2.1 **Infrared Spectrophotometer**

For IR spectra recording Perkin-Elmer model 521 double beam grating spectrophotometer (1) was used. The optical diagram of the instrument is shown in Fig. 2.1. The instrument works on the principle of optical null method. Nernst glower is used as the source providing infrared radiations and the detector is a high speed sensitive thermocouple fitted with a blackened gold leaf strip (2 x 0.2 mm) and CsBr lens. The spectrophotometer records spectra in the frequency range 4000 - 250 cm\(^{-1}\) or 2.5 - 40 \(\mu\) and employs two gratings \(G_1\) and \(G_2\) faced back to back. The first grating has 100 lines per mm and is used in its first and second orders. In the first order it scans in the region 630 - 2000 cm\(^{-1}\) and in the second order in the region 2000 - 4000 cm\(^{-1}\). For the remaining region i.e. from 250 - 630 cm\(^{-1}\), the second grating having 25 lines/mm becomes operative in its first order. Seven automatically adjustable interferential filters operating in different frequency ranges are provided which stop radiations coming from unwanted diffraction orders. The slit-width is coupled with the frequency counter in order to so change that the intensity of the incident radiations remains constant for all frequencies. For a satisfactory and convenient operation of the instrument several adjustable knobs are provided. Thus the scan time can be adjusted anywhere from 2 min to 64 min. A switch is also provided to
control the gain which governs the relative resolution. The resolution of the instrument is 0.3 cm$^{-1}$ at 1000 cm$^{-1}$, with an accuracy of ±0.5 cm$^{-1}$ and a reproducibility 0.25 cm$^{-1}$.

Before recording actual spectrum, the pen position at 100% and 0% transmittance must be checked by fully cutting the reference and the sample beams respectively. The same can be set with the help of the adjustable knobs provided. Further, calibrating the instrument for knowing correct band positions is very important. First the recording pen must fully match with the calibrated markings on the chart paper; for this marker lines must be placed by chopping off the beams at regular frequency intervals throughout the recording range. For calibrating the instrumental frequency scale, some reported standard sharp peak positions have to be compared against those recorded by the instrument. We used the reported sharp peaks of polystyrene (solid) and indene (liquid). The spectra of the first were recorded as a thin film provided by the Perkin–Elmer corporation and, those of the latter were recorded by placing its few drops between two CsBr plates to make out a film.

2.2 Sampling Techniques in Solids:

The biggest difficulty encountered in the recording of the spectra of inorganic compounds is due to high absorptivity of these. To record the transmission spectrum of a crystal (single or poly-) it needs to be made to a thickness of the order of a micron. Hence single crystals are usually studied by reflectance techniques.
To record the transmission spectra of a polycrystalline solid (3,4) the substance is dispersed in an appropriate medium with an appropriate concentration. To avoid scattering losses* the particle sizes of the sample must be extremely small - smaller than a wavelength of radiation. The other considerations are:

(1) the dispersing medium must be transparent in the region of study and (2) the refractive indices of the dispersed and the dispersing media must be matching. On these lines the two techniques in use for dispersing are: (i) suspensions (or mulls) and (ii) pellets or discs. Another method is to make a thin film of the sample having extremely fine particle sizes on some IR transparent plate. In the following we briefly describe these techniques. The various spurious effects in the spectra which could arise are dealt with in detail in a separate section 2.7 (i).

In the suspension (mull) technique, a good paste of a finely powdered sample is made in a mulling agent (liquid) - generally some non-interacting organic chemical which may have its own bands at well known standard positions. The three in general use are: (a) nujol (liquid paraffin), (b) fluorolube (perfluoro kerosene), and (c) hexachlorobutadiene. Of these nujol which has the least number of peaks in the IR region (strong absorption around 3000 cm\(^{-1}\), three weaker bands at \(-1450\) cm\(^{-1}\) and

* Rayleigh scattering is mainly operative in the infrared region. If the particle sizes are comparable to the wavelengths in the region, the scattering losses increase as we go towards low wavelength (high frequency) region, leading to a general loss in the spectral resolution as also a tilt in the base line.
and a very weak band at 720 cm\(^{-1}\), is the most commonly employed. The paste is placed in between two plates (windows) of some IR transparent substance, and pressed to spread to a fine film. The windows are then placed before the sample beam of the instrument for final recording.

As regards the windows the considerations are that the material should be transparent and should not react with the sample to be studied; also the refractive index should be low which otherwise would lead to reflection losses. Some of the window materials in common use are NaCl (>600 cm\(^{-1}\)), KBr (>400 cm\(^{-1}\)), CsBr (<200 cm\(^{-1}\)), CsI (>200 cm\(^{-1}\)). KRS-5 is a compound material (ThBr 57% + ThI 43%) and despite its high refractive index is widely used, because of its non-hygroscopic and less reactive nature.

In the pellet or disc technique the sample is mixed with some non-interacting solid (like KBr, KCl, CsCl) in a proper proportion (say 1:20 to 1:100) and ground to very fine particle size. This mixture is then finely dispersed in a pellet making die and pressed to a high pressure. We used the evacuable die provided by Perkin-Elmer corporation. The pressure was applied by a hydraulic decimal press DP 36 provided by Carl Zeiss Jena. This press reads pressure in the units 'Kp/cm\(^2\)' which is equivalent to 'atm gauge'.

In the thin film technique a suspension is made of finely ground sample powder in some highly volatile non-interacting liquid like CCl\(_4\) or CHCl\(_3\). A drop of this suspension is put on some appropriate window and a plane glass plate is slid back and forth on it while gently pressing at the same
time. This is done until all the CCl₄/CHCl₃ evaporates out leaving a fine thin film of the sample. In some cases an aqueous solution may also be used to produce a thin film.

As regards the relative merits of the three techniques, thin film should give spectra without any interference from any other source. However, preparing a thin film is not always easy and the involved scattering losses are generally high. More particularly in the case of those hydrates where the state of hydration is a sharp function of temperature, thin film preparation would require highly controlled conditions and instrumental precision. Making pellets is easier than making thin films, but here various other factors may be operative like ion exchange, Christiansen effect, stress relaxation etc. The mull technique has the drawback of introducing some foreign bands. But if these do not overlap with the region of interest, there is no difficulty. The method gives fairly neat spectra for inorganic compounds with the minimum of scattering and other effects.

2.3 **Low Temperature Cell**

For spectra recording at low temperatures a slightly modified version of a conventional Wagner Horn type cell (5) was used (Fig. 2.2). Windows with nujol mull, or KBr pellets could be placed in the cold finger block. The cell was connected to a vacuum system (Fig. 2.3). Liquid nitrogen was used as the agent to cool the metallic rod and the sample attained a low temperature by conduction through the cold finger. The temperature at the cold finger was measured using a copper-constantan thermocouple. The accuracy of the temperature reading may be
placed to $\pm 5K$. But the sample temperature (the mull, pellet or thin film) could be higher than that of the cold finger by as much as 15K due to continuous heating by the absorbed infra-red radiations.

2.4 Crystallization and Preparation of Different Hydrates:

The hydrates with different degrees of hydration were prepared by the method of recrystallization from the aqueous solutions at appropriate temperatures. The starting material in every case was either Analar grade or 'Guaranteed reagent' grade chemical. For compounds soluble in water the smooth running solubility-temperature (S-t) curves show an abrupt change in curvature at temperatures where states of hydration change. Thus experimental S-t plots have also been used to determine and characterize the various stages of hydration. The reported curves for the various salts under study were taken from literature and the aqueous solution was maintained at a temperature above or below the transition temperature according to the hydrate desired.

The saturated solution was made in distilled water and its temperature was maintained by putting it in a water bath. The temperature could be controlled to $\pm 2^\circ C$. In cases where the hydrates were stable at room temperature, the solution was just left in the open atmosphere. In every case the solution was appropriately covered to control the rate of evaporation.

From the crystallised material some crystals were taken out for spectral work. These were dried at the proper temperature in an oven where the temperature could be maintained from RT to 250$^\circ C$ with an accuracy of $\pm 5^\circ C$. The hydrates thus prepared and dried were sealed in sample tubes to ensure that
the samples did not absorb atmospheric water; these tubes were opened only in a relatively dry atmosphere provided by a heater placed around where samples were prepared finally for spectral recording. In every case, the crystals were prepared independently several times to check the reproducibility of their spectra.

2.5 Deuteration of the Samples:

For preparing the deuterated analogs of the studied hydrates, the principle of vacuum distillation was used. The vacuum system used for this purpose is shown in Fig 2.3. A rotatory oil vacuum pump provided by Cencos Instruments Corp. U.S.A. was used which provided a vacuum of the order of \(10^{-4}\) mm of Hg. The oil (Stillex) diffusion pump (not shown in figure) provided with the vacuum system could further carry the vacuum level to \(10^{-5}\) mm of Hg.

The salt to be deuterated was first thermally dehydrated in an oven but only to an extent so that unwanted processes like oxidation or hydrolysis did not occur. Thus while in case of \(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}\), dehydration was carried up to the anhydrous stage \((\text{CuSO}_4)\) by heating the pentahydrate at \(-170^\circ\text{C}\), in the case of \(\text{CoCl}_2 \cdot 6\text{H}_2\text{O}\) dehydration was carried only to the dihydrate stage.

Amongst the three flasks—in one was taken pure \(\text{D}_2\text{O}\), in the other the dehydrated salt and the third was attached empty. The whole system was evacuated by freezing \(\text{D}_2\text{O}\) using liquid \(\text{N}_2\). The vacuum pump was now disconnected from the system and under low pressure \(\text{D}_2\text{O}\) was transferred to sample flask to make the solution in \(\text{D}_2\text{O}\) at an appropriate temperature maintained by dipping the flask in a oil bath. In the third
stage D₂O from the aqueous solution was transferred to the empty flask. The sample would now contain the H and D contents in a proportion depending on the H₂O : D₂O proportion in the solution (cf. Sec. 1.54 (ii), Chapter I). Every time the process is repeated the deuteration content percentage increases geometrically. This point has to be paid attention. A much higher deuteration level will be achieved if a particular bulk of D₂O is used in steps than if used in one single cycle. The process of dissolution in D₂O and evaporation was repeated therefore several times to attain increasing deuteration level. The trap was kept invariably dipped in liquid N₂. This is very important to ensure that no water vapor goes into the pump oil lest it should be spoiled.

To take the dry deuterated sample out, a little precaution has to be taken while evacuating the sample flask. The atmospheric air to be circulated should be gently passed and kept for some time in contact with the liquid N₂ trap in order to make the air dry. Only then it should be allowed to enter in. This is a necessary step to ensure that the deuteration level does not decrease due to moisture in the atmospheric air.

The practical method for determining the deuteration content percentage is the spectroscopic one and involves a comparison of the intensities of the internal mode fundamental bands of the different species of water. (cf. sec. 1.54 (ii), Chapter I).

2.6 Resolving the Overlapping Bands:

In case of solids, a Lorentzian shape is found to be justified for IR band contours (cf. sec. 1.4). The observed
spectra were subjected to Lorentzian analysis in order to gain information about the half-width and the intensity parameters. The Lorentzian function is expressed in Eqn. 1.7 and the intensity and half-width parameters are illustrated in Fig. 1.8 (Chapter I).

While in the case of isolated bands the two parameters are directly determinable, in the case of convoluted envelopes only an analysis would resolve the component bands and give the parameters for each separately. The criterion used in such cases was to try for a minimum number of components warranted by the observed contour. The peak positions were maintained quite close to the observed ones. Extra bands were introduced when and only when there were definite evidences from other spectral criteria as well as from repeated Lorentzian trials. Although the analysis is not always unique, several trials were made to obtain the best fit in each case.

Choosing a proper baseline for the spectrum to be resolved is a thing of crucial importance (6). In Fig. 2.4 is shown a typical water stretching envelope in MCl₂.2H₂O (M = transition metal) in nujol to demonstrate the choice of the proper baseline. Some considerations are as noted here (1). The baseline should not be just tangential to the spectral envelopes because whatsoever the correct band shape, the absorption at tails will always go to zero only asymptotically. A margin should therefore be left to accommodate for the combined absorption at tails due to all the components involved. Thus in Fig. 2.4 taking (A) as the baseline is to be avoided. (2) If a particular absorption region is to be excluded from analysis,
it is improper to take the baseline ignoring that absorption. But the better thing will be to take that absorption into account during the analysis and analyse it out; if the unwanted absorption has a fairly sharp band even a free hand sketch to account for it will serve the purpose. Thus in Fig. 2.4 ignoring the nujol absorption N and taking (B) as the baseline is improper. One must take 'C' as baseline, carry the analysis including the nujol absorption and then leave out the nujol band. (3) Higher scattering on high frequency side may tilt the base line, from higher toward lower absorption side in passing from high to low frequency region. But selecting a baseline tilted in the opposite sense is to be avoided. This will at once rule out 'B' as a proper baseline in Fig. 2.4.

Now taking the baseline as the zero absorption level the spectral profile is replotted on a linear absorption scale (the absorbance scale on the chart paper is logarithmic). The plots were made with absorption increasing in the positive ordinate direction and thus the spectral profiles would look peak to base inverted. Analysis is now made starting with the more obvious components, affixing some \( I_0 \) and \( 2bc \) parameters to them, obtaining the residues, proceeding to more bands, and so on. The assigned \( I_0 \) and \( 2bc \) may have to be altered several times to get the best fit, and in some cases the baseline may have to be shifted up or down on the absorption scale to get a good fit.

A comment is needed about the reproducibility and accuracy of the derived parameters. Regarding the frequencies (i) in case of sharp peaks the positions were not shifted in the analysis from the observed ones so that the accuracy is \( \pm 1 \text{ cm}^{-1} \), (ii) for broad but distinct bands an uncertainty up to \( \pm 5 \text{ cm}^{-1} \)
is involved, and (iii) in case of shoulders, bulges and bands with weak evidence the inaccuracy may be as large as say \( \pm 10 \text{ cm}^{-1} \).

The level of uncertainty in \( I_0 \) and \( \Delta \nu \) depends on the number of components involved, the extent of overlapping, the relative intensities of the components and their half-widths. The broader and weaker the band with several components overlapping with it, the larger will be the uncertainty level. It may be only 5\% to 10\% in case of envelopes with weak overlapping (stretching mode and envelope of water in \( \text{MCl}_2 \cdot 2\text{H}_2\text{O}, \) Chapter IV) to say 20\% to 40\% in case of envelopes with strong overlapping (bands \(<1200 \text{ cm}^{-1} \) in \( \text{BeSO}_4 \cdot 4\text{H}_2\text{O}, \) Chapter V).

The integrated intensity \((I_t)\) of a band is given by

\[
I_t = 2I_0 \int_{-\infty}^{\infty} \frac{b_0^2}{b_0^2 + x^2} \, dx = \frac{\pi}{2} (I_0) (2b_0) = \frac{\pi}{2} (I_0 \Delta \nu) \]

Now since we are interested in comparing the relative integrated intensities of various bands, the constant \( \pi/2 \) can be removed from calculations. The relative integrated intensities in each case were thus computed as the product \( I_0 \times \Delta \nu \). These figures were then normalized to 100 for the most stable or the strongest component in a particular set.

2.7 Influence of Various Spurious Effects on Recording the IR Spectra of Hydrates:

2.7.1 General: In section 2.2 while discussing the sampling techniques in solids we made some mention of the spurious effects that may arise with different techniques. From time to time attention has been drawn by various
workers towards these (7,11). Duyckaerts (12) in an extensive review dealt with the spurious effects encountered in the mull and the pellet techniques. Lima and Piedade (13) also emphasized the care needed in the pellet preparation for IR studies.

(i) Physical Factors: The various physical factors that may influence the spectra are: polymorphism, orientation effects, dimension of the individual absorbing particles, and the difference between the refractive indices of the absorbing substance and the dispersing medium (nujol, KBr etc.). Of these the last two are more frequently encountered and in hydrates only these are of significance.

The particle size influences the spectra in two ways. Firstly for large particle sizes the apparent intensities of different components in the spectra may appear to be all similar irrespective of their absolute intensity ratios. Such is the case for calcite as illustrated by Duyckaerts (12). Further for larger particles the radiation losses due to scattering are high. It has been shown that a limiting absorption for strong bands may be obtained for particles of a diameter 'below' 0.1μ. Achieving such fine particle size is difficult and hence means have to be devised to yield such small particle sizes as giving reproducible spectra.

As regards the effect of the refractive index (13) the better the matching between values for the absorbing and the dispersing medium the more dependable are the peak positions and the band-widths. If the ratio of the μ values is high, anomalous dispersion near the absorption band will
cause the shape of the band to become asymmetric and the peak position may get apparently shifted. This effect is the well known Christiansen Effect (14).

Chemical Factors: The possible chemical factors influencing the spectra are:

1. Absorption of the substance on the particles of the dispersing medium,
2. Polymorphism,
3. Chemical reaction between the absorbing substance and other medium like KBr in pellet technique and window in mull technique,
4. Mixed crystal formation and formation of complexes,
5. Distortion of the crystalline structure.

The first two are of relevance mainly in the context of organic samples. In hydrates while the third one may influence in all the three recording techniques, the last two are of especial significance in the pellet technique where pressures are needed for the pellet formation.

Apart from the physical and chemical factors listed above, another difficulty of particular significance in the hydrates arises due to the possibility of a change in the stage of hydration either in contact with the window material in nujol and thin film techniques or under pressure in contact with the dispersing solid in the pellet technique. For this reason the salts studied in the present work were studied using different techniques to check on the reproducibility of the spectra. This is separately discussed for each of the studied salts in the related chapters.

In particular the changes observed in the spectra of CoCl₂·2H₂O and MnCl₂·2H₂O using nujol mull (CsBr window).
and KBr pellet techniques, were critically analyzed and in each case reasons were attributed to the observed changes.

2.72 Changes Observed in the Spectra of CoCl$_2$·2H$_2$O and MnCl$_2$·2H$_2$O using Nujol Mull and KBr Pellet Techniques*

Experimental: Preparation of these hydrates and the corresponding deuterates is discussed in section 4.2, Chapter IV. The spectra were recorded at room temperature in Perkin-Elmer 521 spectrophotometer.

(i) Spectra in nujol mull:

Results: Intimate nujol mulls were prepared grinding with an agate mortar and pestle. To check their time behaviour the spectra using different window materials were recorded at different intervals after placing the mull on the windows. The windows with the mull pressed between them were left in the sample compartment of the instrument, or in open atmosphere or inside a dessicator. Windows of CsBr, AgCl and KRS-5 were used. In case of CoCl$_2$·2H$_2$O, the spectra showed changes with CsBr only and the MnCl$_2$·2H$_2$O spectra did not change with any of the three windows.

The spectrum of CoCl$_2$·2H$_2$O as nujol mull with CsBr windows taken within first 45 minutes is reproducible and is called the 'instant spectrum' hereafter. But with further passage of time the spectrum shows some characteristic changes. These in the different regions

of interest are depicted in Fig. 2.5. There is a general
loss in the structure throughout. In particular the
stretching envelope becomes progressively weaker and
shows a shift of \( \approx 40 \) cm\(^{-1} \) towards higher frequency side.
It is also worth noting that the \( 2v_2 \) band distinctly
in the present instant spectrum almost vanishes with the
passage of time. The bending mode band also shows a shift
towards high frequency side. Its position at 1597 cm\(^{-1} \)
in the 'instant spectrum' shifts to \( \approx 1630 \) cm\(^{-1} \). This
band also shows an increase in half-width by over two-
fold. In the librational mode region (300-700 cm\(^{-1} \))
the wagging and the rocking mode bands show a differential behaviour. While the wagging mode at 360 cm\(^{-1} \)
weakens out much faster and vanishes completely, the
rocking mode at 620 cm\(^{-1} \) shows a slow and small fall in
intensity and only flattens out instead of vanishing
altogether. It is also observed that the colour of the
sample changes from violet to one with a greenish tinge.

The spectrum of the corresponding deuteratedeuterate
shows identical changes in all the regions. The corres-
ponding spectra for the \( \nu_2 \) band only are shown in
Fig. 2.6 as a representing case.

The data for the bending mode of water in the
two isotopic analogues are included in Table 2.1. In
column 1 are noted the time intervals after placing the
mulls on the windows. Columns 2, 3 and 4 give the
position, half-width and the peak absorbance respectively
for the \( \nu_2 \) band in CoCl\(_2\).2H\(_2\)O. The corresponding
Quantities for the $v_2$ band in $\text{CoCl}_2 \cdot 2\text{D}_2\text{O}$ are listed in columns 5 to 7. Table 2.2 gives the data for the bands in the librational mode region of water in $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ only. Here we do not give the data for the deuterated analogues. Again column 1 gives the time intervals after placing the mull on the windows. Columns 2 to 4 give the band position, half-width and the peak absorbance for the rocking mode and the same are given in columns 5 to 7 and 8 to 10 for the wagging mode band and the new appearing band (at $-310 \text{ cm}^{-1}$) respectively.

**Discussion**: The observed behaviour could arise either due to an ion exchange or due to dehydration of the sample in contact with the CsBr windows since these are known to be of a hygroscopic nature. To check over the first of these a spectrum of $\text{CoBr}_2 \cdot 2\text{H}_2\text{O}$ was recorded using the same technique with the CsBr windows. This spectrum also showed progressive changes with the ageing of the mull but neither did its instant spectrum match with the instant spectrum of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ nor did the delayed spectra match in the two cases. Also in the case of $\text{CoBr}_2 \cdot 2\text{H}_2\text{O}$ no band was observed near $310 \text{ cm}^{-1}$. On these grounds ion exchange was ruled out to be operative in the present case.

Dehydration is the second plausible effect. We note that the anhydrous $\text{CoCl}_2$ is known to be of blue colour while the violet coloured dihydrate changes to greenish. Further the $v_2$ band in free water falls at $1595 \text{ cm}^{-1}$ while with the passage of time this band has
shifted to \(-1630\) cm\(^{-1}\). It is plausible to assume that in the dehydrating environment of the CsBr windows an unstable monohydrate is formed. Further the progressive weakening of all the bands would show that with time the salt slowly converts to anhydrous state or some other complex.

The differential behaviour of the wagging and the rocking bands needs some further comments. With dehydration one would expect both of them to weaken together but quite interestingly while the one due to wagging mode disappears, that due to rocking mode still persists though with a lower intensity. It may be inferred that the potential well for the wagging is considerably shallower than for rocking. Thus in the dehydrating environment, while the wagging may tend towards free rotation, the rocking may still be hindered though near the top of the well so that it flattens out and becomes broader.

About the new sharp band at \(310\) cm\(^{-1}\), it is difficult to give it any assignment in the unstable monohydrate. In fact its intensity increases progressively with the weakening of the \(\nu_2\) band and attains a maximum when that of \(\nu_2\) band touches the minimum. It may also not be attributed to Co-Cl stretching in the anhydrous compound where it is reported to occur at 272 and 210 cm\(^{-1}\). However we note that metal-oxygen stretching falls generally at \(~300\) cm\(^{-1}\), typically the one at \(308\) cm\(^{-1}\) in Co(NO\(_3\))\(_2\). This would imply the plausibility of the formation of an oxy-complex in the present case to which the new band could belong.
Further when AgCl and KRS-5 windows were used, no changes were observed even after some 24 hour contact of the mull with the windows. As regards the band positions and their relative integrated intensities, these spectra were identical with the instant spectrum taken with CsBr windows. However due to high refractive indices (1.8) of KRS-5 and AgCl the bands in general were a little broader.

The stability of the spectrum of MnCl₂·2H₂O even with CsBr windows needs an explanation. The direct implication would be that water in this hydrate is more tightly bound in the lattice than in CoCl₂·2H₂O so that neither a monohydrate nor an oxy-complex is formed. To have an idea of the same, one could compare the temperature for the transition dihydrate \( \rightarrow \) anhydrous in the two cases. For CoCl₂·2H₂O this is known to be 135-140°C and for MnCl₂·2H₂O it is 170°C. These would favour a stronger binding for water molecules in MnCl₂·2H₂O.

(ii) Spectra in KBr Pellets:

Results: Spectra as KBr pellets of both the hydrates (CoCl₂·2H₂O and MnCl₂·2H₂O) were recorded for pellets made under different pressures and after allowing them different times. In all the cases a mixture of the salt with KBr was ground in a ball-mill vibrater for ~2 minutes and transparent good pellets were made by keeping the mixture under pressures varying from 60 to 100 Kp/cm²* for 3 to 4 minutes. While the spectra showed changes with

\[ *1Kp/cm^2 = 1 \text{ atm.} \]
pellet life and pressure, grinding time did not make any difference.

In Fig. 2.7 we have compared in the $\nu_2$ mode region the KBr pellet spectra of MnCl$_2$.2H$_2$O with its nujol null (CsBr) spectra. These for CoCl$_2$.2H$_2$O are not shown. In the stretching mode and the librational mode region of water in both the salts there are no noticeable changes except a general loss of structure in the pellet spectrum due to broadening of all the bands. In the bending mode ($\nu_2$) region apart from a broadening of the band, there is a shift to higher frequency side in both the salts. In the high pressure pellets ($\geq$100 Kp/cm$^2$) the shift is observed on the instant recording, being $\approx$ 20 cm$^{-1}$ for CoCl$_2$.2H$_2$O and $\approx$10 cm$^{-1}$ for MnCl$_2$.2H$_2$O. In the low pressure pellet ($\leq$60 Kp/cm$^2$) no position shift is observed on instant recording but when these were stored in a dessicator or left in the open atmosphere for several hours shifts in $\nu_2$ band positions were observed, being of the same order as in case of high pressure pellets on their instant recording (Fig. 2.7).

**Discussion:** The $\nu_2$ band position in KBr pellets formed at higher pressures and the changes in the low pressure pellets with ageing could arise because of any of the following reasons: dehydration, distortion of crystalline structure, ion exchange, and formation of mixed crystals.

Now, it will be noted from Fig. 2.7 that there is no weakening of bands with ageing of the pellet and
also there is no noticeable change in the stretching mode and librational mode bands. This excludes dehydration. Further if the structure were distorted under pressure, time delay would permit relaxation and consequent restoration of the spectrum. Contrary to this in the present case the low pressure pellet shows a drift in the spectrum with ageing. That rules out distortion under high pressure as the origin for the observed changes. To check over ion exchange the nujol mull spectra of the corresponding bromides (CoBr$_2$·2H$_2$O and MnBr$_2$·2H$_2$O) were recorded. They did not show any identity with the KBr pellet spectra of their chloride counterparts. Thus ion exchange is also ruled out. Mixed crystal formation, therefore, appears to be the origin for the spurious effect in the present case. It is also worth noting that KBr is more hygroscopic than CsBr. Hence the absence of dehydration in the present case of KBr pellets, in contrast with the observations using nujol mulls with CsBr windows, could only be explained if there be a competing process like mixed crystal formation.

(iii) Conclusion: From the above discussion it is concluded that apart from the spurious effects due to various known physical and chemical factors, in the hydrates one has to be cautious about the dehydration also. To arrive at reproducible spectra, the spectra must be repeated with different techniques particularly if the window material or the dispersing solid is of a hygroscopic nature. Under such circumstances it is advisable to make a compromise and non-hygroscopic window material must be used, though it may have a higher refractive index, like KRS-5.
REFERENCES


12. G. Duyckaerts, Analyst. 84, 201 (1959).


Table 2.1: Positions, half-widths and the peak absorbance of the $\nu_2$ band of water in the IR spectra of CoCl$_2$.2H$_2$O and CoCl$_2$.2D$_2$O recorded at room temperature (300 K) in nujol mull over CsBr windows with the passage of time.

<table>
<thead>
<tr>
<th>Time</th>
<th>CoCl$_2$.2H$_2$O</th>
<th></th>
<th></th>
<th>CoCl$_2$.2D$_2$O</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\nu$</td>
<td>$\Delta\nu_{1/2}$</td>
<td>$I_m$</td>
<td>$\nu$</td>
<td>$\Delta\nu_{1/2}$</td>
<td>$I_m$</td>
</tr>
<tr>
<td>a</td>
<td>1597</td>
<td>30</td>
<td>1.00</td>
<td>1183</td>
<td>20</td>
<td>1.00</td>
</tr>
<tr>
<td>b</td>
<td>1625</td>
<td>80</td>
<td>0.34</td>
<td>1183</td>
<td>50</td>
<td>0.80</td>
</tr>
<tr>
<td>c</td>
<td>1630</td>
<td>80</td>
<td>0.24</td>
<td>1205</td>
<td>50</td>
<td>0.44</td>
</tr>
</tbody>
</table>

$v'$: peak position (cm$^{-1}$); full width at half the maximum intensity (cm$^{-1}$); $I_m$: peak absorbance; a, b, c refer to spectra taken at 0 hr, 2 hr, and 4 hr respectively after the mull is placed on CsBr windows. $I_m$ values for all bands are on a relative scale normalised to 1.00 for spectrum 'a'.

Table 2.3: Time variations in the bands of water in its librational mode region in CoCl₂.2H₂O in nujol mull over CsBr windows at room temperature.

<table>
<thead>
<tr>
<th>Time</th>
<th>Rocking</th>
<th>Wagging</th>
<th>Co-0 Stretch?</th>
</tr>
</thead>
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<tr>
<td></td>
<td>ν</td>
<td>Δν₁/₂</td>
<td>Iₘ</td>
</tr>
<tr>
<td>1</td>
<td>520</td>
<td>80</td>
<td>0.27</td>
</tr>
<tr>
<td>a</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>625</td>
<td>~80</td>
<td>0.19</td>
</tr>
<tr>
<td>c</td>
<td>?</td>
<td>vd</td>
<td>?</td>
</tr>
</tbody>
</table>

ν: peak position (cm⁻¹); Δν₁/₂: full-width at half the maximum intensity (cm⁻¹); Iₘ: peak absorbance. a, b, c refer to spectra taken at 0 hr, 2 hr, and 4 hr respectively after placing the mull on the windows. Iₘ values are on a relative scale normalized to 1.00 for the ν₂ mode band (Table 2.1) in spectrum 'a'.
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Glower (Source); Mirrors (M₁, M₂, M₃, M₄, M₅, M₆, M₇, M₈, M₉, M₁₀, M₁₁, M₁₂, M₁₃ and M₁₄); Entrance slit (S₁); Exit slit (S₂), Grating (G₁ and G₂).

Fig. 2.1
Fig. 2.2 Low temperature cell
Fig. 2.5: Vacuum system used for deuterating the samples and also with the low temperature cell. The oil diffusion pump is not shown.
Fig. 2.4: Illustration for choosing a proper base taking the case of a typical water stretching envelope in the IR spectra of $\text{MCl}_2 \cdot 2\text{H}_2\text{O}$ ($\text{M} =$ transition metal). Only 'C' is a proper base line.
Fig. 2.5: IR spectra (at room temperature) of CoCl₂·2H₂O recorded by nujol mull technique using CsBr windows. a, b, c refer to spectra recorded at 0 hr, 2 hr, and 4 hr respectively after placing the mull on the windows.
Fig. 2.6: IR absorption at room temperature, of CoCl₂·2D₂O in the bending mode region of D₂O, using nujol mull technique with CsBr windows. a, b, c refer to spectra recorded at 0 hr, 2 hr, 4 hr after placing the mull on the windows.

Fig. 2.7: Bending mode band of water in the room temperature IR spectrum of KBrCl₂·2H₂O. 'a' is instant spectrum in air low pressure pellet, 'b' is spectrum after 20 hr in the same KBr pellet, and 'c' is nujol mull spectrum over CsBr windows (for comparison).