学校编码：10384　　分类号_____密级_____
学号：B200025032　　UDC _____

厦　门　大　学

博　士　学　位　论　文

液体核磁共振中分子间多量子相干及其应用

Intermolecular Multiple-Quantum Coherences in Liquid NMR and Their Applications

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论文提交日期：2004 年 11 月

论文答辩时间：2004 年 12 月

学位授予日期：

答辩委员会主席：_____

评　　阅　　人：_____

2004 年 11 月

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声明人（签名）：

2004 年 11 月 20 日

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中　文　摘　要

1990 年当简单的 CRAZED 脉冲序列作用于简单的高极化核自旋体系时，在一维实验时间域中发现了多自旋回波现象(Multiple Spin Echo，MSE)，在二维实验频率域中发现了令人诧异的分子间多量子相干现象(Intermolecular Multiple Quantum Coherence，iMQC)，这引起了核磁共振工作者极大的研究兴趣，同时也给核磁共振界带来争论。随着研究的深入，理论和实验均表明这两种现象的本质是一样的，都是由远程偶极相互作用引起的。

本论文采用经典的偶极场和量子力学的密度矩阵理论方法，并利用脉冲梯度场与选择激发相结合的实验手段，对 iMQC 的性质和机理进行了系统的研究，还建立了利用 iMQC 在不均匀场下获得高分辨率 NMR 谱的方法。本论文主要研究成果有：

一、采用偶极场和量子力学积算符相结合的理论方法，并利用脉冲梯度场与选择激发相结合的实验手段，首次系统地定量研究了单组分单自旋和双组分双自旋体系的分子间多量子相干信号的相对强度、优化脉冲翻转角、扩散、纵向弛豫和横向弛豫的性质。

二、首次提出了分子间单量子相干(iSQC)概念，采用偶极场和 Torrey 方法相结合的有效方法对同核 iSQC 进行了定量的研究，利用选择激发技术首次从实验上分离出纯的二自旋阶 iSQC 信号，并对其信号强度、优化脉冲翻转角、扩散和弛豫等性质进行了定量表征，为其在不均匀和不稳定磁场中获得高分辨率 NMR 谱奠定了坚实的理论和实验基础。

三、在国际上首次成功分离出来自纵向三自旋阶的分子间多量子相干信号，并系统地分析和表征了其相对强度、优化脉冲翻转角、分子扩散和弛豫等特性。

四、系统地提出了一系列基于分子间多量子相干的在不均匀磁场下获得高分辨率 NMR 谱的方法。首先，提出了改进的基于分子间零量子相干的 SEL-HOMOGENIZED 方法。其次，率先提出了基于分子间双量子相干的 IDEAL 和 IDEAL-II 方法以及基于分子间单量子相干的 IDEAL-III 方法。这些方法可从不均匀磁场中获得常规高分辨率 NMR 谱所具有的化学位移、*J* 耦合常数、多重峰结构、信号强度等信息，又各具特色、优点，可互为补充。

关键词：核磁共振；分子间多量子相干；高分辨率谱

Intermolecular Multiple-Quantum Coherences in Liquid NMR and Their Applications

Chen Zhiwei

ABSTRACT

Over the past decade or so, the multiple spin echo (MSE) or intermolecular multiple quantum coherence (iMQC) phenomena in highly polarized nuclear spin systems have seemed to contradict conventional NMR theory and drawn great attention in NMR research community. In the subsequent deliberate research, these experimental phenomena were referred to be resulted from intermolecular dipole-dipole interaction. In this work, classical dipolar field theory and quantum-mechanical density matrix formalism were employed to analyze the coherences of spin dynamics. Techniques based on pulsed-field gradients and selective excitations were used to study the signals from iMQCs. Several pulse sequences were designed to achieve 1D high-resolution NMR spectra in inhomogeneous fields. The main results are summarized as follows:

1. Liquid NMR behaviors related to intermolecular dipolar interactions were investigated theoretically and experimentally in highly polarized single-component and two-component spin systems. The properties of molecular diffusion, transverse relaxation, longitudinal relaxation, and optimal RF flip angles were quantitatively characterized.
2. For the first time, the concept of intermolecular single-quantum coherences (iSQCs) was proposed. A combination of dipolar field treatment and Torrey equation was used to derive a general theoretical expression for the time evolution of spins with arbitrary flip angles of RF pulses. Signals from pure

homonuclear two-spin iSQCs and intermolecular iSQC cross peaks in homonuclear pulsed-field gradient COSY experiments were observed and characterized, in one- and two-dimensional experiments, respectively.

3. Signals originating from a pure specific coherence of intermolecular three-spin orders were separated and characterized experimentally in highly polarized two-component spin systems. For the first time, relaxation and diffusion properties of pure intermolecular single-, double-, and triple-quantum coherences of three-spin orders were characterized and analyzed in one-dimensional experiments.
4. Several pulse sequences based on the iMQCs were proposed to obtain high-resolution 1D NMR spectra in inhomogeneous fields, including the SEL-HOMOGENIZED based on intermolecular zero-quantum coherences, IDEAL and IDEAL-II methods based on intermolecular double-quantum coherences, and IDEAL-III based on intermolecular single-quantum coherences. Chemical shifts, *J* couplings, multiplicity patterns, and relative areas are retained with these methods. Each method has its own advantages and plays a complementary role in different cases.

Keywords: nuclear magnetic resonance; intermolecular multiple-quantum coherence; high-resolution spectra