CHAPTER VII

SUMMARY OF CONTRIBUTIONS OF THE PRESENT WORK TOWARDS USEFUL DATA AND INTERPRETATIONS.

7.1. Background of the Work

The hydrates of divalent transition metal sulfates \( MSO_4 \cdot xH_2O \) (\( M = Mn, Co, Ni, Zn \)) were chosen for comprehensive IR absorption studies to examine the variations in the librational modes of water. The monohydrates are isostructural; also the H-bond length happens to be the same in all the four monohydrates. Thus the changes must be attributed to changes in \( M \) and it should be possible to quantify such changes.

Earlier studies in IR on these salts existed only at room temperature and only up to \( 600 \text{ cm}^{-1} \). Deuteration studies for \( MnSO_4 \cdot H_2O \) were not available. No attempts had earlier been made to deduce half-widths and relative integrated intensities of the bands.

We also noted that although water librations are more sensitive to crystal field, one must not see its effect in isolation. Hence \( SO_4^{2-} \) modes needed a simultaneous study.

Earlier IR spectra of the anhydrous salts below \( 400 \text{ cm}^{-1} \) were not available, nor were half-widths and relative integrated intensities of the bands in the observed regions available.

Raman spectra of neither the hydrates nor the anhydrous salts of the series were available earlier.

* 400 in some cases
7.2 Contribution of the Present Work

(a) New data presented

1. The infrared spectra of the following salts have been extended from 400 cm$^{-1}$ to 250 cm$^{-1}$:

MSO$_4$ (M = Mn, Co, Ni, Zn), Room Temperature (RT)

MSO$_4$·H$_2$O (M=Mn,Co,Ni,Zn), RT spectra.

2. The infrared spectra of the following salts have been studied at low temperature (~120K, LT) for the first time in the region 4000-250 cm$^{-1}$.

MSO$_4$·H$_2$O (M = Mn, Co, Ni, Zn)

3. An analysis of the observed IR spectra in the region 400-250 cm$^{-1}$ to deduce the band half-widths $\Delta\nu/2$, and relative integrated intensities (RI) have been made for the first time:

MSO$_4$ (M = Mn, Co, Ni, Zn) - RT spectra only

MSO$_4$·H$_2$O (M=Mn,Co,Ni,Zn) - RT and LT spectra

MSO$_4$·4H$_2$O (M=Mn) - RT spectrum only

4. The following infrared spectra in the entire region 400-250 cm$^{-1}$ were studied in the present work for the first time:

MSO$_4$·D$_2$O (M=Mn) both RT and LT spectra

MSO$_4$·4H$_2$O (M=Mn) - RT spectrum only.

5. The following Raman Spectra in the region 1400-200cm$^{-1}$ are being presented for the first time

MSO$_4$ (M=Mn) - RT spectrum only

MSO$_4$·H$_2$O (M=Mn) - RT spectrum only

Of course, in the regions overlapping with earlier work the present studies led to a revision and improved data due particularly to the analysis, vide para 3 above.
In two particular situations a librational band completely overlapped with the sulfate \( \nu_4' \) bands—one in NiSO\(_4\)·H\(_2\)O were the wagging mode of water overlapped with \( \nu_4' \); the other in MnSO\(_4\)·D\(_2\)O were the rocking mode of D\(_2\)O overlapped with \( \nu_4' \).

These represent extreme cases of usefulness of the Lorentzian analysis we applied all through.

(b) Interpretation regarding Librational Modes of Water.

1. The assignments of the bands due to librations of water were placed on a firm footing, using frequency shifts on deuteration to distinguish between Rocking and Wagging modes. For the wagging mode the presence of two components was established on this basis. The twisting mode was also observed and assigned in case of MnSO\(_4\)·H\(_2\)O (§ 3.53).

2. Variations in the absorption band (re: intensity and frequency) on lowering of temperature have been interpreted by applying Boltzmann canonical distribution law and assuming the librational potential to be anharmonic. It explains why the effect is distinctly more in the wagging mode than in the rocking mode (§ 5.51).

3. Evidence for a possible phase change in MnSO\(_4\)·H\(_2\)O at ~ -100°C has been obtained by the study of variation of librational modes with lowering of temperature (§ 3.53).

4. The following correlation curves have been tried: (i) between \( \nu_R \) and \( \nu_W \), (ii) between \( \nu_R \) or \( \nu_W \) and \( \nu(H-O_w \) stretch), and (iii) between \( \nu_R \) or \( \nu_W \) and M-O\(_W\) distance. The following conclusions have been drawn (§5.4):

   (a) With change of M, the fields governing R and W modes change together almost in the same proportion.

   (b) M-O\(_W\) coordination is the primary factor governing both R and W modes of water in these monohydrates.
(c) In quantifying the influence of $\text{M-O}_w$ coordination we find
that the $\gamma'_w$ versus $r(\text{M-O}_w)$ graph is a straight line:

$$\gamma'_w = 1460 - r(\text{M-O}_w) \times 410 \text{ cm}^{-1}.$$ where $r$ is in Å.

5. The internal mode frequency $\gamma'_2$ of water in these hydrates
is near the lowest among all hydrates, implying dominance
of $\text{M-O}_w$ coordination. We find a smooth correlation of $\gamma'_2$
with $\text{M-O}_w$ distance, so that one can quantify the effect.

(§ 5.22a).

6. It has been shown that the changes in librations of water
cannot be treated in isolation from the changes in $\text{SO}_4^{2-}$
internal modes as we change M. For both these we find Mn
and Ni at the extreme ends, with Co and Zn sitting close
together in the middle. (Chapter VI).

(c) Assignments and Interpretation of Internal modes of $\text{SO}_4^{2-}$
in $\text{MSO}_4$ and $\text{MnSO}_4\cdot\text{H}_2\text{O}$ ($\text{M} = \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}$).

1. Whereas earlier workers had only grouped together all bands
in the region 1250-1050 cm$^{-1}$ under $\gamma'_3$ of $\text{SO}_4^{2-}$
we have isolated three components in each case to assign them to $\gamma'_3$, $\gamma''_3$, $\gamma''''_3$, and the rest have been separately assigned to
combinations.

2. Whereas earlier workers only listed together the bands in
$\gamma'_4$ region of $\text{SO}_4^{2-}$, we specifically examined whether all
three site split components appear or only two of them
appear, with correlation splitting in one or both site
components. Though final conclusions would need polariza-
tion studies, some initial guidelines have been laid
down. The Raman Spectra of MnSO$_4$ and MnSO$_4\cdot$H$_2$O were par-
cularly helpful in this.
3. In understanding the strength and asymmetry of the crystal field around \( \text{SO}_4^{2-} \), quantities shift parameter \( F_1 \) and splitting parameters \( G_1 \) have been introduced, and evaluated for MnSO\(_4\)·H\(_2\)O for all the internal modes of \( \text{SO}_4^{2-} \) in ir as well as Raman. The same have been discussed also for the ir spectra of Co, Ni and Zn salts.

7.3 Suggestions for Further Work

(a) Through partial deuteration spectra for the monohydrates one must get a closer view at the water stretching modes. Since H-bonding, as measured by H-bond lengths, is equal in these salts, one can isolate the effect of M-O\(_w\) coordination on the stretching bond of water.

(b) Through Raman Spectra of the Co, Ni, Zn salts (both anhydrous and monohydrates) one could see if more light can be thrown on the components of \( \gamma_4 \) mode of \( \text{SO}_4^{2-} \). Then combining the effects of A\(\rightarrow\)MH for the shifts of \( \gamma_1^1 \) and \( \gamma_4 \) and on the split of \( \gamma_4 \) modes in the salts with different M one can get a fuller view of variations of the field around \( \text{SO}_4^{2-} \) ion. Work with single crystals will be needed.

(c) One must then consider a model in which the interdependence of all the fields are taken into account to give the total picture of librations of water. Since oxygens of \( \text{SO}_4^{2-} \) enter in the H-bonds as also in the coordination around M, as does H\(_2\)O, the field around \( \text{SO}_4^{2-} \) cannot be unrelated with the librations of water.
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