NUCLEAR MAGNETIC RESONANCE IN PARAMAGNETICS

Thesis Submitted for the Degree of Doctor of Philosophy (Science) of the University of Calcutta

By
MANORANJAN BHATTACHARYYA, M. Sc.
SAHA INSTITUTE OF NUCLEAR PHYSICS CALCUTTA - 9.
CHAPTER 2 : MAGNETIC HYPERFINE INTERACTIONS

2.1 Hyperfine Interaction Hamiltonian

2.1.1 Hyperfine Field and Hyperfine Coupling Constant

2.1.2 Isotropic and Anisotropic Parts of Hyperfine Coupling

2.1.3 Transition Probability for Nuclear and Electronic Spins on the same Atom

2.2 Nuclear Hamiltonian

2.2.1 Hyperfine Coupling Constant A

2.2.2 Isotropic A

2.2.3 Anisotropic A

2.3 Fractions of Unpaired Spins

2.4 Isotropic Shifts

2.4.1 Contact Shift

2.4.2 Pseudo Contact Shift

2.4.2.1 Isotropic Shift in Solid

2.4.2.2 Isotropic Shift in Solution

References

---

CHAPTER 3 : EXPERIMENTAL DETAILS

3.1 Spectrometer and Magnet Assembly

3.2 Calibration Procedure
3.2.1 Field Modulation .. 55
3.2.2 Frequency Modulation .. 56
3.2.3 Calibration in the Case of Weak Signals .. 56
3.3 Shift Measurement .. 57
3.4 Temperature Variation Work .. 58
3.4.1 Difficulties Encountered in Temperature Variation Work .. 59
3.4.2 Modifications .. 59

CHAPTER 4 : INTERACTION OF PHOSPHATE LIGAND WITH TRANSITION METAL ION 61
4.1 Introduction .. 62
4.2 Effect of Paramagnetic Ion on the Relaxation Process in Solution .. 63
4.3 Temperature Effect on Relaxation .. 66
4.3.1 Effect of Chemical Exchange on NMR .. 67
4.3.2 Modified Bloch Equation for the Temperature Effect .. 68
4.4 31P NMR Studies in Solutions of Phosphoric Acid Containing Paramagnetic Ions .. 71
4.4.1 Experimental Considerations .. 73
4.4.2 Methods of Analysis .. 73
4.4.3 Results and Discussion .. 76
References .. 82
CHAPTER 5 : STUDIES ON RPO₄ SYSTEM : PHYSICAL AND CHEMICAL INVESTIGATIONS

5.1 Introduction ........................................ 86
5.2 Atomic and Ionic Properties ...................... 87
  5.2.1 Crystal Structure of Rare-Earth Compounds .... 92
  5.2.2 Crystal Structure of RPO₄ ....................... 93
5.3 Present Structural Investigation on RPO₄ ......... 96
  5.3.1 Preparation of Samples ....................... 98
  5.3.2 Experimental Work on RPO₄ : Physical and Chemical 102
    5.3.2.1 Methods of Analysis of Rare-Earth and Phosphates 102
    5.3.2.2 On the Dehydration of Phosphates .......... 104
References ............................................. 108

CHAPTER 6 : NUCLEAR MAGNETIC RESONANCE INVESTIGATION IN RPO₄ SYSTEMS .................................. 109
6.1 Role of f Electrons in Bonding .................. 110
6.2 Properties of Rare-Earth Ions in Crystals ...... 113
6.3 NMR in Paramagnetics ......................... 118
6.4 NMR Studies in RPO₄ Systems .................. 120
6.5 Results and Discussions ....................... 123
  6.5.1 Experimental Conditions .................... 123
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5.2 $^{31}$P Investigations on some Diamagnetic and Paramagnetic Phosphorous Compounds</td>
<td>126</td>
</tr>
<tr>
<td>6.5.3 $^{31}$P NMR Studies of Hydrated vs. Anhydrous Phosphates</td>
<td>130</td>
</tr>
<tr>
<td>6.5.3.1 Line Widths</td>
<td>132</td>
</tr>
<tr>
<td>6.5.3.2 Asymmetry</td>
<td>137</td>
</tr>
<tr>
<td>6.5.3.3 Temperature Variation Work</td>
<td>141</td>
</tr>
<tr>
<td>6.5.3.4 Shifts</td>
<td>143</td>
</tr>
<tr>
<td>6.5.4 Proton Resonance in Hydrated Phosphate</td>
<td>153</td>
</tr>
<tr>
<td>6.6 Magnetic Resonance Studies of Reported Antiferromagnetic Transition in a no. 1 of Rare-Earth Phosphates</td>
<td>160</td>
</tr>
<tr>
<td>6.6.1 Results, 6.6.2 Discussion</td>
<td>166</td>
</tr>
<tr>
<td>References</td>
<td>166</td>
</tr>
<tr>
<td>CHAPTER 7 : LINE SHAPE ANALYSIS FOR ASYMMETRIC LINES</td>
<td>172</td>
</tr>
<tr>
<td>7.1 Line Shape</td>
<td>173</td>
</tr>
<tr>
<td>7.2 Fine Structure of Spectral Lines (Strongly Coupled Two Spin System)</td>
<td>175</td>
</tr>
<tr>
<td>7.3 Axially Symmetric Anisotropic Interaction</td>
<td>177</td>
</tr>
<tr>
<td>7.4 Different Cases of Axial Interaction</td>
<td>179</td>
</tr>
<tr>
<td>7.5 Expressions for Absorption Lines and its Derivatives</td>
<td>180</td>
</tr>
<tr>
<td>7.6 Method of Analysis</td>
<td>183</td>
</tr>
</tbody>
</table>
7.6.1 Effect of Parameter on the Line Shape

7.6.2 Fitting Procedure

7.6.3 Sign of Parameter

7.6.4 Discussion on the Parameters from Computer Fitting

7.7 On the Results of Line Width, \( \beta, \alpha_y \) and \( \alpha_\phi \) from Computer Fittings

References