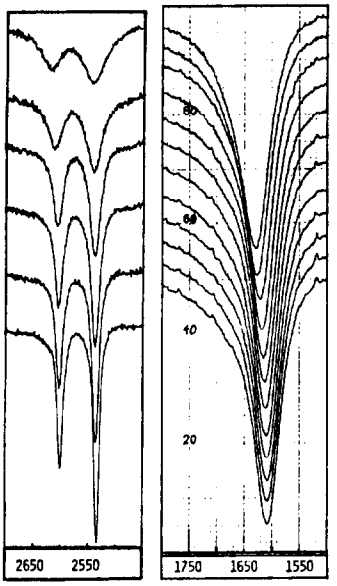

Fig. 3. The effect of lowering the temperature from RT to LNT on the OD stretching and HOH bending in the selenate

It was proposed, namely, that in order to have such very low frequencies (in some cases even lower than 1500 cm^{-1}), the bending of the water molecules should take place in an environment which "assists", so to say, the motion of the protons in the course of the vibration. This would happen, it was reasoned, if the H-O-H angle is large but the O...Ow...O one is much larger, if both angles are small (the acceptor-donor-acceptor one being smaller than the H-O-H angle) or if the H-bonds are biffurcated in a way similar to the one which is apparently present in magnesium potassium phosphate monohydrate [17] and in the related compounds (a more detailed account of the spectra of this extremely interesting series of compounds and of our interpretation of the origin of the lowering of the bending HOH frequencies far below the gas-phase value will be published [18]). As shown [1], in lithium sulfate monohydrate the HOH angle is rather large (108.6° at RT) and is increasing when the temperature is decreased (the value at LNT is 109.7°), whereas the O...Ow...O one is much larger (146.8 and 144.9° at RT and LNT respectively). It is the increase in the value of the H-O-H angle which is believed, in agreement with the outlined above explanation, to be responsible for the decrease of the bending HOH frequency on lowering the temperature.

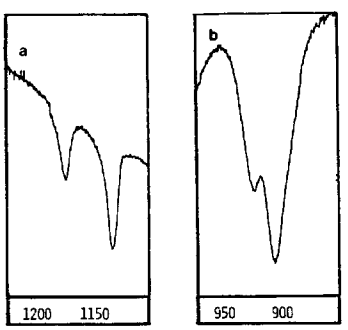

Fig. 4. The antisymmetric XO_4 region in the spectra of the selenate doped with sulfate (a) and the sulfate doped with selenate (b)

The isomorphism between lithium sulfate monohydrate and its selenate analogue made it possible to prepare mixed crystals. In order to study the infrared spectra in the solid state free, so to say, from solid-state effects, samples with low sulfate or low selenate content were studied. Under such conditions the sulfate ions surrounded exclusively by selenate ones or vice versa become "isomorphously isolated" (the term being analogous to the familiar "isotopically isolated" one) and their vibrational spectra should reflect their effective symmetry. As can be seen in Fig. 4, in both cases the appea-

rence of the bands in the antisymmetric stretching region is such that symmetry higher than the crystallographic C_1 one is strongly indicated (it should be at least close to C_{3v} or some other under which the triply degenerate antisymmetric stretch would split into two components). Such a conclusion is in perfect agreement with the determined [1] S-O distances whose values are 146.6, 148.1, 148.1 and 148.0 pm at LNT - the one at which the spectra in Fig. 4 were recorded. It should be mentioned that Shchukarev et al. [3] arrived to the same conclusion on the basis of their analysis of the spectra of the pure compounds where additional effects may, in principle, alter and complicate the picture.

It is to be noted that the half-widths of the bands in the spectra of the isomorphously isolated ions are much less than those in the spectra of the pure compounds and shifts are observed when the frequencies of the guest ions are compared with those for the pure corresponding compound. Space does not permit to go into detailed explanation of the possible causes for the observed effects.

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