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# INFRARED SPECTRA OF DICESIUM *trans*-TETRAAQUADICHLOROCHROMIUM(III) CHLORIDE

KEY WORDS : *trans*-tetraaquadichlorochromium(III) chloride; infrared spectra.

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## ABSTRACT

The infrared spectra of *trans*-$Cs_2[CrCl_2(H_2O)_4]Cl_3$ and its deuterated isotopomers were investigated at room and liquid nitrogen temperature and at intermediate temperatures as well. The spectra of the partly deuterated analogues are not in agreement with the crystallographic data [1], perhaps because of the incorrect choice of the space group in which the structure was solved and refined or the presence of disorder in the structure.

## INTRODUCTION

The vibrational spectra of *trans*-$Cs_2[CrCl_2(H_2O)_4]Cl_3$ have already been investigated. Thus, the room temperature (RT) infrared (IR) spectrum and the Raman spectrum recorded at liquid nitrogen temperature (LNT) of this compound were studied by Michalska-Fong *et al.* [2]. To the best of our knowledge, the spectra of the deuterated isotopomers have not been investigated so far and the LNT infrared spectrum of the protiated compound has not been studied either.

The crystal structure of the title compound was determined by X-ray diffraction [1]. The systematic absences observed in zero and upper level Weissenberg photographs, were found to be consistent with each of the space groups $C2$, $Cm$ and $C2/m$. Simply disregarding the existence of space groups with lower symmetry, the structure was solved [1] in the space group $C2/m$ and was refined to an $R$ value of 9.9 % for the observed and 12.5 % for all reflections. Only one type of water molecules (coordinated to the $Cr^{3+}$ ions) was found in the structure, the $H_2O$ molecules being located at sites with $C_1$ symmetry.

Some time ago we published the results of our LNT infrared study of slightly deuterated (≈ 5 % D) *trans*-$Cs_2[CrCl_2(H_2O)_4]Cl_3$ [3], concluding that the spectra are not consistent with the structural data. A phase transition, disorder of the water molecules and/or incorrectly determined space group symmetry of the crystals were suspected as possible causes for this finding.

A more thorough analysis of the infrared spectra of protiated and deuterated samples (studied at RT and LNT) in the 4000-200 $cm^{-1}$ region is presently given. As shall be seen, the new data show that two types of water molecules are present even at room temperature, thus ruling out, almost unequivocally, the phase transition as a possible cause. In order to explain the existence of more than one type of water molecules, one is left with the remaining two possibilities : a true space group having a symmetry lower than $C2/m$ (in which all water molecules would not be crystallographically equivalent) or, alternatively, a disordered structure.

## EXPERIMENTAL

The crystals of *trans*-$Cs_2[CrCl_2(H_2O)_4]Cl_3$ were synthesized according to the method described by McCarthy *et al.* [1]. Stoichiometric quantities of cesium chloride and *trans*-$[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$ (known as green $CrCl_3 \cdot 6H_2O$) were dissolved in aqueous hydrochloric acid [$c(HCl)$ = 2 mol/L]. Upon slow evaporation, stable, non-hygroscopic, dark green crystals were formed. Deuterated samples were obtained in an analogous way, using DCl and $D_2O$ as solvents. In order to prevent the H-for-D exchange with the atmospheric moisture, all operations were carried out in a dry box.

The chemical and thermogravimetric analyses gave the following results :

| | w(Cr) | w(Cl) | $w(H_2O)$ | w(Cs) |
|---|---|---|---|---|
| calculated : | 9.17 % | 31.26 % | 12.71 % | 46.87 % |
| found : | 9.30 % | 32.10 % | 12.56 % | |

The IR spectra were recorded, in the 4000-200 $cm^{-1}$ region, on a Perkin-Elmer 580 grating infrared spectrophotometer from CsCl and CsI pellets and from mulls in Nujol and Fluorolube. No significant difference was detected between the two sets of spectra. However, the samples with a high deuterium content could be recorded only from Nujol mulls. For the LNT work a VLT-2 low-temperature cell, equipped with KBr (4000-350 $cm^{-1}$) and polyethylene (500-200 $cm^{-1}$) windows was used.

## RESULTS AND DISCUSSION

The IR spectra of *trans*-$Cs_2[CrCl_2(H_2O)_4]Cl_3$ recorded at RT and LNT are presented in Fig. 1. Our room-temperature spectrum agrees well with that published by Michalska-Fong *et al.* [2].

### *Assignments*

The assignment of the majority of the observed infrared bands in the spectra of the title compound (cf. Fig. 1) is a straightforward task and will be only briefly summarized below.

The intense bands in the high-frequency region are undoubtedly related to the water stretching modes and the assignment of the bands around 1650 $cm^{-1}$ to the HOH bending vibrations is also beyond doubt. However, it should be noted that at least three bands are observed in the former and two in the latter. The bands in the $\delta$(HOH) region are better resolved in the LNT spectrum where they appear at 1650 and 1619 $cm^{-1}$. In a section presented later on, we shall return to the problem of the number of bands in various spectral regions and its implications. Taking into account the polyatomic groups present in the structure, the bands observed in the 2400-2100 $cm^{-1}$ region, as well as those appearing between 1500 and 900 $cm^{-1}$ should be assigned to second-order transitions.

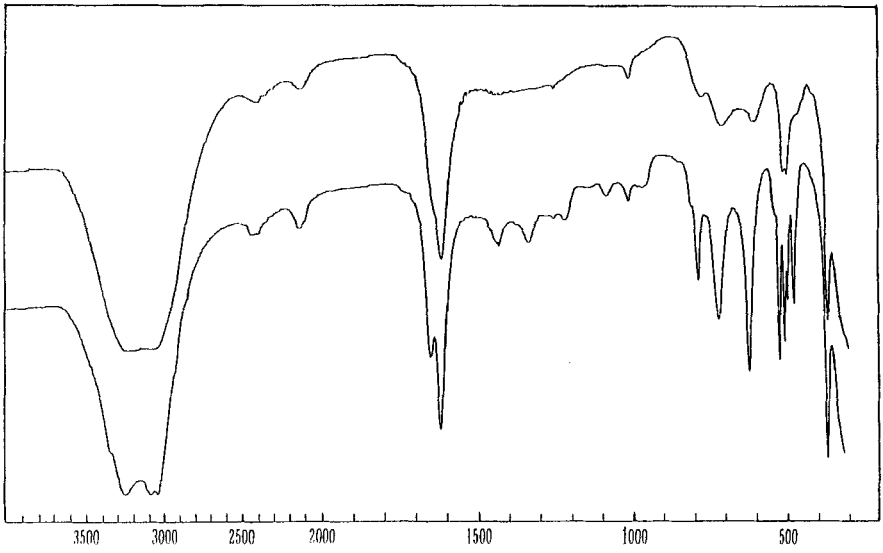


FIG. 1. Infrared spectra of *trans*-$Cs_2[CrCl_2(H_2O)_4]Cl_3$ recorded at room temperature (upper curve) and at LNT (lower curve)

Somewhat more complicated is the assignment of the bands which, in the RT IR spectrum of the title compound, appear in the 800-200 $cm^{-1}$ region. As seen in Fig. 2 (a and b), ten bands are present in this region. Of these, Michalska-Fong *et al.* [2] assigned (on the basis of the result of their normal coordinate analysis) the bands at 515/504, 369, 279 and 228 $cm^{-1}$ to Cr-O and Cr-Cl stretching, $\delta$(O-Cr-O) and $\pi(CrO_4)$ modes, respectively. In fact, the appearance of the doublet at 515/504 $cm^{-1}$ was attributed to a site-group splitting of the complex $[CrCl_2(H_2O)_4]^{2+}$ ion. The small departure from $D_{4h}$ symmetry, according to these authors, was caused by the rather strong hydrogen bonding of the water molecules. The RT IR bands at around 780, 720 and 610 $cm^{-1}$ were assigned to water librations, the two higher frequency bands being attributed, on the basis of the criteria of Adams and Lock [4], to the wagging $H_2O$ modes. The rather broad shoulder at about 480 $cm^{-1}$ was left unassigned and no band was attributed to the twisting mode which is infrared active for $H_2O$ molecules under $C_1$ symmetry.

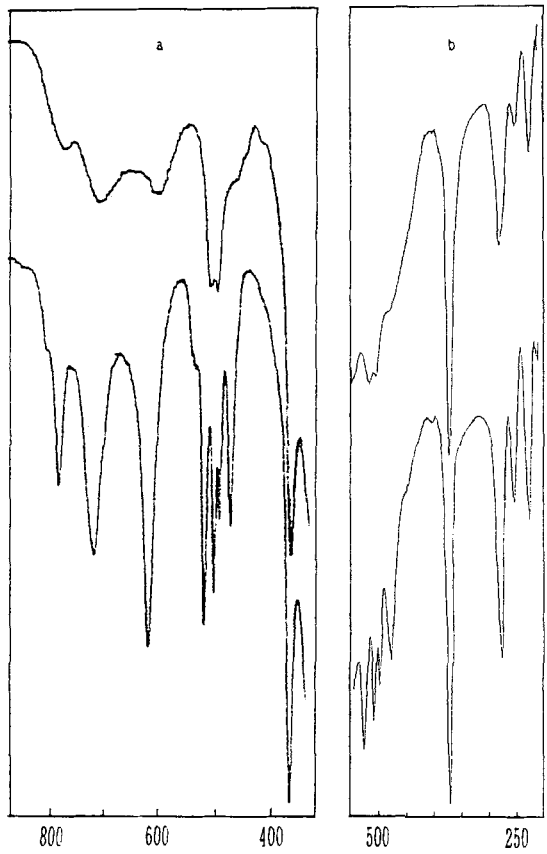


FIG. 2. The low-frequency region in the spectra of the title compound at RT (upper curve) and LNT (lower curve) recorded from CsI pellets : a - with KBr windows; b - with polyethylene windows on the variable-temperature cell

The attribution of bands to water librational modes is simplified by a parallel analysis of the RT and LNT infrared spectra. It is now a common knowledge that, as a rule, on lowering the temperature the bands due to water librations are shifted towards higher frequencies and gain (at least - apparently) in intensity. On the basis of such a behavior and their shift on deuteration (Fig. 3), to $H_2O$ librations we attribute the LNT bands at around 790, 725, 625, 500 and 480 $cm^{-1}$ and, perhaps, also the shoulder around 545 $cm^{-1}$.

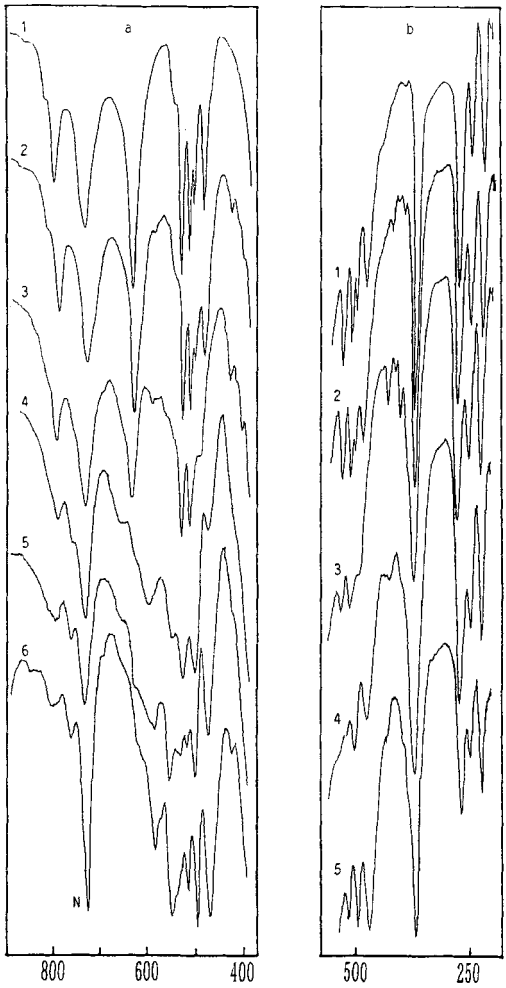


FIG. 3. The low-frequency region in the LNT spectra of protiated *trans*-$Cs_2[CrCl_2(H_2O)_4]Cl_3$ (curve 1) and of partially deuterated samples (curves 2-6; the deuterium content increases from top to bottom) : a - with KBr windows; b - with polyethylene windows on the variable-temperature cell

On increasing the deuterium content in the sample, the bands at 526 and 508 $cm^{-1}$ are gradually shifted towards lower frequencies (to 512 and 494 $cm^{-1}$ in the spectrum of the sample deuterated to a very high degree). In fact, they are only broadened at first, but this broadening disappears at higher degrees of deuteration. The isotopic frequency ratios for the two bands are 1.027 and 1.028 respectively so that their assignment to Cr-$OH_2$ stretches seems confirmed. The assignment made by Michalska-Fong [2] of the 369 $cm^{-1}$ RT band (our LNT value is 371 $cm^{-1}$) to a Cr-Cl stretching mode is also confirmed by the constancy of the position of this band on changes in the deuterium content. All bands at still lower frequencies exhibit shifts on deuteration so that they must involve motions of the water molecules.

*Improperly chosen space group or a disordered structure?*

As pointed out in the introductory part of this article, in our previous paper [3] the improper choice of the space group in which the structure was solved was taken as one of the possible reasons for the observed disagreement between the spectroscopic and the crystallographic data. An alternative explanation would involve the existence of some kind of disorder (static or dynamic) in the structure and a phase transition at some temperature below the ambient one should also be taken into account. On the basis of our new spectroscopic results (particularly the analysis of the spectra of the whole series of partially deuterated analogues), we intend to show that this last possibility is the least likely since even at room temperature two types of water molecules are present in the structure (although the real cause for this finding is not entirely clear). In the discussion which follows, we shall analyze the O-H and O-D stretching regions in the spectra of the partially deuterated analogues of *trans*-$Cs_2[CrCl_2(H_2O)_4]Cl_3$, the regions of H-O-H, H-O-D and D-O-D bendings and, finally, the water librational region.

It should be recalled that according to the available crystallographic data [1], only one type of water molecules with crystallographic symmetry $C_1$ exists in the structure of *trans*-$Cs_2[CrCl_2(H_2O)_4]Cl_3$, the two protons of a given water molecule being non-equivalent. In such cases (and in absence of correlation-field effects), two water stretching and one H-O-H bending bands are expected to appear and the number of bands due to water librations should be either two or three, depending on whether or not the effective symmetry is high enough to have an essentially pure twisting mode with infrared

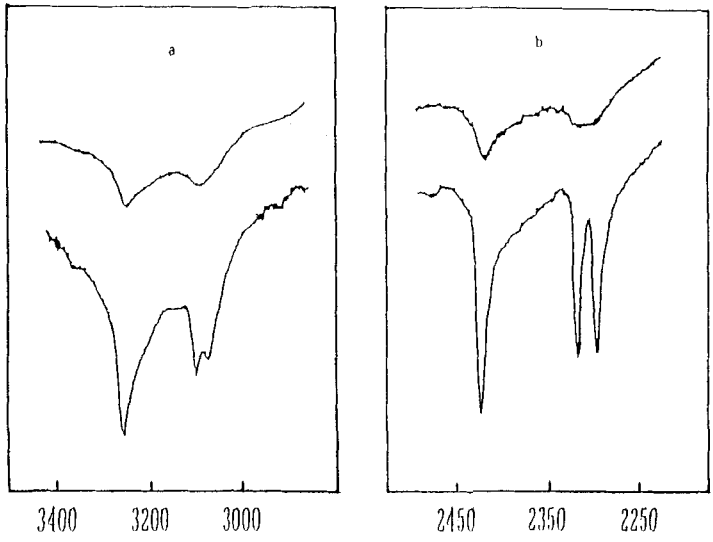


FIG. 4. RT (upper curves) and LNT (lower curves) spectra of partially deuterated analogues of *trans*-$Cs_2[CrCl_2(H_2O)_4]Cl_3$ : a - $w(D) \approx 95$ %; b - $w(D) \approx 5$ %

activity comparable to that of water molecules with $C_{2v}$ symmetry when the twisting libration is inactive.

Because of the non-equivalence of the two protons, the partially deuterated samples should contain two types of $H_2O$-$d_1$ species which can conveniently be labeled as HDO and DHO, depending on the proton which has been exchanged. Since in the case of the semideuterated water molecules the two stretching vibrations become decoupled (i.e. they become practically pure O-H and O-D stretchings [5] respectively), for isotopically isolated semideuterated water molecules two OH and two OD stretching bands are expected to appear. Also expected is the appearance of two bands in the region around 1400 $cm^{-1}$, one of them being due to the HOD and the other to the DOH bending.

Needless to say, correlation-field splitting effects can augment the number of observed bands, but these effects will not be operable if species containing isotopically isolated molecules are studied.

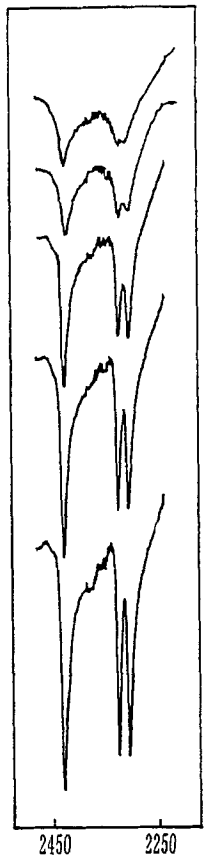


FIG. 5. The O-D stretching region in the spectrum of the partially deuterated analogue of *trans*-$Cs_2[CrCl_2(H_2O)_4]Cl_3$ with $w(D) \approx 5$ % recorded at temperatures from RT (uppermost curve) to LNT (bottom curve)

Contrary to the expectations based on the crystallographic results, *three* O-D stretching bands were found (at 2425, 2319 and 2299 $cm^{-1}$) in the LNT spectrum of a sample containing ≈ 5% D [3]. Three bands are also present (at 3255, 3098 and 3069 $cm^{-1}$) in the O-H stretching region of the spectrum of the almost perdeuterated (≈ 95% D) compound, as seen in Fig. 4. Actually, three bands could be identified even at RT (Fig. 5) and when the temperature is lowered, the number of observed bands does not change, but they become better resolved.

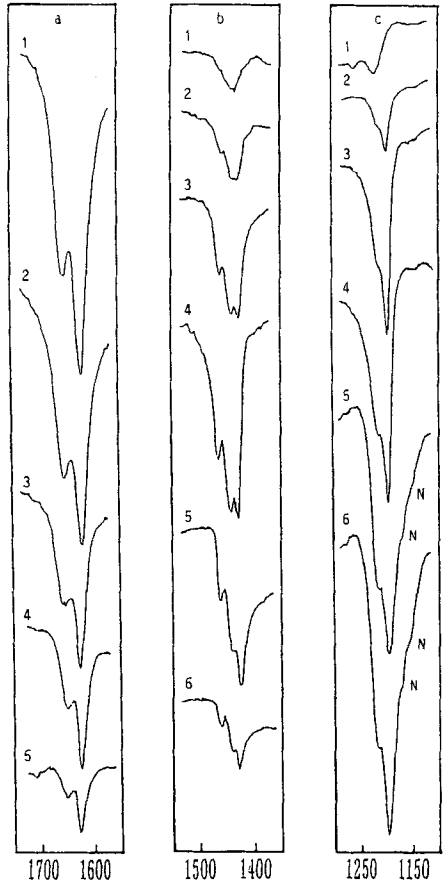


FIG. 6. The δ(HOH) (a), δ(HOD) (b) and δ(DOD) (c) regions in the LNT infrared spectra of the partially deuterated analogues of *trans*-$Cs_2[CrCl_2(H_2O)_4]Cl_3$; the deuterium content increases from top to bottom; the Nujol bands are marked by N

The fact that, irrespectively of the degree of deuteration there are two δ(H-O-H) bands and that more than two δ(H-O-D) bands exist, shows that the correlation-field effects are not responsible for the observed number of bands. Thus, two bands exist in the H-O-H bending region even in the spectra of the highly deuterated compound (cf. Fig. 6 a) *i.e.* when the HOH molecules are isotopi-

cally isolated with DOD and HOD molecules and practically no interaction between identical oscillators is possible. Unfortunately, the spectra of the slightly deuterated samples in the δ(DOD) region are of little value (*cf.* Fig. 6 c) since intense bands exist in the same region of the protiated compound. When the deuterium content is increased, two bands (as expected) are clearly visible, their frequencies being 1215 and 1197 $cm^{-1}$ in the highly deuterated compound.

Since there are at least four librational bands in the RT infrared spectrum (see above) and it is not likely that any of them is due to correlation-field splitting effects, the existence, even at room temperature, of more than one type of water molecules in the structure seems to be certain.

As already mentioned [3], the existence of more than one type of water molecules in the structure might be due to a phase transition at temperatures lower than the ambient one (the structure was solved at room temperature), to disorder in the structure (*cf.* [6]) or, simply, a result of incorrectly determined space group (as in the case of $Cs_3[VCl_2(H_2O)_4]Cl_4$ [7,8]). The possibility of a phase transition at temperatures below RT seems to be ruled out by the presence of three O-D stretching bands even at room temperature.

It is more difficult to chose the correct one of the two remaining possibilities : a disordered structure or a space group different from the one chosen by McCarthy *et al.* [1]. In any case, additional evidence that the crystal structure of the compound is incorrectly determined is provided by the values of the root-mean-square amplitudes of the thermal motion (calculated by us from the published [1] anisotropic temperature factors). Most atoms, namely, show highly anisotropic thermal motion and, furthermore, for some atoms (Cl and O) the thermal ellipsoid is even not real. This last finding is consistent with incorrectly determined structure (space group), with a disorder of the water molecules or may, simply, be due to the modest accuracy with which the structure was determined and refined by McCarthy *et al.* [1]. However, it should be borne in mind that a structure which appears disordered in a high-symmetry space group may be perfectly ordered if a space group with lower symmetry is chosen (e.g., in our case, *C*2 or *Cm*).

If the structure is ordered, but the space group is incorrectly determined, then the water molecules must occupy different sets of positions in the structure. The

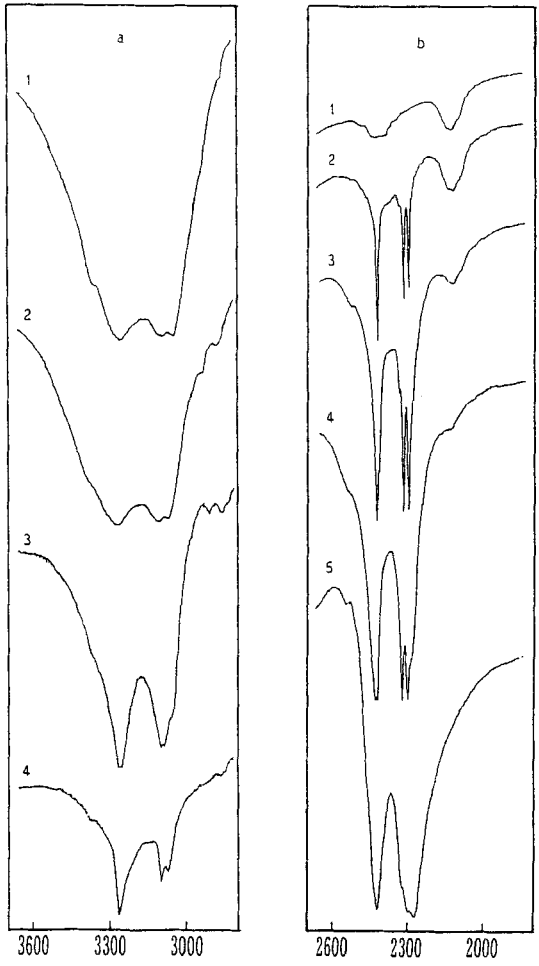


FIG. 7. The O-H stretching region (a) and O-D stretching region (b) in the LNT spectra of protiated *trans*-$Cs_2[CrCl_2(H_2O)_4]Cl_3$ (curve 1) and of partially deuterated samples (curves 2-5; the deuterium content increases from top to bottom)

deuteration results (Fig. 7) are not consistent with the existence of symmetrically bonded water molecules. In the case of existence of such water molecules, namely, the $D_2O$ stretchings should appear as pairs of bands flanking, at relatively high degrees of deuteration, the O-D stretching bands of the HDO molecules [9]. Since this is not the case, then the positions occupied by the water molecules are likely to be the general ones (sites with $C_1$ symmetry) which are fourfold in the $C2$ or $Cm$ space group. Consequently, only two types of water molecules would be present in the structure.

However, two types of water molecules could exist also as a result of the presence of disorder of some kind. Thus, two non-equivalent sets of sites could be only partly occupied by the water oxygens (this would lead to a static disorder of the structure) or, alternatively, only the water hydrons may undergo some kind of reorientational motion.

For an unambiguous answer to the dilemma : incorrectly determined space group or a disordered structure, it would be advantageous to use the same set of data in solving and refining the structure in the $C2/m$ space group and in some of those with lower symmetry ($C2$ and $Cm$). Alternatively, the carefully calibrated Raman and infrared spectra could be compared in order to check whether or not the space group is centrosymmetric. The structure might also be determined by neutron diffraction which would allow a precise determination of the positions of the hydrogen atoms. Neither of these checks is, unfortunately, presently available to us.

*Temperature dependence of the bands*

The comparison of the spectra recorded at different temperatures shows that many bands are temperature sensitive. This is a commonly encountered effect and the sharpening of the bands at low temperatures and their consequent more clearly visible splitting is something that is *a priory* expected. It is, therefore, no surprise that the barely visible shoulder on the high-frequency side of the H-O-H bending band at around 1650 $cm^{-1}$ becomes, at LNT, a well separated band. The bands in the O-H and O-D stretching regions are also sharpened on lowering the temperature.

The temperature dependence of the librational band has already been mentioned and it is well-known that the shift to higher frequency and the increase in the intensity serves as the most reliable criterion for assigning

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