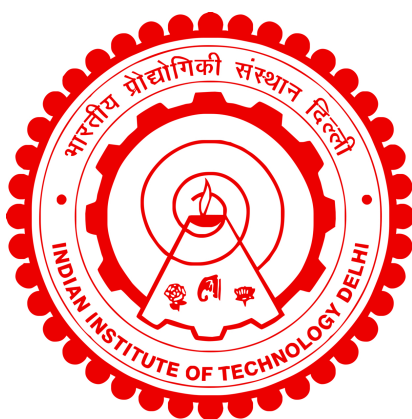


**EXPLORATIONS IN LONG-LIVED NUCLEAR
SPIN ORDER, CROSS-POLARIZATION IN
QUADRUPOLEAR SOLIDS, AND SPHERICAL
TENSOR ANALYSIS OF FID**

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**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
JULY 2024**

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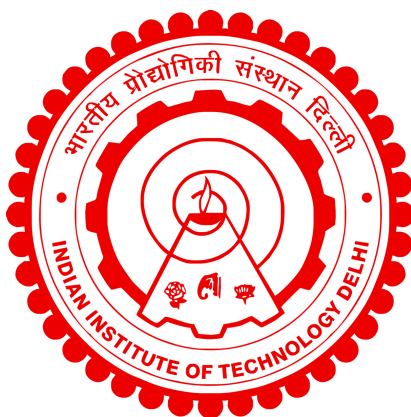
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Submitted

in partial fulfillment of the requirements
of the degree of
Doctor of Philosophy
to the



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Certificate

This is to certify that the thesis entitled “**Explorations in Long-lived Nuclear Spin Order, Cross-polarization in Quadrupolar Solids, and Spherical Tensor Analysis of FID**”, submitted by **Mr. Manjeet** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy**, is a record of the original bonafide research work carried out by him under my supervision and guidance. The thesis has reached the standards fulfilling the requirements of the regulations related to the award of the degree.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma to the best of my knowledge.

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Abstract

Long-lived spin-order or state (LLS) possesses lifetime that is much longer than the longitudinal relaxation time. Since its first demonstration in molecules lacking symmetry, LLS has found application in areas such as slow diffusion, chemical exchange, protein-ligand interactions, quantum computation, and hyperpolarization. LLS methodology has also advanced in parallel and now numerous methods exist that can excite LLS from thermal magnetization and convert it to an observable state. The first half of this thesis details an exploration performed for a geometrical description of LLS excitation during spin-locking pulses. This exploration has been successful in providing a geometrical description for weak coupling regime and also reveals novel pulse sequences for a diverse range of coupling regimes. The findings and implications of this investigation open new opportunities for further advancing the LLS methodology and extending the range of LLS applications. In addition to this exploration, a new two-dimensional J-resolved sequence is also presented in the first half. Based on the concept of LLS, this new sequence provides a faster and simpler way of accessing selective scalar couplings from highly congested spectra.

The second half entails cross-polarization (CP) that is now a well-established phenomenon and has become an integral part of solid-state NMR for investigating nuclei with low gyromagnetic ratios and natural abundance. However, cross-polarization in quadrupolar systems is still challenging under magic-angle spinning (MAS). A new pulse sequence for CPMAS in half-integer quadrupolar systems is proposed that has the potential to emerge as a successful alternative to the conventional sequence. In addition to cross-polarization, a somewhat different and relatively

unknown concept—*Spherical Tensor Analysis of Free Induction Decay*—is also explored in the second half. This exploration suggests the possibility of free induction decay decomposition into spherical harmonic functions and anticipates its use for shimming of magnets.

सारांश

लॉग-लिब्ड स्पिन ऑर्डर अथवा स्टेट (एल एल एस) का जीवन काल अनुद्ध्य जीवन काल की अपेक्षा अधिक होता है। जब इसे पहली बार असममिति वाले अणुओं में प्रदर्शित किया गया, तत्पश्चात एल एल एस का उपयोग धीमे विसरण, रसायनिक विनिमय, प्रोटीन-लिगेण्ड अंतरक्रिया, क्वांटम गणना एवं हाइपरपोलराइजेशन जैसे क्षेत्रों में किया गया है। समय के साथ अल अल एस् विधि में भी प्रगति हुई है एवं अब अनेक विधियाँ ज्ञात हैं जिनके माध्यम से थर्मल चुम्बकत्व का एल एल एस में उत्तेजन एवं इसका अवलोकन संभव है। इस थीसिस के पहले भाग में स्पिन-लॉकिंग पल्स के दौरान एलएलएस उत्तेजना के ज्यामितीय विवरण के लिए किए गए अन्वेषण का विवरण दिया गया है। यह अन्वेषण कमजोर कपलिंग प्रणाली के लिए एक ज्यामितिय विवरण प्रदान करने में सफल रहा है और नवीन पल्स अनुक्रमों की खोज भी करता है जो विभिन्न कपलिंग प्रणालियों के लिए हैं। इस अन्वेषण के नतीजे नई संभावनाओं के द्वार खोलते हैं जो एल एल एस विधि को और आगे बढ़ाने एवं एल एल एस अनुप्रयोगों की श्रेणी को विस्तारित करने में सहायक हैं। इस अन्वेषण के अलावा, पहले भाग में एक नया दो-आयामी J-रेज़ोलवड विधि भी प्रस्तुत की गई है। एल एल एस के अवधारणा पर आधारित, यह नई विधि अत्यधिक भीड़बाड़ से भरे स्पेक्ट्रम में विशेष रूप से चयनात्मक स्कैलर कपलिंग्स को ज्ञात का एक तेज एवं सरल तरीका प्रदान करता है।

इसका दूसरा भाग क्रॉस-ध्रुवीकरण को सम्मिलित करता है, जो अब एक सिद्ध तथ्य है एवं सॉलिड-स्टेट एन एम आर का एक अभिन्न अंग बन गया है, जिसका उपयोग कम जायरोमैग्नेटिक अनुपात एवं कम प्राकृतिक प्रचुरता वाले नाभियों की जांच के लिए किया जाता है। हालांकि, कुआडरूपलोर निकाय में क्रॉस-ध्रुवीकरण अब भी मैजिक-एंगल स्पिनिंग (MAS) के अंतर्गत चुनौतीपूर्ण है। आधा पूर्णांक कुआडरूपलोर निकाय में CPMAS के लिए एक नयी पल्स विधि प्रस्तुत की गई है जो पारंपरिक अनुक्रम का सफल विकल्प बन सकती है। क्रॉस-ध्रुवीकरण के अतिरिक्त, दूसरे भाग में कुछ अपेक्षाकृत अलग अवधारणा—फ्री इंडक्शन डिके का स्फेरिकल टेंसर विश्लेषण—को भी अन्वेषित किया गया है। यह अन्वेषण संभावना दिखाता है कि फ्री इंडक्शन डिके को स्फेरिकल हार्मोनिक फलन में विभाजित किया

जा सकता है एवं यह मैग्नेटों के शिमिंग के लिए उपयोग के संकेत करता है।

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