

## WATER-ANION VIBRATIONAL COUPLING IN SOME CRYSTALLOHYDRATES

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## ABSTRACT

In treating the vibrational spectra of crystallohydrates, it is usually assumed that the water molecules vibrate independently (or nearly so) from the rest of the structural units and, consequently, the bands which shift on deuteration are automatically assigned to water modes (internal or external). In a number of hydrates of metal carboxylates, however, we were able to detect indications of water-anion vibrational coupling.

## INTRODUCTION

An assumption which is usually made, explicitly or implicitly, when the vibrational spectra of crystallohydrates are studied is that water molecules in the structure vibrate more or less independently from the structural units which make up the structure with the exception of alike, symmetry related, water molecules and the metal atoms to which water is coordinated. Consequently all bands which significantly change their position on deuteration are assigned to water modes, provided that the other present ions or molecules do not contain exchangeable protons. An additional criterion used to assign water librations is based on the examination of the temperature sensitivity of the bands - the librational ones are, namely, shifted to higher frequencies when the temperature is lowered, their width is appreciably decreased and the intensity is, at least apparently, increased [1]. In the course of our study of the vibrational spectra of hydrates of various metal carboxylates (acetates and formates) [2], however, we encountered some rather unexpected effects on deuteration and/or lowering the temperature which could not fit into the established scheme but could be satisfactorily interpreted if water-anion vibrational coupling was assumed. In the case of some investigated by us metal formate dihydrates, similar conclusions were reached by Tewary *et al.* [3,4].

## EXPERIMENTAL

All studied compounds were either commercially available or were prepared by standard laboratory methods. Repeated recrystallization from  $D_2O$  or solvent media containing deuterioacetic or deuterioformic acid was used to prepare the deuterated samples. The infrared spectra were recorded on a Perkin-Elmer 580 instrument, while a JEOL JRS S1B spectrophotometer was used to record the Raman spectra. For low-temperature infrared measurements a VLT-2 (RIIC) cell was used.

## RESULTS AND DISCUSSION

Among the examples where, we believe, water-anion vibrational coupling is present, that of nickel acetate tetrahydrate is probably the most convincing. Neither Stoilova *et al.* [5] nor Baraldi and Fabri [6] who recently reported on the infrared spectra of this compound have considered such a possibility, however.

Thus, in the protiated form of this compound the bands around  $970$  and  $920\text{ cm}^{-1}$  exhibit thermal sensitivity characteristic for water librational bands (Fig. 1A) and are absent from the infrared spectrum of the deuterate in which a single, rather weak and sharp band is found instead (Fig. 1B). The frequency of this latter band ( $\approx 945\text{ cm}^{-1}$ ) is almost exactly the average of the two above-menti-

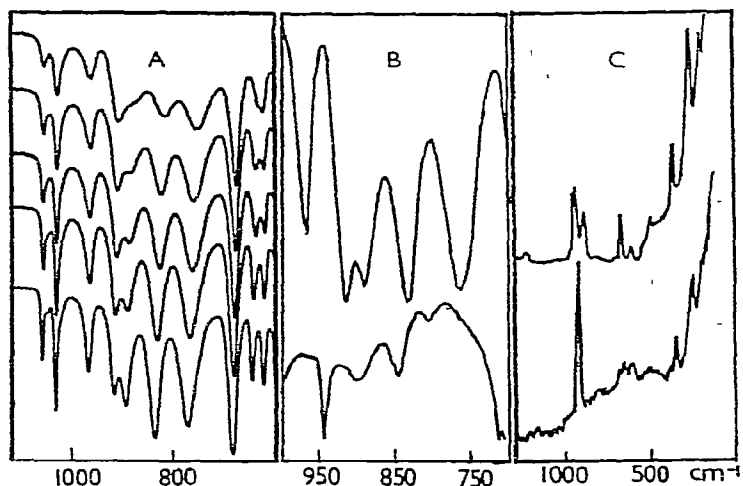


Fig. 1. The low-frequency part of the spectra of nickel acetate tetrahydrate : (A) Variation of the IR spectra on lowering the temperature. (B) Infrared spectra of protiated and deuterated form. (C) Raman spectra of protiated and deuterated form.

oned frequencies.

A doublet at about the same (only somewhat lower) frequencies is observed also in the Raman spectrum of the protiated form, where as in that of the deuterate a single, sharp and strong band is observed a little below  $945\text{ cm}^{-1}$  (see Fig. 1C).

This latter band and its infrared counterpart must be due to an acetate vibration, the only candidate being the  $\nu_4$  mode. On the other hand, the behaviour of the two bands around  $970$  and  $920\text{ cm}^{-1}$  in the spectrum of the protiated compound (their temperature sensitivity and their position with respect to the single band in the spectrum of the deuterate) can simply be explained if vibrational coupling between the  $\nu_4$  acetate vibration and a water librational mode with a close unperturbed frequency is assumed.

Several factors make such an interaction plausible. Thus, the carboxylate groups and the water molecules are mechanically coupled by coordination to the same metal ion and by hydrogen bonds (one of them being only  $261.9\text{ pm}$  long [7]); the force field around the water molecules is very asymmetric, probably making their librations highly anharmonic and, finally, the site symmetry of both the water molecules and the acetate ions is low, so that mixing of vibrational states with similar energies is not hindered by strict symmetry requirements.

The vibrational coupling is apparently not limited to the low-frequency region. As seen in Fig. 2, the strong acetate band found around  $1530\text{ cm}^{-1}$  in the spectrum of the protiated form (it belongs to the acetate  $\nu_6$  mode perturbed by interaction with the  $\delta(\text{HOH})$  vibration) is gradually shifted towards higher frequencies, "returning" to its normal position as the deuterium content in the samples is increased and the interaction is destroyed because of the shift of the water bending vibration towards lower frequencies.

The situation is, in all respects, similar with cobalt acetate tetrahydrate, except that the interaction of the vibrations with frequencies above  $900\text{ cm}^{-1}$  seems to be less complete, probably because of the lower water li-

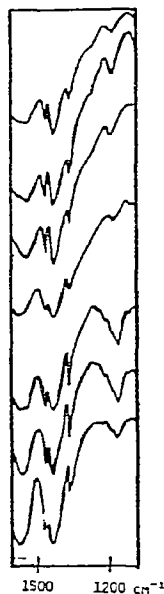


Fig. 2. Changes, on deuteration, in the acetate  $\nu_6$  region.

brational frequencies. It has, namely, been shown [8] that in series of isomorphous compounds the water librational frequencies decrease, on changing the metal to which water is coordinated, in the order Ni, Co, Fe, Mn, i.e. following the order of the increase in the ionic radii of the metal ions.

We have observed coupling between carboxylate vibrations and water librations also in the case of cobalt acetate dihydrate (the spectra of which are discussed in an accompanying paper), of strontium formate dihydrate [2] and, as already discussed, in the series of isomorphous metal formate dihydrates (for two members of this series the same findings were reported by Tewary *et al.* [3,4], as mentioned earlier).

There is, of course, no reason to believe that interactions of the described type would be limited to carboxylates only, so that care should be taken in interpreting the vibrational spectra of crystallohydrates in general, especially in situations when vibrations of the anion are expected to appear in the same region(s) as the H<sub>2</sub>O librations or some other water vibrational mode (e.g. HOH bending).

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