## NMR SPECTROSCOPY IN LIQUIDS AND SOLIDS

## **VLADIMIR I. BAKHMUTOV**



CRC Press is an imprint of the Taylor & Francis Group, an Informa business

## Contents

Preface			•••••	ix	
Introduction	1			xi	
Author				xv	
Chapter 1	Physical Basis of Nuclear Magnetic Resonance1				
	1.1	Nuclei	in the External Magnetic Field	2	
	1.2	Radiof	requency Irradiation: Continuous-Wave		
		and Ra	diofrequency Pulses	7	
	1.3	From I	Nuclear Relaxation to Shapes of NMR Signals	11	
	1.4	1.4 Registration of NMR Signals: General Principles			
		and NI	MR Equipment	14	
		1.4.1	Magnets, Decouplers, and NMR Probes	16	
		1.4.2	Dead Time in NMR Experiments:		
			Influence on NMR Data	18	
		1.4.3	Spectral Resolution	19	
	1.5	Enhan	cement of Sensitivity in NMR Experiments	20	
	1.6	Two-D	vimensional and Multi-Quantum		
		NMR	Experiments: General Aspects	21	
		1.6.1	Artifacts in 2D NMR	24	
		1.6.2	Multi-Quantum NMR	24	
	Refe	rences a	nd Recommended Literature	26	
Chanter 2	Cher	nical Shi	fts and Nuclear Coupling		
Chapter 2	Theory and Practical Consequences				
	Thee	Jy and I			
	2.1	Phenor	menology of Chemical Shift	27	
		2.1.1	Chemical Shift in Diamagnetic Molecular Systems	30	
		2.1.2	Relationship Chemical Shift and Atomic Charge	32	
		2.1.3	Predicting Chemical Shift Values.	34	
		2.1.4	Isotropic Chemical Shift	35	
	2.2	Chemi	cal Shifts in the Presence of Unpaired Electrons	37	
		2.2.1	Knight Shifts	38	
	2.3	Spin-S	Spin Coupling	39	
		2.3.1	Strongly Coupled Spin Systems	40	
		2.3.2	Spin-Spin Coupling via Chemical Bonds	43	
		2.3.3	Spin-Spin Coupling through Space	46	
		2.3.4	Proton-Proton Exchange Coupling	46	
	2.4	Dipola	r Coupling	48	
	2.5	Quadr	upolar Coupling	49	
	References and Recommended Literature				

Chapter 3	Nuclear Relaxation: Theory and Measurements				
	3.1	Molecular Motions: Common Characteristics			
		3.1.1 Isotropic and Anisotropic Molecular Reorientations 56			
	3.2	Mechanisms of Spin–Spin and			
		Spin-Lattice Nuclear Relaxation			
		3.2.1 Intraniolecular Dipole-Dipole Relaxation			
		3.2.2 Intermolecular Dipole Dipole Relaxation			
		3.2.4 Relaxation by Chemical Shift Anisotropy			
		3.2.5 Spin-Rotation and Scalar Relaxation Mechanisms			
		3.2.6 Cross-Relaxation and Coupled Relaxation			
	3.3	Spin Diffusion in Solids			
	3.4	Paramagnetic Relaxation			
	3.5	Relaxation Time Measurements			
		3.5.1 Non-Selective, Selective,			
		and Bi-Selective $T_1$ Times			
		3.5.2 Measuring $T_{1\rho}$ and $T_2$ Times			
	3.6	Experiments and Measurements:			
		Errors and Problems75			
		3.6.1 Instrumental Errors75			
		3.6.2 Treatment of Relaxation Curves:			
		Approaches and Problems76			
	3.7	3.7 Artifacts in Relaxation Time Measurements			
	References and Recommended Literature				
Chapter 4	NMR and Molecular Dynamics: General Principles				
	4.1	Kinetics of Chemical Reactions by NMR Spectroscopy85			
	4.2	Chemical Exchange			
		4.2.1 Line-Shape Analysis87			
		4.2.2 Slow Chemical Exchange90			
		4.2.3 Exchange NMR Spectroscopy92			
		4.2.4 Carr-Purcell-Meiboom-Gill			
		Relaxation Dispersion93			
	4.3	Molecular Mobility from Relaxation Times95			
		4.3.1 Dipole–Dipole Relaxation, Nuclear			
		Overhauser Effect, and Molecular Mobility			
		4.3.2 Effects of Molecular Motional			
		Anisotropy on Nuclear Relaxation			
		4.3.3 Molecular Dynamics in the Presence			
		of Correlation Time Distributions			
	1 1	4.5.4 Distribution of Activation Energies			
	4.4	Molecular Dynamics from Low Field NMD			
	4.5 MORECULAR DYNAMICS FIOLIN LOW-FIELD INVIK				

Chapter 5	NMR Spectroscopy in Solutions: Practice and Strategies of Structural Studies			
	5.1	Prepara 5.1.1	tion of NMR Samples: Minimal Requirements 113 Adjustment of Spectral Resolution	
			and Spectral Manipulations 114	
		5.1.2	Reference Lines	
	5.2	Structu	ral Studies by Solution NMR: General	
		Strategi	ies and 1D and 2D NMR Experiments 116	
		5.2.1	From 1D NMR to 2D Correlation Spectroscopy 116	
		5.2.2	Multi-Quantum NMR 119	
		5.2.3	Examples of Structural Studies 121	
		5.2.4	Ultrafast NMR 128	
	5.3	Conform	mational (Isomeric) Analysis	
		by NM	R in Solutions129	
		5.3.1	Common Principles	
		5.3.2	Determination of Molecular Geometry	
			(Conformations, Isomers) via Chemical Shifts	
			and Spin-Spin Coupling Constants through	
			Chemical Bonds	
		5.3.3	Molecular Geometry and Spin-Spin	
			Coupling through Space	
		5.3.4	Conformational Analysis in the	
			Presence of Fast Interconversions	
	5.4	NOE ar	nd Residual Dipolar Coupling	
		Measur	ements in Structural Studies 141	
	Refe	rences an	d Recommended Literature 145	
Chapter 6	NMR Relaxation in Solutions: Applications			
	6.1	Partiall Unreso	y Relaxed NMR Spectra: Resolving the ly local sector of the ly local	
	6.2	Relaxat	ion Times in Solutions: Quadrupolar	
	0.2	Couplin	ng Constants and Chemical Shift Anisotropy 149	
		6.2.1	OCC Values from Variable-Temperature	
		0.211	Relaxation Experiments and $T_{\rm eff}$ Times 151	
		622	T. Relaxation and DOCC Values	
		0.2.2	in Mobile Structural Units 156	
		623	Chemical-Shift Anisotrony Values from T. Data 159	
	63	NMR F	Relaxation and Intermolecular Interactions 160	
	0.5	631	Weak Bonding 160	
		632	Ion Pairing 162	
		633	Complexation 164	
	64	Solvent	Relavation 165	
	65	Relevet	ion in Molecular Systems	
	0.5	with CL	amical Exchanges 167	
		with CI	iennear Exchanges 10/	

	6.6 Refer	Structural Aspects Obtained from Relaxation in Solutions 170 $6.6.1$ <sup>1</sup> H $T_1$ Criterion in Structural Assignments			
Chapter 7	Special Issues in Solution NMR 181				
	7.1 7.2 7.3	Optical Isomers in NMR Spectra181Solution NMR of Biomolecules: General Principles184Dynamics of Liquids by NMR1907.3.1Diffusion NMR Spectroscopy in Liquids1917.3.2High-Pressure NMR: Structure and Dynamics of Liquids194			
	7.4 7.5	<ul> <li>para-Hydrogen and NMR Spectroscopy in Solutions</li></ul>			
	7.6 Refer	Free Radicals in NMR Spectra of Solutions			
Chapter 8	Solid-State NMR Spectroscopy: General Principles and Strategies 213				
	8.1	Detection of NMR Signals in Solids			
	8.2 8.3	General Approaches and Strategies         of NMR Studies in Solids			
		8.3.1 Resolving Signals from Different Structural Units in Solids via Paramagnetic Effects			
	8.4	<ul> <li>Assignments of Signals</li></ul>			
	8.5	vs. Isotropic Chemical Shifts			

	Refer	8.5.2.2 <sup>14</sup> N NMR in Static Powders       247         8.5.2.3 <sup>14</sup> N MAS NMR       247         8.5.3       Alkali Metal Ions Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> ,       247         8.5.4 <sup>14</sup> N MAS NMR       249         8.5.5 <sup>35,37</sup> Cl, <sup>78,81</sup> Br, <sup>127</sup> I, and <sup>17</sup> O Solid-State NMR       252         8.5.6 <sup>51</sup> V, <sup>93</sup> Nb, and <sup>181</sup> Ta Solid-State NMR       256         ences and Recommended Literature       257				
Chapter 9	Molecular Dynamics and Nuclear Relaxation in Solids: Applications					
	9.1	Temperature Control and Calibration				
	02	In Solid-State INMR				
	9.2	Molecular Dynamics in Solida Determined				
	2.5	by Full Line Shape A polycis				
	94	One- and Two-Dimensional Exchange NMP				
	7.4	Spectroscopy in Solids: Slow Molecular Dynamics 266				
	9.5	Dynamics in Solids by Cross-Polarization				
	110	NMR Experiments 268				
	9.6	Molecular Dynamics in Solids by NMR Relaxation				
		Measurements: Common Aspects of Applications 271				
		9.6.1 Nuclear Relaxation in Spinning Solids 277				
		9.6.2 Methodology of Solid-State Relaxation Studies 274				
		9.6.3 General Comments on Non-Exponential				
		Relaxation in Solids277				
	9.7	Dynamics in Heterogeneous and Disordered				
		Solids: NMR Spectra and Relaxation Dispersion				
	9.8	Dynamics in Solids under High Pressure				
	Refer	ences and Recommended Literature				
Chapter 10	Solid-	State NMR: Special Issues				
	10.1	Solid-State NMR of Proteins 287				
	10.1	10.1.1 Chemical Shift Tensors in Proteins 200				
	10.2	Solid-State NMR in Metals and Allovs 292				
	10.3	Porous Diamagnetic Solids: Porosity via NMR				
		Experiments				
		10.3.1 NMR Cryoporometry 296				
		10.3.2 NMR Relaxometry				
		10.3.2.1 NMR Relaxometry for Gases				
		10.3.2.2 Low-Field NMR Relaxometry				
		under High Pressure				
	10.4	Solid-State NMR and Paramagnetic Molecular Systems 303				

10.4.1	Spin Echo Mapping Technique
	for Detection of Invisible Nuclei
10.4.2	Detection of Nuclei at Paramagnetic Centers:
	Paramagnetic Metal Ions
10.4.3	NMR Spectra of Paramagnetic Solids:
	General Aspects and Study Strategies
	10.4.3.1 NMR Spectra of Quadrupolar
	Nuclei in Paramagnetic Solids
	10.4.3.2 Common Strategies in Structural
	Studies of Paramagnetic Solids
10.5 Nuclea	r Relaxation in Paramagnetic Solids: Applications 316
10.5.1	Strategy for Relaxation Studies
	of Paramagnetic Solids
References an	d Recommended Literature
Concluding Remarks	
Index	