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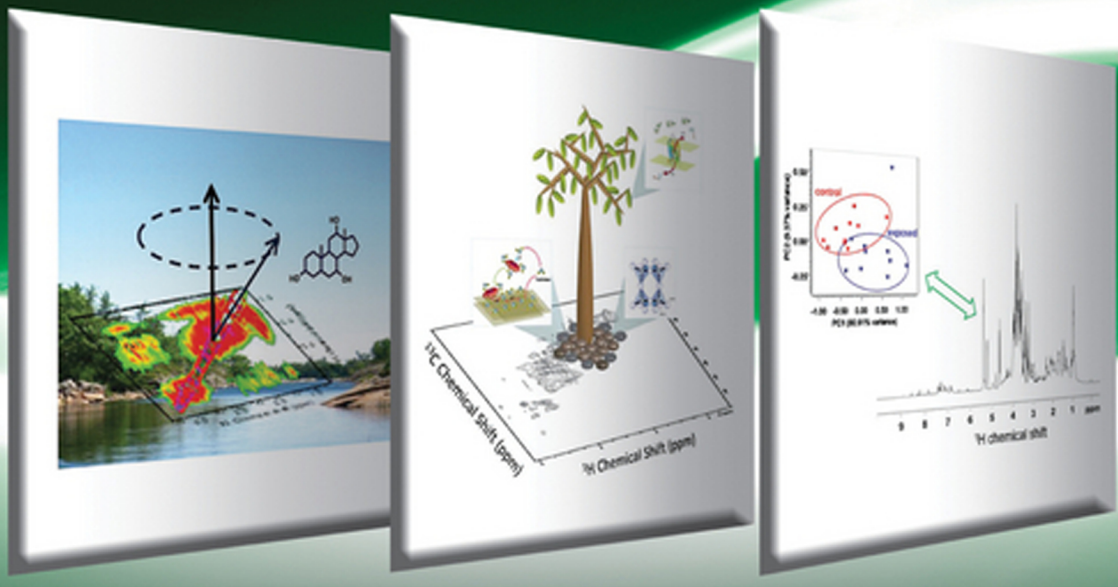

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NMR Spectroscopy: A Versatile Tool for Environmental Research

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Series Preface

The *Encyclopedia of Nuclear Magnetic Resonance* was published, in eight volumes, in 1996, in part to celebrate the fiftieth anniversary of the first publications in NMR in January 1946. Volume 1 contained an historical overview and 200 articles by prominent NMR practitioners, whilst the remaining seven volumes were constituted by 500 articles on a wide variety of topics in NMR (including MRI). A ninth volume was brought out in 2000 and two "spin off" volumes incorporating the articles on MRI and MRS (together with some new ones) were published in 2002. In 2006 the decision was taken to publish all the articles electronically (i.e. on the world-wide web) and this was carried out in 2007. Since then, new articles have been placed on the web every three months and some of the original articles have been updated. This process is continuing and to recognize the fact the Encyclopedia of Magnetic Resonance is a true online resource, the web site has been redesigned and new functionalities added, with a relaunch in January 2013 in a new Volume and Issue format, under the new name eMagRes. In December, 2012, a print edition of the Encyclopedia of NMR was published in ten volumes (6200 pages). This, much needed update of the 1996 edition of the Encyclopedia, encompasses the entire field of NMR with the exception of medical imaging (MRI).

The existence of this large number of articles, written by experts in various fields, is enabling a new concept to be implemented, namely the publication of a series of printed handbooks on specific areas of NMR and MRI. The chapters of each of these handbooks will be constituted by a carefully chosen selection of Encyclopaedia articles relevant to the area in question. In consultation with the Editorial Board, the handbooks are coherently planned in advance by specially-selected editors, and new articles written (together with updating of some already existing articles) to give appropriate complete coverage of the total area. The handbooks are intended to be of value and interest to research students, postdoctoral fellows and other researchers learning about the topic in question and undertaking relevant experiments, whether in academia or industry. Consult the eMagRes web site (http://onlinelibrary.wiley.com/book/10.1002/9780470034590) for the latest news on magnetic resonance Handbooks.

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Preface

The challenges faced by environmental scientists today are vast, complex, and multi-faceted. For instance, predicting the fate of an environmental pollutant or understanding ecosystem responses to climate change, necessitate a firm understanding of molecular structure and dynamics of environmental media as well as the components that exist and interact within this media. Furthermore, linking information obtained at the molecular-scale to ecosystem-level processes is a major pursuit of modern environmental research. As such, NMR spectroscopy and its scalability from the molecular-scale to the macroscopic-scale, is facilitating rapid growth in environmental science. In addition, the versatility of NMR spectroscopy has resulted in the development and implementation of different types of NMR techniques to examine the structure of various types of environmental samples, living and non-living, as well as the study of critical environmental processes. This handbook is a collection of chapters that span from methods to how NMR is used in environmental research to gain insight into various ecosystem properties. These chapters also highlight the immense potential of NMR spectroscopy which has expanded our fundamental understanding of environmental processes and will likely continue to do so well into the future.

NMR spectroscopy has been used to study environmental samples since the early 1960s. One of the first applications, by Barton and Schnitzer in 1963 (*Nature* 198:217–218), used solution-state ^{1}H NMR to study the composition of isolated soil humic substances. Since this time, the advancements in NMR have resulted in a wide range of methods to be applied to environmental samples and required the development of environment-specific methods, such as comprehensive multi-phase NMR. This handbook is organized into three parts—Part A focuses on methods used in environmental NMR which span from solution-state to magnetic resonance imaging. Part B emphasizes how NMR spectroscopy has played an essential role in understanding various types of environmental components and related processes. These include different forms of organic matter found in soil, water, and air as well as how NMR is used to probe the fate of water, organic pollutants, and metals in the environment. Part C focuses on the growing field of environmental metabolomics which uses NMR as its main discovery platform. NMR-based environmental metabolomics is reshaping the understanding of ecotoxicity of problematic environmental pollutants in different environments.

We sincerely hope that the reader will benefit from the overviews written by experts in the growing and diverse field of environmental NMR spectroscopy. We thank the authors for their important and excellent contributions to this handbook. We also thank Professor Robin K. Harris and Professor Roderick Wasylishen (Editors in Chief for *eMagRes*) for their guidance and support. This handbook would not have been possible without the support and assistance from the *eMagRes* team at Wiley which consists of Elke Morice-Atkinson, Stacey Woods, and Martin Rothlisberger. It is also important to note that many influential people nurtured our early interest in environmental NMR. We thank our PhD mentors (Professor Marvin Dudas, Professor William McGill and Professor Michael H. B. Hayes) and our Postdoctoral research supervisors (Professor William Kingery and Professor Pat Hatcher). Our collaborators at Bruker BioSpin, especially Dr. Manfred Spraul, Dr. Werner Mas, and Dr. Henry Stronks, are also acknowledged because of their keen interest in the co-development of environmental NMR methods and their long-term support

of environmental NMR development and application. We must also thank the generous support for environmental NMR research from the Canada Foundation for Innovation, Krembil Foundation, Natural Sciences and Engineering Research Council of Canada, Ontario Research Foundation, and the University of Toronto. Lastly, we dedicate this book to our four year old twins, Sam and Sophie, who are great admirers of both the environment and our NMR "rockets" (a.k.a. spectrometers).

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June 2014

Abbreviations and Acronyms

1D	One-Dimensional
2D	Two-Dimensional
3D	Three-Dimensional
3QMAS	Triple-Quantum Magic-Angle Spinning
4MTB	4-Methylthiobutylglucosinolate
ACD	Advanced Chemistry Development
A-DNT	Amino-Dinitrotoluene
ADP	Adenosine Diphosphate
AFM	Atomic Force Microscopy
ANOVA	Analysis of Variance
APCI	Atmospheric Pressure Chemical Ionization
ATP	Adenosine Triphosphate
BD	Bloch Decay
BET	Brunauer-Emmett-Teller
BMRB	Biological Magnetic Reference Bank
BPP	Bloembergen-Purcell-Pound
BSM	Biogenic Small Molecule
CA	Concentration Addition
CaB	Cation Bridges
CD	Circular Dichroism
CE	Capillary Electrophoresis
CEC	Cation Exchange Capacity
CEWAF	Chemically Enhanced Water-Accommodated Fraction
CIDET	Canadian Intersite Decomposition Experiment
CPMG	Carr-Purcell-Meiboom-Gill
CMP-NMR	Comprehensive Multiphase-Nuclear Magnetic Resonance
CN	Cetane Number
C/N	Carbon-to-Nitrogen
Cobs	Observable Carbon
CONTIN	CONTINuous Distribution
COSY	Correlation Spectroscopy
CPMAS	Cross Polarization Magic-Angle Spinning
CRAM	Carboxyl-Rich Alicyclic Molecules
CRAMPS	Combined Rotation And Multiple-Pulse Sequence
CSA	Chemical Shift Anisotropy
CSI	Chemical Shift Imaging
μCT	Micro X-ray Tomography
DA	Discriminant Analysis
DAD	Diode Array Detector
DANS	Differential Analysis by Two-Dimensional Nuclear Magnetic Resonance Spectroscopy
DCP	2,4-Dichlorophenol
DCPMAS	Double Cross Polarization Magic-Angle Spinning
DD	Dipolar Dephasing
DE	Diffusion-Edited
DFS	Double-Frequency Sweep
DNA	Dinitroaniline
DNB	Dinitrobenzene
DNBA	Dinitrobenzoic Acid
DNP	2,4-Dinitrophenol
DNT	Dinitrotoluene
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DON	Dissolved Organic Nitrogen
DOP	2-Chloro-1,3,2-Dioxaphospholane
DOSY	Diffusion Ordered Spectroscopy
DP	Direct Polarization
(−)DPBQ	2,5-Di-(*N*-(−)-Prolyl)-*Para*-Benzoquinone
DQF	Double-Quantum-Filtered
DQF-COSY	Double-Quantum-Filtered Correlation Spectroscopy
DQF-STMAS	Double-Quantum-Filtered Satellite Transition Magic-Angle Spinning
ds-4MTB	Desulfated 4-Methylthiobutylglucosinolate
DSC	Differential Scanning Calorimetry
DSS	4,4-Dimethyl-4-Silapentane-1-Sulfonate
DWI	Diffusion-Weighted Imaging
EC_{50}	Effective Concentration to 50% of the Population
ECD	Electronic Circular Dichroism
EDX	Energy-Dispersive X-ray Spectroscopy
ELISA	Enzyme-Linked Immunosorbent Assay
EM	Exponential Multiplication
EOC	Emerging Organic Contaminant
EPA	Environmental Protection Agency
EPS	Extracellular Polymeric Substance
ESEM	Environmental Scanning Electron Microscope
FA	Fulvic Acid
FCA	Fuzzy Clustering Analysis
FFC	Fast-Field Cycling
FFT	Fast Fourier Transformation
FID	Free Induction Decay
FIMS	Field Ionization Mass Spectrometry
FLASH	Fast Low-Angle Shot
FT	Fourier Transform
FT-ICR-MS	Fourier Transform Ion Cyclotron Resonance Mass Spectrometry
FTIR	Fourier Transform Infrared
GABA	γ-Aminobutyric Acid
GC	Gas Chromatography
GC-FID	Gas Chromatography with Flame Ionization Detection
GC-MS	Gas Chromatography-Mass Spectrometry
Gd-DTPA	Gadolinium and Diethylenetriamine Pentaacetic Acid
HA	Humic Acid
HATS-PR	Hierarchical Alignment of Two-dimensional Spectra-Pattern Recognition
HCA	Hierarchical Cluster Analysis

HETCOR	Heteronuclear Correlation
HF	Hydrofluoric Acid
HFB	Hexafluorobenzene
HILIC	Hydrophilic Interaction Liquid Chromatography
HMBC	Heteronuclear Multiple Bond Correlation
HMDB	Human Metabolome Database
HMQC	Heteronuclear Multiple Quantum Coherence
HOC	Hydrophobic Organic Contaminant
HPLC	High Performance Liquid Chromatography
HPLC-MS	High Performance Liquid Chromatography-Mass Spectrometry
HR	High-Resolution
HR-FAB-MS	High-Resolution Fast Atom Bombardment Mass Spectroscopy
HR-MAS	High-Resolution Magic-Angle Spinning
HSQC	Heteronuclear Single Quantum Coherence
HSQCAD	Heteronuclear Single Quantum Coherence Adiabatic
HSQMBC	Heteronuclear Single Quantum Multiple Bond Correlation
IA	Independent Action
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IEA	International Energy Agency
IR	Infrared
IV	Iodine Value
JRES	J-Resolved Spectroscopy
K_d	Soil-Water Distribution Coefficient
KEGG	Kyoto Encyclopedia of Genes and Genomes
K_{oc}	Organic-Carbon Normalized Distribution Coefficient
K_{ow}	Octanol-Water Partition Coefficient
LB	Linebroadening
LC_{50}	Lethal Concentration to 50% of the Population
LC	Liquid Chromatography
LC-LC	Two-dimensional Liquid Chromatography
LC-NMR	Liquid Chromatography Nuclear Magnetic Resonance
LC-SPE	Liquid Chromatography-Solid-Phase Extraction
LMD	Laser Microdissection
MAS	Magic-Angle Spinning
MDLT	Material Derived From Linear Terpenoids
MIC	Minimum Inhibitory Concentration
MMM	Molecular Mixing Model
MOA	Mode of Action
MOUSE	Mobile Universal Surface Explorer
MPNBG	Methyl-4,6-*O*-(*p*-Nitrobenzylidene)-α-D-Glucopyranoside Gel
MRI	Magnetic Resonance Imaging
MRS	Magnetic Resonance Spectroscopy
MS	Mass Spectrometry
MSD	Mean Square Displacement
MTBE	Methyl *tert*-Butyl
NAPL	Nonaqueous Phase Liquid
NBA	Nitrobenzoic Acid
NMRD	Nuclear Magnetic Resonance Dispersion
NOAEL	No-Observable Adverse-Effect Level
NOESY	Nuclear Overhauser Effect Spectroscopy
NOM	Natural Organic Matter
NP	Nitrophenol
NT	Nitrotoluene
O/C	Oxygen-to-Carbon
OM	Organic Matter
OPLS-DA	Orthogonal Partial Least Squares Discriminant Analysis
PA	Picric Acid
PC	Principal Component
PCA	Principal Component Analysis
PCB	Polychlorinated Biphenyl
PCP	Pentachlorophenol
PCR	Principal Components Regression
PET	Positron Emission Tomography
PFG	Pulsed-field Gradient
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctanesulfonic Acid
PFPE	Perfluoropolyether
PG	Peptidoglycan
PIA	Polysaccharide Intracellular Adhesion
PLS	Partial Least Squares
PLS-DA	Partial Least Squares Discriminant Analysis
PP	Pre-Polarized
PSRE	Proton Spin Relaxation Editing
PURGE	Presaturation Utilizing Relaxation Gradients and Echoes
QCPMG	Quadrupolar Carr-Purcell-Meiboom-Gill
RADE	Recovery of Relaxation Losses Arising from Diffusion Editing
RAMP	Ramped Amplitude
RARE	Rapid Acquisition with Refocused Echoes
RESTORE	Restoration of Spectra via T_{CH} and T One Rho Editing
RF	Radio Frequency
RH-STD	Reverse Heteronuclear Saturation Transfer Difference
RMSD	Root Mean Square Displacement
ROESY	Rotating-Frame Overhauser Effect Spectroscopy
SCV	Small Colony Variant
SDBS	Spectral Database for Organic Compounds
SHY	Statistical Heterospectroscopy
S/N	Signal-to-Noise
SNIF	Site-specific Nuclear Isotope Fractionation
SOA	Secondary Organic Aerosols
SOM	Soil Organic Matter
SON	Soil Organic Nitrogen

SOP	Standard Operation Procedure
SPE	Solid Phase Extraction
SSB	Spinning Side Band
SST	Sample Shuttle Technique
STD	Saturation Transfer Difference
STDD	Saturation Transfer Double Difference
STMAS	Satellite Transition Magic-Angle Spinning
STOCSY	Statistical Total Correlation Spectroscopy
STWL	Simulated Tank Waste Leachate
SUS	Shared and Unique Structures
SUVA	Specific Ultraviolet Absorbance
SWIFT	Sweep Imaging with Fourier Transform
SWT	Switching Time
T_1	Spin-Lattice Relaxation Time
T_2	Spin-Spin Relaxation Time
TAME	*tert*-Amyl Methyl
TCA	Tricarboxylic Acid
TCI	Triple-resonance Inverse
TEMPO	2,2,6,6-Tetramethylpiperidine-1-Oxyl
TFS	(3,3,3-Trifluoropropyl)dimethylchlorosilane
TMA	Thermomechanical Analysis
TMDP	2-Chloro-4,4,5,5-Tetramethyl-1,3,2-Dioxaphospholane
TNB	Trinitrobenzene
TNBA	Trinitrobenzoic Acid
TNT	2,4,6-Trinitrotoluene
TOCSY	Total Correlation Spectroscopy
TOSS	Total Sideband Suppression
TPPM	Two-Pulse Phase-Modulated
TRAPDOR	Transfer of Populations in Double Resonance
TSP	3-Trimethylsilyltetradeuteropropionate
UPEN	Uniform PENalty regularization
UPLC	Ultra Performance Liquid Chromatography
UTE	Ultrashort Echo Time
UV	Ultraviolet
UV-VIS	Ultraviolet/Visible
VCT	Variable Contact Time
VIP	Variable's Influence on Projection
VSL	Variable Spin Lock
VT	Variable Temperature
WAF	Water-Accommodated Fraction
WaMB	Water Molecule Bridges
WEFT	Water-Eliminated Fourier Transform
WET	Water Suppression Enhanced through T_1 Effects
WISE	Wideline Separation
WS	Wrinkly Spreader
WS-FSFA	Water-Soluble Forest Soil Fulvic Acid
WSOM	Water-Soluble Organic Matter
WURST	Wide, Uniform Rate, and Smooth Truncation
WWTP	Wastewater Treatment Plant
XOC	Xenobiotic Organic Contaminant
XRD	X-Ray Diffraction

PART A
Fundamentals of Environmental NMR

Chapter 1
Environmental NMR: Solution-State Methods

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1.1 INTRODUCTION

Magnetic resonance spectroscopy is concerned with the splitting of magnetic spins of electrons (ESR) and that of atomic nuclei (NMR) in an external magnetic field B_0.[1–7] The splitting of the NMR transition is not solely an intrinsic atomic and molecular property but also depends on the magnitude of an external magnetic field B_0. Here, an increase in B_0 results in NMR sensitivity enhancement and improved spectral resolution.[3–5] The special role of NMR spectroscopy in the molecular-level characterization of complex mixtures and amorphous materials resides in its ability to provide unsurpassed in-depth, isotope-specific information about short-range molecular order.[7]

NMR offers the capability for quantitative and nondestructive determination of chemical environments across the periodic table with a very few exceptions: only the elements Ar and Ce lack any stable, magnetically active isotope with nuclear spin >0. Quantitative relationships between number of spins and area of NMR resonances operate in the absence of differential NMR relaxation.[1,2,5,6] This key feature of NMR in the de novo analysis of complex systems implies the use of NMR spectroscopy as a quantitative reference for other, complementary analytical methods, in particular, when complex unknowns are to be characterized with molecular precision.[7,8] However, low intrinsic overall NMR sensitivity compared with other analytical methods restricts the accessible signal-to-noise (S/N) ratio in NMR spectra and accuracy of signal definition.

When performed properly on any environmental sample, NMR spectroscopy will provide isotope-specific information in unsurpassed detail on the arrangements of chemical bonds, including connectivities, stereochemistry, and spatial proximity as well as meaningful clues about their dynamics and reactivity.[1–3,9–11] However, elaborate sample

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preparation with attentive consideration of the physical processes initiated by the NMR pulse sequence might become essential to obtain meaningful data from polydisperse mixtures. Common environmental samples are mostly complex mixtures of small and large molecules, related by a continuous range of weak to strong interactions. Typically, formation history is poorly constrained, whereas polydispersity and molecular heterogeneity across various size scales is the norm rather than the exception. NMR spectroscopy offers uniquely versatile options to study liquids, gels (see Chapter 5), solids (see Chapter 4), gases, and any combination thereof, a very beneficial prerequisite to study environmental samples in their native state[10–13] (see Chapter 6).

The impressive contributions of, e.g., solid-state (see Chapter 4) and comprehensive multiphase NMR spectroscopy (see Chapter 6) have been addressed in excellent reviews[10,11] and are not considered in this account, which is concerned with solution-state NMR spectroscopy in environmental sciences. This focus implies a stronger emphasis on studies of extracts and, hence, environmental sample preparation. The often unavoidable extraction selectivity will become an asset when purposeful decrease in heterogeneity and impurities will improve sensitivity and S/N ratio in NMR spectra, which is of perpetual concern in NMR spectroscopy.

Current scientific exploration of biochemical organic molecular complexity in which clearly resolved patterns (and their alterations) are readily observed appears more attractive to many than investigation of the vastly more complex biogeochemical mixtures. Here, analytical data are subject to far more extensive intrinsic averaging and necessarily produce less resolved signatures.[7,14] Here, NMR spectroscopy shows the most unambiguous relationship between NMR observable (NMR with chemical shift, line shape, and couplings) and atomic process (reorientation of nuclei spinning with individual precession frequencies in an external magnetic field B_0). It cannot be overemphasized that NMR spectroscopy alone will provide the most direct evidence on molecular structure of any unknown (amorphous) organic substance and mixture; this degree of immediacy of NMR–structure relationships is not available by any other analytical technique.[8] This allows one to define the relative quantities and remarkable structural detail of fundamental building blocks.[15,16] Here, multinuclear quantitative one-dimensional (1D) NMR spectroscopy provides the key margin for any structural model of a complex unknown environmental sample. The unique capability to generate and analyze data from multiple higher dimensional and multinuclear NMR experiments obtained from a single sample[1,2,8,15–19,] serves to enhance the reliability of NMR assignments and allows definition of rather extended substructures in environmental organic mixtures.[8,18]

The most prominent obstacles to implement the potential intrinsic to NMR in environmental sciences are an often novercal attitude of chemistry toward environmental complexity and a factual and technical inaccessibility of competitive NMR resources to virtually all environmental sciences. This has led to a widespread perception that NMR spectroscopy is not sensitive enough to cope with the low concentrations and diversity of matrices encountered in many environmental reactions.[20] This chapter highlights some of the encouraging conceptual and hardware developments in modern NMR spectroscopy, which may provide about one order of magnitude improved resolution and sensitivity compared with equipment commonly used in environmental sciences. This game-changing evolution should place this most powerful analytical method at the heart of most environmental studies that are aimed at a molecular understanding of archetypical complex environmental unknowns that are poorly amenable to any target analyses.

1.2 GENERAL NMR CHARACTERISTICS OF NUCLEI ACROSS THE PERIODIC TABLE

NMR spectroscopy measures the precession frequencies of individual nuclear magnetic moments in an external magnetic field B_0 and the rate of nuclear spin reorientation after excitation (NMR relaxation).[1,2,5,6,21,29] NMR characteristics depend on the isotope-specific nuclear properties γ_N: gyromagnetic ratio, B_0 applied, and the local chemical environments (Figure 1.1). Therefore, any atom within a molecule will show individual NMR-relevant properties, allowing the assembly of molecular structures from NMR spectra in the case of resolvable mixtures and the reconstruction of key structural principles in the case of nonresolvable biogeochemical mixtures.[7] An increase in B_0 results in NMR sensitivity enhancement and improved spectral resolution (Figure 1.1, panel B). The Larmor equation of NMR [$\omega_i = \gamma_N \cdot B_0 \cdot (1 - \delta_i)$; γ_N: gyromagnetic ratio; δ_i: chemical

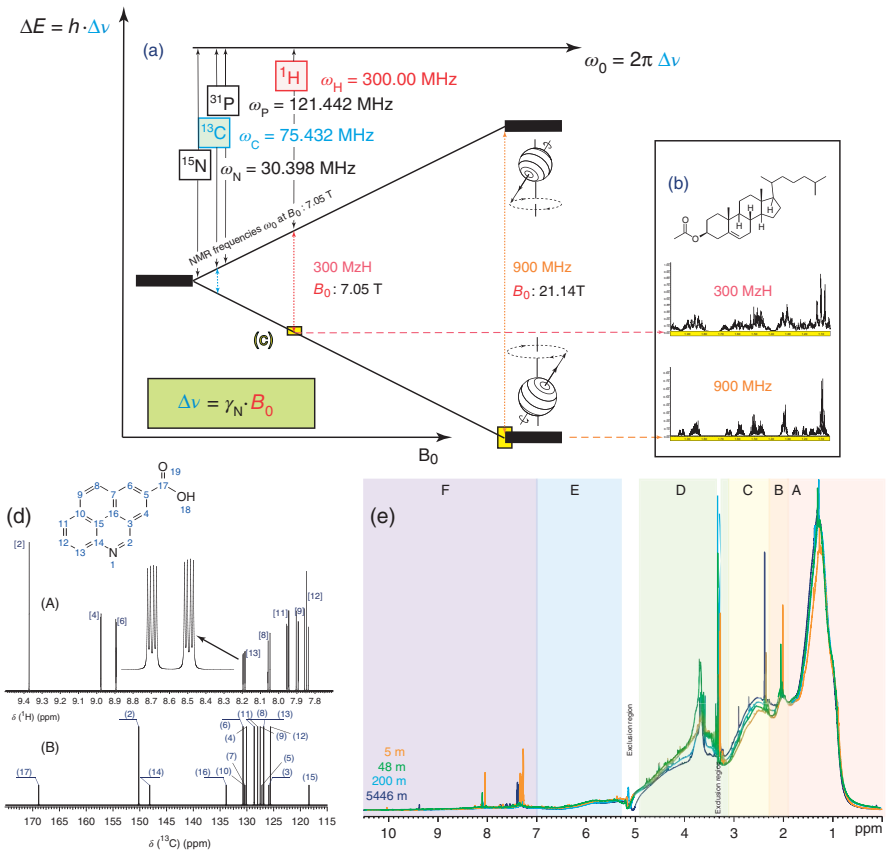

Figure 1.1. Dependence of some magnetic resonance spectral characteristics on the magnetic field B_0.[7] (a) At constant magnetic field B_0, the resonance frequency depends on the relative gyromagnetic ratios of the nuclei γ_N (NMR). (b) Sections of proton NMR spectra of cholesterol acetate at $B_0 = 7.05$ T (300 MHz ^{1}H frequency) and at $B_0 = 21.14$ T (900 MHz ^{1}H frequency); note the *qualitative* difference of high-resolution proton NMR spectra acquired at various B_0. This variation remains the most significant obstacle for automated NMR assignment in organic molecules. Pattern recognition in 2D NMR spectra can be more successfully automated. (c) The relative energy, represented by the chemical shift range, covers a miniscule (ppm) range of the (already tiny) NMR energy transition energy; the ratio of total chemical shift range to total NMR transition energy ranges from ~20 ppm (^{1}H, diamagnetic molecules) up to ~20 000 ppm (^{59}Co and ^{195}Pt NMR; Figure 1.2). Owing to the near equality of the Boltzmann factors for the NMR energy levels, out of 1 000 000 proton nuclei, only 81 participate in the ^{1}H NMR experiment at $B_0 = 11.7$ T and 283 in the NMR experiment at $B_0 = 21.14$ T (at room temperature: 300 K). All other proton nuclei remain silent throughout the NMR experiment. This ratio is even worse for other nuclei, explaining the relative insensitivity of NMR spectroscopy when compared to higher energy spectroscopic methods. (d) Mid-sized molecules produce individual NMR signatures for any atom as shown for ^{1}H (A) and ^{13}C NMR (B) NMR spectra of carboxyazapyrene, which allow reconstruction of unambiguous structures; the coupling of H13 is shown in expansion: the vicinal coupling ^3J(H12–H13) = 7.9 Hz generates the large dublett splitting; further splitting is effected by ^4J(H12–H14) = −1.3 Hz with favorable W-shaped geometry, which reflects a succession of two near 180° dihedral angles (cf. Karplus equation) and even ^6J(H13–H9) = 0.6 Hz is observable, in which two separate long-range coupling pathways coadd to result in a detectable splitting of the H13 NMR. ((a-c) Reproduced from Ref. 32.) (e) Complex environmental mixtures similar to this marine organic matter depth profile (800 MHz ^{1}H NMR spectra), normalized to identical integral area, exhibit low-resolution NMR signatures resulting from extensive superposition of NMR resonances.[8] Integration provides quantities of coarse substructure regimes; NMR spectra of environmental samples acquired at increased B_0 show enhanced sensitivity and resolution as well as improved assignment options from combinations of multinuclear and higher dimensional NMR spectra. (Reproduced from Ref. 8. Distributed under the Creative Commons Attribution 3.0 License)