

VIBRATIONAL SPECTRA OF HEXAAQUA COMPLEXES :
IV. MULTIPLE BANDS IN THE HOH BENDING REGION OF SOME ALUMS

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The IR and Raman spectra of a number of sulfate and selenate alums were recorded at room and liquid nitrogen temperature (LNT). At room temperature, the HOH bending vibrations appear as an unsymmetrical, poorly resolved band. When the temperature is lowered, remarkable changes in the number of bands and their shape take place. In the LNT spectra of α alums, a progression of bands could be seen, with an almost regular spacing ($\approx 100 \text{ cm}^{-1}$) between the individual components. In the spectra of the β alums, the spectral picture is more complicated and no regularity is readily detectable. In both cases bands related to the water bending modes appear in a very wide spectral region (from ≈ 2000 to $\approx 1200 \text{ cm}^{-1}$). It is possible that an acceptable explanation for the appearance of multiple bands is based on the assumption of anharmonic coupling of the HOH bending vibration with a low-frequency mode via a mechanism similar to that discussed by Bertie and Falk [1].

1. INTRODUCTION

The alums are a very large and common class of double salts, having a general formula $M^I M^{III} (RO_4)_2 \cdot 12H_2O$. M^I is a univalent cation (such as Na^+ , K^+ , Rb^+ , Cs^+ , NH_4^+ etc.), M^{III} is a trivalent cation (an ion of Al, Ga, In, Fe, Cr etc.) and R is S or Se. Standardized abbreviations consisting of the chemical symbols for M^I , M^{III} and R and the letter D standing for dodecahydrate will be used throughout the text. Thus, the abbreviation CsAlSeD will stand for $CsAl(SeO_4)_2 \cdot 12H_2O$, AAlSD for $NH_4Al(SO_4)_2 \cdot 12H_2O$ etc.

The alums have been very extensively

studied by both crystallographic and spectroscopic methods (see [2-7] and the references given therein). It is known that two types of trigonally coordinated water molecules exist in the structure. The water molecules coordinated to the M^{3+} ions are strongly hydrogen bonded and those from the $M^I(H_2O)_6$ groups form hydrogen bonds of moderate strength only.

Some time ago [8], we observed that the HOH bending bands in the IR and Raman spectra of the alums show multiple structure. Despite the numerous published spectroscopic studies, no mention was made (either before or after our communication) of this peculiarity. In fact, either

only the region below 1200 cm^{-1} was discussed or the HOH bending bands were simply disregarded. The problem with the multiple bands appearing in the HOH/DOD bending region of some crystallohydrates, however, seems to be far from uninteresting. Therefore, in this paper we present our results on the multiple HOH bending bands in the spectra of the alums.

2. EXPERIMENTAL

The studied compounds were prepared by crystallization from stoichiometric mixtures of aqueous solutions of $M^{II}_2\text{RO}_4$ and $M^{III}_2(\text{RO}_4)_3$. The IR spectra were recorded from KBr pellets on a Perkin Elmer 580 IR spectrophotometer. A VLT-2 (RIIC, London) cell was used for the LNT work. The Raman spectra were recorded on a Carry 81 spectrophotometer. The source was a Spectra-Physics Ar^+ laser, operating at 514.52 nm .

3. RESULTS AND DISCUSSION

The room temperature (RT) and LNT IR spectra of CsCrSD are presented in Fig. 1. The broad and poorly resolved HOH bending band at room temperature splits into a number of subbands at LNT. The temperature effect is, as seen, very pronounced.

The subbands cover a very wide range of frequencies ($1900 - 1300\text{ cm}^{-1}$ in this particular case). Obviously, they can not be interpreted as due to the correlation field splitting components, since no examples of hydrates in which the HOH bending frequency is above 1750 or below 1470 cm^{-1} are known so far.

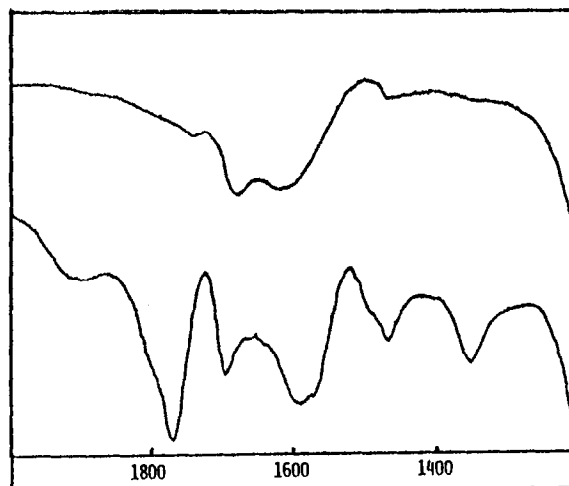


Fig. 1. The HOH bending region in the RT (upper) and LNT (lower curve) IR spectra of CsCrSD

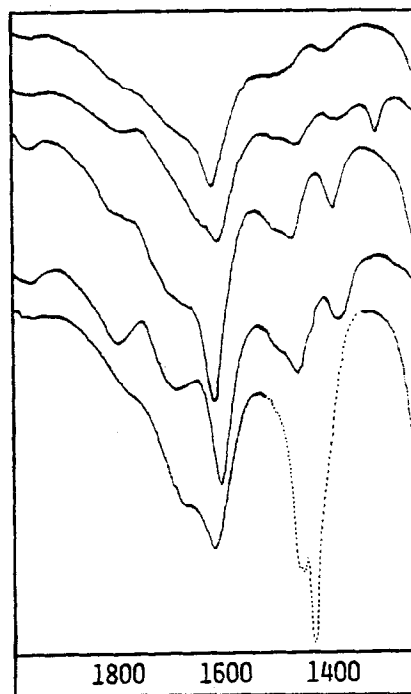


Fig. 2. HOH bending bands in the LNT IR spectra of some sulfate alums :
1 - KAlSD; 2 - KCrSD; 3 - RbAlSD;
4 - RbCrSD; 5 - AAlSD

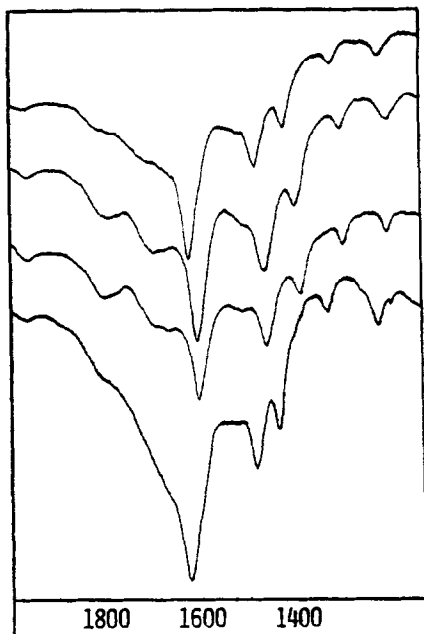


Fig. 3. HOH bending bands in the LNT IR spectra of some selenate alums :
1 - RbAlSeD; 2 - RbCrSeD; 3 - CsCrSeD;
4 - KAlSeD

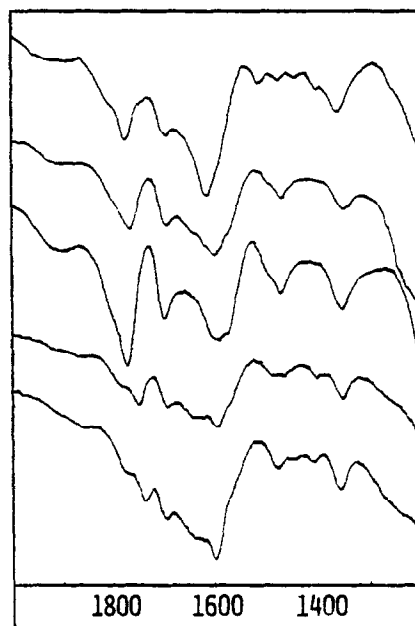


Fig. 4. HOH bending bands in the LNT IR spectra of some sulfate β alums :
1 - CsAlSD; 2 - CsGaSD; 3 - CsCrSD;
4 - CsVSD; 5 - RbVSD

Further examples are given in Figs. 2 - 4 where the LNT infrared spectra of several sulfate and selenate alums of the α and β types are presented. Multiple bands in the $2000 - 1200 \text{ cm}^{-1}$ region could be seen in all these cases.

Despite the different selection rules and the excitation mechanisms, multiple bands exist in the low-temperature Raman spectra as well. As an example, the Raman spectrum of RbAlSeD is presented in Fig. 5.

In the case of α alums (Figs. 2 and 3), an almost regular sequence of bands is found, with an average spacing of some 100 cm^{-1} . On the other hand, the spectral picture in the case of the β alums is more involved (cf. Fig. 4).

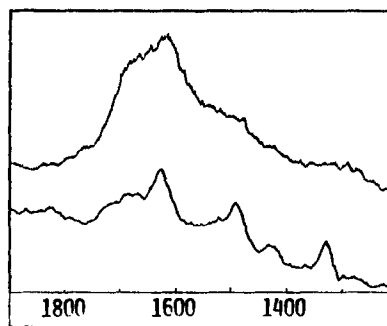


Fig. 5. The HOH bending region in the RT (upper) and LNT (lower curve) Raman spectra of RbAlSeD

Second-order transitions, involving librational modes of the water molecules (possibly in Fermi resonance with the HOH bending mode) may, of course, be invoked as an explanation for the origin of these peculiar bands. However, the sequence of

bands found in the α alums would, in that case, be a mere coincidence and this does not seem as an acceptable explanation.

Alternatively, these bands could be regarded as a *progression*, similar to the Frank-Condon progressions which sometimes appear in the electronic spectra. The acceptance of such an explanation would lead to a mechanism similar to that described by Bertie and Falk [1]. These authors, namely, studied the multiple bands in the bending Cl-H...O (not HOH) region of some ether - HCl complexes and concluded that the bands are due to combinations of the fundamental bending vibration with the low-frequency (50 cm^{-1}) mode assigned to the *rocking* H-Cl vibration. The observed temperature-induced changes in the case of alums, however, are not in a full agreement with the model since all "hot" transitions should vanish at low temperatures (in the alum spectra the corresponding bands are found below 1600 cm^{-1}).

In any case, the temperature effects do suggest that an extensive anharmonic coupling of the HOH bending bands and some low frequency mode(s) occurs since the "pure" HOH bending (expected to appear at $\approx 1600\text{ cm}^{-1}$) should not be temperature sensitive. This frequency is, namely, so high that the excited states at RT could be treated as unpopulated and thus, as mentioned, no remarkable temperature effect is possible.

So, the mechanism of Bertie and Falk [1] does not seem to be integrally applicable in the present case, but its basic idea (anharmonic coupling with low frequency motions) seems to be operative. Unfortunately, it provides no explanation for the regula-

rity of the sequence found in the spectra of the α alums.

Further work, based on quantum-mechanical model calculations, is needed in order to reveal the true cause for the appearance of multiple HOH bending bands.

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