

VIBRATIONAL SPECTRA OF HEXAAQUA COMPLEXES. II. EXTERNAL MOTIONS
OF WATER MOLECULES IN THE SPECTRA OF $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$

Viktor Stefov, Bojan Šoptrajanov and Vladimir Petruševski

Institut za hemija, PMF, Univerzitet "Kiril i Metodij",
P.O. Box 162, 91001 Skopje, Yugoslavia

ABSTRACT

The infrared spectra of powdered samples of various $\text{AlCl}_3 \cdot 6(\text{H},\text{D})_2\text{O}$ isotopomers were recorded at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT). The RT Raman spectrum of the protiated compound was also studied. It appears that despite the low site symmetry (C_1), the force field around H_2O has approximately C_{2v} symmetry.

The librational bands were assigned according to the criteria of Eriksson and Lindgren [1]. The rocking (*r*) mode was found at highest frequency ($\approx 840 \text{ cm}^{-1}$), the twisting (*t*) and wagging (*w*) bands being close to each other (≈ 600 and $\approx 540 \text{ cm}^{-1}$, respectively).

A strong band at around 1150 cm^{-1} was found in both infrared (IR) and Raman spectra. It was assigned to second-order transitions of wagging and twisting motions of the water molecules. Strong mechanical anharmonicity in the *w*(H_2O) and *t*(H_2O) motions is apparently present, arising probably from large quartic terms in the potential energy expansion.

INTRODUCTION

The external motions of water molecules (librations, i.e. hindered rotations and hindered translations) in crystallohydrates were extensively studied from both theoretical and experimental point of view and that work has been reviewed [2,3].

It is generally agreed that the librational motions of water molecules (H_2O and/or D_2O) may be classified as *rocking* (an in-plane mode), *wagging* and *twisting* (the latter two are out-of-plane modes). Needless to say, the librational modes, if the symmetry permits, may be *mixed*. In the case of HDO molecules, according to Falk *et al.* [4], the out-of-plane motions are better described as H- and D-motion, respectively. This proposal was later developed by Eriksson and Lindgren [1] and supported by the results of their normal-coordinate treatment of model

systems. Lutz [3], however, argues that in the case of tetrahedrally coordinated, non-distorted water molecules, wagging and twisting librations may be present for *all* three water isotopomers.

In our previous report [5] we have studied the librational motions of the water molecules in some aluminium alums and concluded that the assignments which were made were in line with the criteria of Eriksson and Lindgren [1]. The present paper is devoted to a similar analysis of the spectra of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$.

According to the crystallographic data [6], $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ crystallizes in the hexagonal space group $R3c$ with $Z = 6$. There is only one type of water molecules which occupy sites of C_1 symmetry. The water molecules are coordinated to Al, forming almost perfect octahedra. The site symmetry of the complex $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ cations is S_6 . Each water molecule forms two strong hydrogen bonds with the chloride anions, the corresponding $\text{Ow} \cdots \text{Cl}$ distances being almost equal (302(2) and 303(1) pm respectively). The hydrogen bonds are almost linear. The water molecule, the proton acceptors and the Al atoms lie, approximately, in the same plane.

Structurally speaking, the water molecules in $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ are closely related to those in the alums, the main structural unit in all these cases being the complex $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ cations [6,7]. Thus, it seemed worthwhile to study the external motions of the water molecules in $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and to compare the results with those obtained for the alums [8].

The vibrational (infrared and Raman) spectra of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ have already been studied by Adams and Hills [9], but their assignment could not be supported by the present investigation, particularly by the study of the spectra of partly deuterated compounds.

The polarized infrared reflection spectra of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ single crystals and of partly deuterated analogues have been studied by Wäschenbach and Lutz [10]. The spectroscopic study of these authors shows that the frequencies of the two OD stretching bands of the isotopically *isolated* HDO molecules differ for about 20 cm^{-1} . Our results are in complete agreement with these findings and we found, furthermore, that the splitting of the two observed HDO bending bands is less than 10 cm^{-1} . It is, thus, almost irrelevant which of the protons is substituted by a deuteron, suggesting that not only the geometry [6], but also the force field around H_2O have approximately C_{2v} symmetry.

EXPERIMENTAL

$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was a commercial product (Riedel, Hannover) and was recrystallized from water before use. Deuterated samples were prepared by recrystallization of the salt from $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures of appropriate composition.

The infrared spectra were recorded from KBr pellets on a Perkin-Elmer 580 spectrophotometer. A VLT-2 low-temperature cell cooled with liquid nitrogen was used for the low-temperature studies. The Raman spectra were recorded from polycrystalline samples, on a JEOL JRS-S1B spectrophotometer. The light source was a Coherent Radiation Ar⁺ ion laser. The laser operated at 514.52 nm.

RESULTS AND DISCUSSION

The RT and LNT infrared spectra of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ are presented in Fig. 1 a and the RT Raman spectrum is given in Fig. 1 b. Only the region below 1400 cm^{-1} is shown.

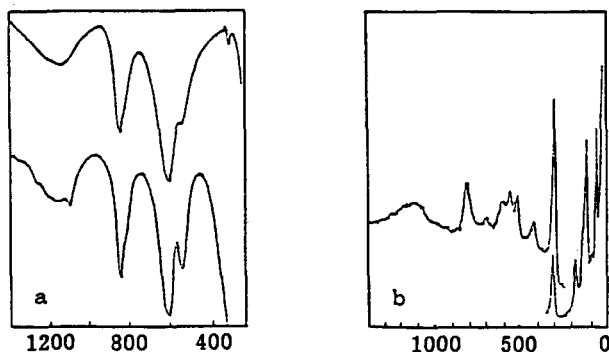


Fig. 1. RT and LNT infrared spectra (a) and RT Raman spectrum (b) of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$

We shall start with the assignment of the AlO_6 vibrations. Since, as mentioned, the relevant structural units as well as their site symmetry in both Cs-Al alum and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ are the same, it is expected that the frequencies of the AlO_6 normal modes in $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ will be close to those found in the Cs-Al alum spectrum [8]. The results of the assignment are summarized in Table I.

TABLE I
Assignment of the AlO_6 modes in $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ *

Compound	$\nu_1 (A_{1g})$	$\nu_2 (E_g)$	$\nu_3 (F_{1u})$	$\nu_4 (F_{1u})$	$\nu_5 (F_{2g})$	$\nu_6 (F_{2u})$
$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$	530	430	600	310	315	< 250
Cs-Al alum	542	443	600	335	347	265

* All values are in cm^{-1} . The frequencies for the Cs-Al alum [8] are given for comparison.

Except for the case of mode ν_3 , these values are in a fair agreement with those given by Adams and Hills [9].

The remaining bands in the region below 950 cm^{-1} are due to H_2O librations. Therefore, the bands at ≈ 840 , 540 and, probably (as suggested by the Raman spectrum of the compound), 600 cm^{-1} correspond to the three expected librational modes.

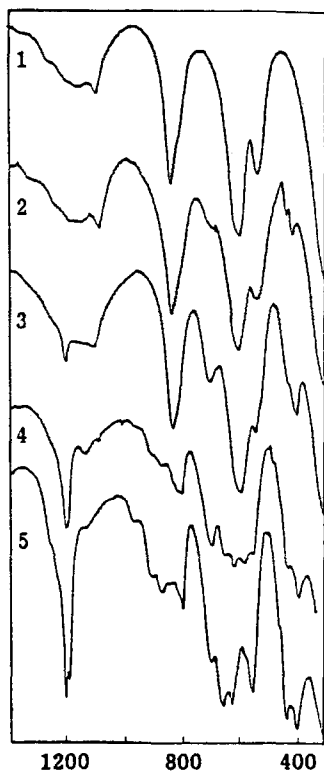


Fig. 2. LNT IR spectra of a series of partially deuterated analogues of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$

found at 440 and 405 cm^{-1} . The strong band at around 555 cm^{-1} is certainly the D_2O analogue of the band observed, in the spectrum of the protiated compound, around 600 cm^{-1} .

The LNT spectra of the partly deuterated compounds (Fig. 2) clearly show that the band at $\approx 840\text{ cm}^{-1}$ is not due to the $w(\text{H}_2\text{O})$ mode as proposed by Adams and Hills [9]. In fact, even in the case of the spectra recorded from samples with low deuterium content, a new band is found around 710 cm^{-1} (the isotopic ratio is 1.18). The intensity changes of this band on increasing the deuterium content in the samples is in line with the expectations for a $r(\text{HDO})$ band. This, then, implies that the 840 cm^{-1} band is due to $r(\text{H}_2\text{O})$. It is not clear whether both components of the $655/625\text{ cm}^{-1}$ doublet in the perdeuterated compound (or only one of them) should be attributed to $r(\text{D}_2\text{O})$.

The band at $\approx 540\text{ cm}^{-1}$ in the LNT IR spectrum of the protiated compound is assigned to $w(\text{H}_2\text{O})$. The $t(\text{H}_2\text{O})$ band is most probably hidden by the intense 600 cm^{-1} band (the latter being due to the $\nu_3(\text{AlO}_6)$ mode). Such an assignment is confirmed by the appearance of the $435/415\text{ cm}^{-1}$ doublet (spectrum 2 of Fig. 2), the components of which are assigned to the D-motions of the HDO molecules in which different protons have been substituted by deuterons (HDO and DHO respectively). The frequency of the H-motion is 570 cm^{-1} (cf. spectrum 4 of Fig. 2), only one such band being detected. The bands assignable to $t(\text{D}_2\text{O})$ and $w(\text{D}_2\text{O})$ are

The assignment of the H_2O , HDO and D_2O librational bands in the spectra of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and its deuterated analogues is summarized in Fig. 3.

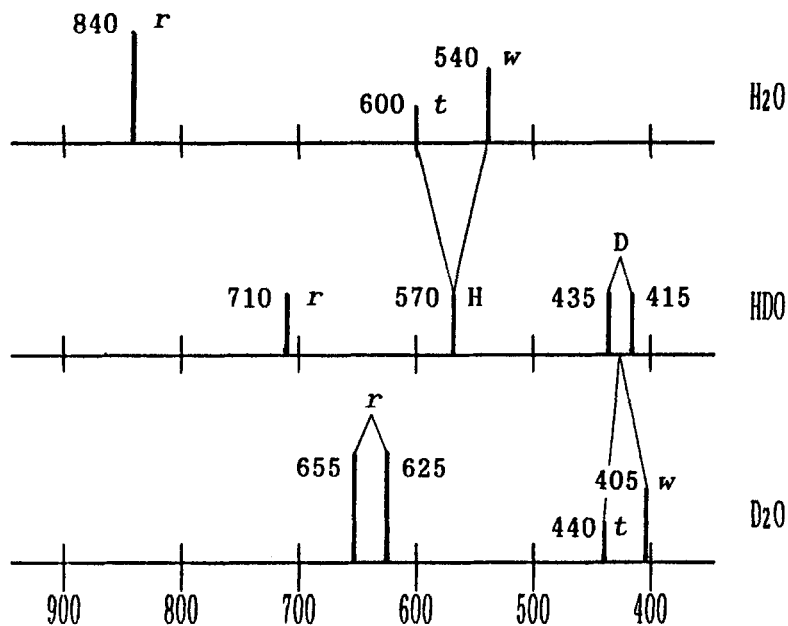


Fig. 3. Schematic representation of the position and intensity of the H_2O , HDO and D_2O librational bands

An interesting feature worth mentioning is the appearance, in both infrared and Raman spectra, of a rather strong band centered around 1150 cm^{-1} . Some structure is evident in the LNT IR spectrum (Fig. 1 a) so that it is clear that not one, but a number of bands are present in this region.

On deuteration (cf. spectrum 5 of Fig. 2), the complex of bands shifts to $\approx 850\text{ cm}^{-1}$, this being the frequency of the centroid of the feature. It is important to note that no new bands appear, in the spectra of the samples with low deuterium content, around 1000 cm^{-1} .

The bands giving rise to the broad feature described above were attributed to second-order transitions involving *wagging* and *twisting* motions of water. As seen from the absence of bands around 1000 cm^{-1} , namely, there is no indication for the existence of second-order transitions involving the $r(\text{HDO})$ mode(s).

The width and structure of the feature are apparently a consequence of the relaxed selection rules for the multiphonon transitions. The wave vectors of the individual phonons, namely, may be anywhere in the first Brillouene zone, the intensity distribution of the bands, then, mapping the combined two-phonon density of states [11].

The intensity of the 1150 cm^{-1} band suggests strong mechanical and/or electrical anharmonicity of the wagging and twisting motions. In the LNT IINS (incoherent inelastic neutron scattering) spectra, however, there is again a strong band centered around 1150 cm^{-1} [12]. Since the selection rules in the IINS spectroscopy are not related to either the dipole moment or the polarizability changes, it must be concluded that the anharmonicity is *mechanical* in character with important anharmonic terms in the potential-energy expansion of the out-of-plane water librations. Most probably, the *quartic* terms are dominant since for water molecules of C_{2v} symmetry all *odd* terms in the potential energy expansion are equal to zero.

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