

VIBRATIONAL SPECTRA OF HEXAAQUA COMPLEXES : I. ASSIGNMENTS OF WATER
 LIBRATIONAL BANDS IN THE SPECTRA OF SOME ALUMS

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SUMMARY

The IR and Raman spectra of a number of alums were recorded at both room temperature and LNT. In order to make a reliable assignment of the librational bands of the water molecules, special attention was paid to $\text{CsAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and its partly deuterated analogues. Assuming that the hindered rotations of the water molecules are of the rocking, wagging and twisting type, the bands were assigned in line with the criteria given by Eriksson and Lindgren [1]. It was found that the frequency of the librational bands decreases in the order $\omega > \tau > \rho$, for the water molecules coordinated to the trivalent cation and $\tau > \omega > \rho$, for the water molecules coordinated to the univalent cation. The wagging libration of the water molecules coordinated to Al shifts, on deuteration, by a factor close to 1.5. Some of the possible reasons for this high isotopic ratio are discussed.

INTRODUCTION

Alums are compounds with a general formula $\text{M}^{\text{I}}\text{M}^{\text{III}}(\text{RO}_4)_2 \cdot 12\text{H}_2\text{O}$ (M^{I} is a univalent metal such as Na, K, Rb, Cs etc., M^{III} is a trivalent metal : Al, Ga, In, Fe, Cr, Ir etc. and R is S or Se).

According to the crystallographic data (see [2] and the references therein), all alums are cubic and crystallize in the space group $\text{Pa}\bar{3}$ with $Z = 4$. The site symmetry for both the univalent and trivalent cation is S_6 , the tetrahedral anions occupy C_3 sites and the site symmetry of the two crystallographically distinct types of water molecules is C_1 . The water molecules coordinated to M^{III} (W^3 hereafter) form, in all known cases, almost perfect $\text{M}^{\text{III}}\text{W}_6$ octahedra and are strongly hydrogen bonded ($\text{O}_w \dots \text{O}$ distances close to 260 pm). The other type of water molecules (W^1 - these are 'coordinated' to M^{I}) are more weakly hydrogen bonded, the geometry around M^{I} being dependent on the alum type. There are, namely, three types of alums, denoted by Lipson [3] as α -, β - and γ -alums. A clear-cut distinction between the three types can be made, as shown by Beat-

tie *et al.* [2] on the basis of the details in their crystal structure.

The vibrational spectra of alums have been extensively studied (see [4] and the references therein). Despite that, no definite assignment of the water librational bands exists so far. The aim of the present paper is to give a reliable assignment of the H₂O librations, based on the study of the IR and Raman spectra of protiated and partly deuterated alums, recorded at both room temperature and LNT.

EXPERIMENTAL

A number of different alums were prepared by standard methods, i. e. by slow crystallization from water solution of the corresponding M^I₂RO₄ and M^{III}₂(RO₄)₃·xH₂O salts taken in equimolar amounts. Deuterated samples were prepared by recrystallization of the alums from H₂O/D₂O mixtures of appropriate composition. The IR spectra (KBr pellets) were recorded on a Perkin-Elmer 580 spectrophotometer. For LNT IR studies a VLT-2 low-temperature cell was used. Raman spectra were recorded on CARRY 81 Raman spectrophotometer. The light source was a Spectra-Physics Ar-ion laser operating at 514.52 nm.

RESULTS AND DISCUSSION

CsAl(SO₄)₂·12H₂O (CASD) and RbAlSeO₄)₂·12H₂O (RASED) were chosen as case examples because these compounds are very stable (no loss of water or any reaction with KBr could be detected). The IR spectra of CASD are shown at Fig. 1. All temperature-sensitive bands are in some way connected to motions of the water molecules (librational or translational modes). The application of group theory shows that as a result of correlation-field splitting, up to three components of each librational mode could be expected in the IR spectra. However, one should expect doublets rather than triplets if the interactions of the four equivalent MW₆ groups in the unit cell are neglected. As seen in Fig. 1, this is what is in fact observed.

Both theoretical [1] and experimental [5] studies suggest that if a water molecule occupies a site of C_{2v} symmetry, one should expect almost equal frequencies of the wagging (ω) and twisting (τ)

H₂O or D₂O librations, but the related librations for the HDO isotopomer can best be described as H and D out-of-plane motions. Furthermore, the frequencies of these H and D motions should fall around the mean-values of the frequencies of $\omega(\text{H}_2\text{O})$ and $\tau(\text{H}_2\text{O})$ i.e. $\omega(\text{D}_2\text{O})$ and $\tau(\text{D}_2\text{O})$ respectively. The frequency of $\rho(\text{HDO})$ should be roughly an arithmetic mean of the frequencies of $\rho(\text{H}_2\text{O})$ and $\rho(\text{D}_2\text{O})$. According to the model calculations of Eriksson and Lindgren [1] $\rho(\text{H}_2\text{O})$ should have the highest frequency for trigonally coordinated water molecules, whilst the opposite is expected if the water molecules are tetrahedrally coordinated. On the other hand, Lutz and Christian [6] have found examples where the hindered rotations of all three water isotopomers can be described as ω -, τ - and ρ -type librations.

Our working assumption was that the effective symmetry of the water molecules in CASD does not deviate appreciably from C_{2v} . After a careful inspection of the IR spectra of both protiated and partly deuterated samples (cf. Figs. 1 and 2) it appeared possible to assign the librational bands in CASD in line with the criteria given by Eriksson and Lindgren [1]. We started with the assignment of the resonant doublet at around $975/945\text{ cm}^{-1}$. There is no doubt that these bands should be attributed to librations of the strongly hydrogen-bonded water molecules W^3 , as done in all previous assignments (see [4] and the references therein). The study of the partly deuterated compounds shows that this pair of bands is not due to the ρ -libration, whereas their intensity

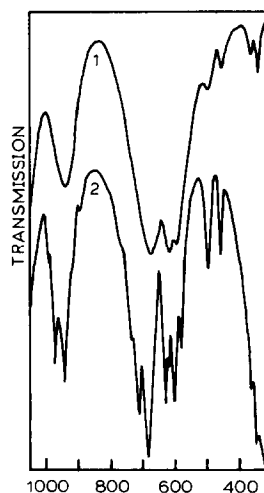


Fig. 1 : IR spectra of CASD recorded at RT (1) and LNT (2)

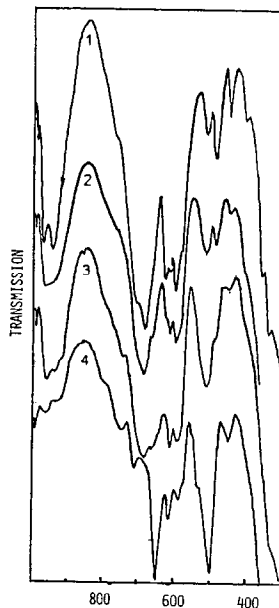


Fig. 2 : LNT IR spectra of CASD (deuterium content increases, going from 1 to 4)

eliminates the possibility that they are due to τ -librations either. Therefore, they must originate from the ω -librations of the water molecules coordinated to Al. The shoulder at 920 and the very weak band at 890 cm^{-1} were assigned to the τ -modes of the same type of water molecules. If this is correct, then in the IR spectrum of the compound deuterated to highest degree (around 80% D) a band (or pair of bands, because the protons are not crystallographically equivalent) due to the H-motions of the HDO molecules should appear at around 930 cm^{-1} . The doublet at 955/925 cm^{-1} seen in the deuterated compound (cf. spectrum no. 4 of Fig. 2) is in a very good agreement with these expectations.

By similar reasoning, the doublet at 715/685 cm^{-1} in the LNT IR spectrum of the protiated compound was assigned to the ω -librations, whilst the shoulders at 770/730 cm^{-1} must be due to the τ -librations of the water molecules 'coordinated' to Cs. The deuteration behaviour is, again, in line with this assignment. The $\omega(\text{D}_2\text{O})$ librations of the W^3 and W^1 molecules lie at 645 and 500 cm^{-1} respectively. The high-frequency shoulders of the 500 cm^{-1} band may correspond to the $\tau(\text{D}_2\text{O})$ of W^1 ; the corresponding bands of W^3 fall in the region where $\nu_4(\text{SO}_4)$ bands appear and hence could not be identified with certainty.

The doublet at around 495/455 cm^{-1} was assigned to $\rho(\text{H}_2\text{O})$ of W^1 . Its HDO analog is found around 405 cm^{-1} (spectrum 1 of Fig. 2), in a fair agreement with the model of Eriksson and Lindgren [1]. The $\rho(\text{D}_2\text{O})$ band is obscured by the window-absorption of the LNT cell. It was not quite clear where should the $\rho(\text{H}_2\text{O})$ librations of W^3 fall. We assumed that they are in the region around 600 cm^{-1} . However, in the same region strong absorptions of $\nu_3(\text{SO}_4)$ and $\nu_3(\text{AlW}_6)$ exist, the latter being deuteration-sensitive. So, in the IR spectra of CASD the $\rho(\text{H}_2\text{O})$ bands could not be identified. For this reason we turned our attention to the Raman spectra of RASeD. The $\nu_4(\text{SeO}_4)$ mode is, namely, found around 430 cm^{-1} and the $\nu_3(\text{AlW}_6)$ is Raman inactive. Thus the band at around 625 cm^{-1} in the LNT Raman spectrum of RASeD (Fig. 3) proves that, really, there is a H_2O libration in this region. Keeping this in mind, the bands at 630/580 cm^{-1} in the IR spectrum of CASD were assigned to $\rho(\text{H}_2\text{O})$ of W^3 . The probable D_2O analogs of these bands were found at around 460 cm^{-1} . The complete assignment of the librational bands is given in Table 1. Somewhat unexpectedly [1], the $\rho(\text{H}_2\text{O})$ mode appears at the lowest frequency, although the water molecules are trigonally coordinated.

TABLE 1 : Assignment of the librational bands in the LNT-IR spectrum of CASD (frequencies in cm^{-1} ; pairs of numbers refer to correlation-field components; H_{Oop} and D_{Oop} denote H and D out-of-plane motions respectively)

$\omega(\text{H}_2\text{O})$	$\omega(\text{D}_2\text{O})$	$\tau(\text{H}_2\text{O})$	$\tau(\text{D}_2\text{O})$	$\rho(\text{H}_2\text{O})$	$\rho(\text{D}_2\text{O})$	$\rho(\text{HDO})$	H_{Oop}	D_{Oop}
w^1								
715	500	770	560	495	?	405	750	510
685	-	730	535	455	-	-	710	-
w^3								
975	645	920	?	630	460	500?	955	?
945	-	890	-	580	-	-	925	-

On deuteration, very high frequency shifts for the ω -libration of w^3 was found, the isotopic ratio being 1.49. According to van der Elsken and Robinson [7] this may indicate a rather high degree of anharmonicity for this libration. Another possibility is that, due to the isotopic effect on the $O_w \dots O$ distances [8,9], after deuteration the hydrogen bonds of w^3 become weaker. Since the librations are sensitive to the hydrogen-bond strength [10], this could also be an explanation for the rather high isotopic ratio. Unfortunately, the structure refinements [8,9] were made more than 20 years ago and no accurate neutron diffraction data are available for both protiated and deuterated CASD (or, for that matter, any other alum). Thus, it seems desirable to have the structures of CASD and CASD-d determined by neutron diffraction in order to be sure that a considerable isotopic effect really exists.

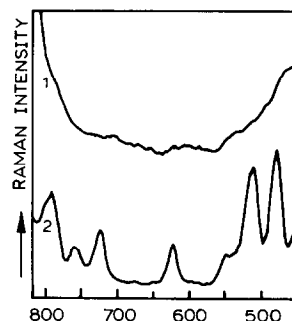


Fig. 3 : Raman spectra of RASd recorded at RT (1) and LNT (2)

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REFERENCES

1. A. Eriksson and J. Lindgren, *J. Mol. Struct.* **48**, 417 (1978).
2. J.K. Beattie, S.P. Best, B.W. Skelton and A.H. White, *J. Chem. Soc. Dalton Trans.*, 1973 (1983).
3. H. Lipson, *Proc. Roy. Soc.* **A151**, 347 (1935).
4. S.P. Best, J.K. Beattie and R.S. Armstrong, *J. Chem. Soc. Dalton Trans.*, 2611 (1984).
5. G.H. Thomas, M. Falk and O. Knop, *Can. J. Chem.* **52**, 1029 (1984).
6. H.D. Lutz and H. Christian, *J. Mol. Struct.* **101**, 199 (1983).
7. J. van der Elsken and D.W. Robinson, *Spectrochim. Acta* **17**, 1249 (1961).
8. A.C. Larson and D.T. Cromer, *Acta Crystallogr.* **22**, 793 (1967).
9. D.T. Cromer and M.I. Kay, *Acta Crystallogr.* **22**, 800 (1967).
10. C.L. Thaper, A. Sequeira, B.A. Dasannacharya and P.K. Iyengar, *Phys. Status Solidi* **34**, 279 (1969).