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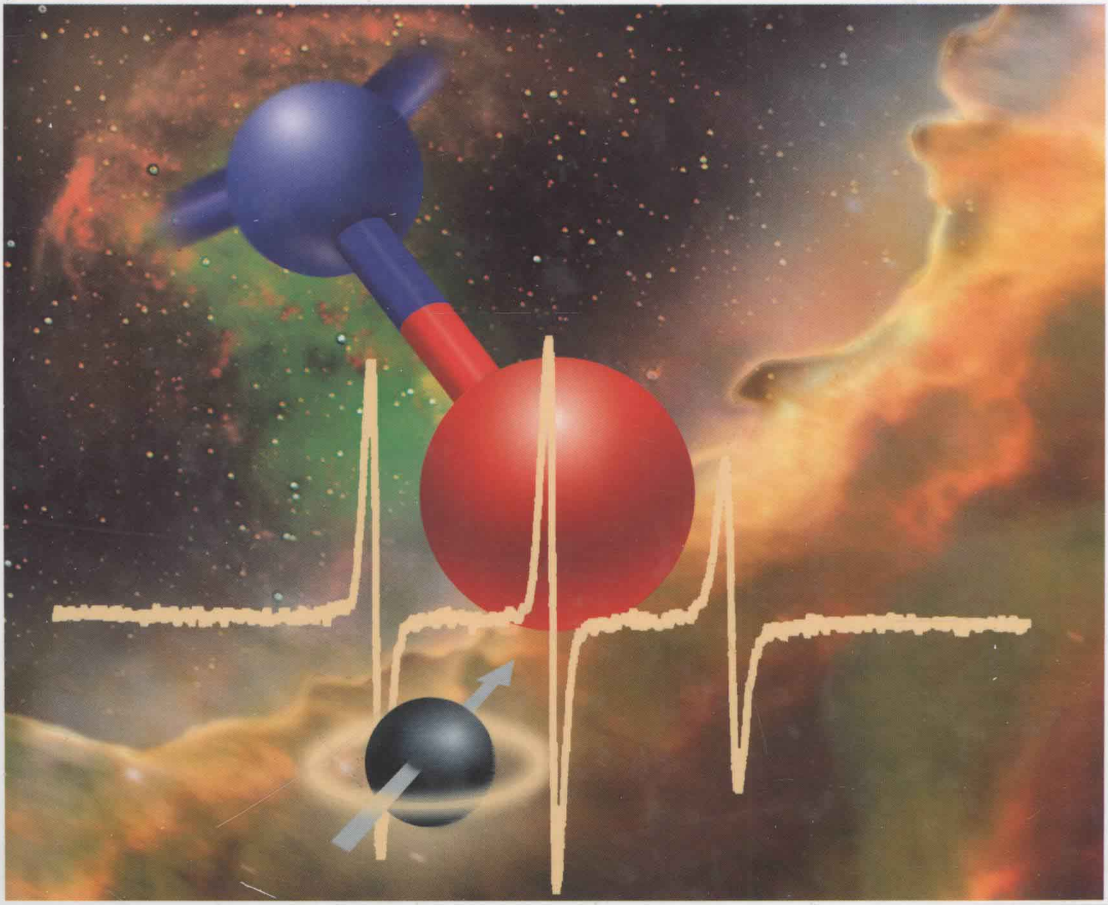
Applications in Chemistry, Biomedicine, and Materials Science



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Shin'ichi Nakatsuji, Alex I. Smirnov,
and Rui Tamura

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Further Reading

M. Kaupp, M. Bühl, V. G. Malkin (Eds.)

Calculation of NMR and EPR Parameters

Theory and Applications

2004

ISBN 978-3-527-30779-1

P. G. Wang, T. B. Cai, N. Taniguchi (Eds.)

Nitric Oxide Donors

For Pharmaceutical and Biological Applications

2005

ISBN 978-3-527-31015-9

R.-A. Eichel, S. Weber

Introduction to EPR Spectroscopy

Applications from Life to Materials Science

2009

ISBN 978-3-527-31849-0

Preface

Stable nitroxide radicals have proved to be effective tools in solving many problems in chemistry, physics, biology, and biomedicine at the molecular level. The nitroxide labels are used as "molecular rulers" to measure the distances between chosen groups and to measure the size, form, and micro-relief of objects of interest. The labels provide information that helps the scientist to understand the structure and molecular dynamics of individual molecules, polymers, liquid crystals, enzymes, proteins, membranes, and nucleic acids and how they function. Recently, new important developments of nitroxides as redox-probes, spin-traps, imaging and pharmokinetic reagents, and magnetic materials have been reported. Nitroxide derivatives are successfully used for the investigation of chemical kinetics, photophysical, and photochemical processes. Therapeutic and clinical applications of nitroxides appear to be a new advance in medicine.

This volume covers all aspects of this field. It also critically discusses recent results obtained with the use of nitroxides and gives an analysis of developments in the field in the future.

This book is a view of the area by a group of scientists with long-term experience in the investigation of chemistry, physicochemistry, biochemistry, and biophysics of nitroxides. It is not intended to provide an exhaustive survey of each topic but rather a discussion of their theoretical and experimental background, and recent developments. The literature of nitroxides is vast and many scientists have made important contributions in the area so that it is impossible in the space allowed in this book to give a representative set of references. The authors apologize to those they have not been able to include. More than 1100 references are given, which should provide a key to essential relevant literature.

In Chapters 1 to 3 (J. Yamauchi) of the present monograph, the general theoretical, and experimental background is expounded for magnetic properties and ESR techniques. Chapter 4 (A. Smirnov) describes recent advances in modern ESR technique and related areas, which to a considerable extent were stimulated by the growing requirements of nitroxide application in biology and biomedicine. Fundamentals, recent results in preparation, and basic chemical properties of nitroxides are the main subject of Chapter 5 (S. Nakatsuji)

Chapters 6 and 7 (G.I. Likhtenshtein) offer a brief outline of principles and current results in nitroxide application as spin-labels and spin-probes in the

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investigation of the molecular dynamics and microstructure of biological and non-biological objects, and as redox-probes and spin-traps. An important role of nitroxides as spin pH-meters, spin oximeters, and reactive radical–nitron adducts is elucidated. These chapters form the basis for subsequent profound studies of molecular properties of various objects such as polymers, inorganic materials, complexes of nitroxides with paramagnetic metals, photochemical systems, and so forth (Chapter 8 by G.I. Likhtenshtein). Advantages in a new area, the construction and investigation of magnetic materials on the basis of nitroxides are the subjects of Chapter 9 (R. Tamura). Chapter 10 (G.I. Likhtenshtein) discusses recent results from the utilization of the spin-labeling method for the investigation of molecular structure, dynamics, and functional activity of proteins, enzymes, biomembranes, nucleic acids, and polysaccharides. The concluding Chapter 11 (G.I. Likhtenshtein) considers biomedical, therapeutic, and clinical applications of nitroxides in areas which appear to be of great importance for human wellbeing.

Chemical, biochemical, biomedical, and material researchers may find in this book knowledge about fundamentals, instrumentation, data interpretation, capacity, and recent advances in nitroxide applications. It will help them to understand how nitroxides can help to solve their own problems. Physicists and experts in ESR instrumentation may learn about current problems and achievements in various areas of chemistry and molecular biology, and in the rapidly developing field of the application of nitroxides in biomedicine and medicine in particular. The book is also suited as a subsidiary text for instructors, graduate, and undergraduate students of university biochemical and chemical departments.

The authors are very grateful to Drs A. Rockenbauer, V. Khramtsov, F. Villamena, and A. Wasserman for their valuable advice and fruitful discussions. Finally, the authors are deeply indebted to Dr H. Tsue for his generous help in the preparation of the manuscript.

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Symbols and Abbreviations

Symbols

α	electron spin quantum number $m_S = 1/2$
	angle, alternating parameter
	anisotropic exchange parameter
α_n	nuclear spin quantum number $m_I = 1/2$
β	spin quantum number $m_s = -1/2$
	angle
β_n	nuclear spin quantum number $m_I = -1/2$
δ_{ij}	Kronecker δ
θ	angle
	Curie-Weiss constant
ΔH	line-width
$\Delta H_{1/2}$	half height line-width
ΔH_{pp}	peak-to-peak line-width
ΔH_{msl}	maximum-slope line-width
$\Delta H_{\omega 1/2}$, $H_{\omega pp}$	line-width in frequency
ε_0	dierectric constant
ε_F	Fermi energy
η	$\|J'/J\|$
Γ	molecular field coefficient
γ	gyromagnetic ratio
	exchange interaction parameter
	anisotropic exchange parameter
γ_n	nuclear gyromagnetic ratio
ϕ	molecular orbital
	relaxation function
Ψ	molecular orbital
ψ	atomic orbital
ν	frequency
μ	magnetic permeability
μ_0	magnetic permeability of free space

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μ_B	Bohr magneton
μ_n	nuclear Bohr magneton
$\mathcal{H}$	Hamiltonian
ρ	spin density, life-time probability
Λ	$\Lambda_{\mu\nu}$-tensor
$\Lambda_{\mu\nu}$	second order perturbation of spin–orbit interaction
λ	spin–orbit coupling constant
τ, τ_c	correlation time, life time
τ_C	correlation time
ω	(angular) frequency
ω_C	cyclotron frequency
ω_L	Larmorfrequency
χ	magnetic susceptibility
$\chi_{//}$	parallel magnetic susceptibility
$\chi_{\perp}$	perpendicular magnetic susceptibility
χ_{dia}, χ_{para}, χ_{TIP}	diamagnetic, paramagnetic, and temperature-independent paramagnetic magnetic susceptibility
A	hyperfine coupling constant
A_{aniso}	anisoptpic hyperfine splitting
	A_x, A_y, A_z or A_{xx}, A_{yy}, A_{zz}
$\mathbf{A}_{dip}$	dipolar hyperfine tensor
A_{iso}	average of **A**-tensor
A_{sol}	hyperfine coupling constant in solution
$\mathbf{A}_0$	hyperfine tensor of Fermi contact term
A_0	Fermi contact hyperfine coupling constant
$\mathbf{B}$	magnetic induction
B_J	Brillouin function
C	Curie constant
	Coulomb integral
c	light velocity
$\mathbf{D}$	**D**-tensor
D	zero-field splitting parameter
E	energy,
	zero-field splitting parameter
F	force
FT	Fourier transformation
G	Gaussian (function)
	complex magnetization
	autocorrelation function
g	g-value
g_e	free electron g-value
g_n	nuclear g-value
g_{iso}	average of g-tensor
g_{sol}	g-value in solution
h	Planck constant

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$\boldsymbol{H}$, H	magnetic field (strength)
H_1	oscillating magnetic fiel
H_a	anisotropic field
H_e	exchange field
H_C	coercivity (coercive force)
H_{cr}	critical field
H_{eff}	effective field
H_{dip}	dipolar field
H_{ex}	exchange field
$\boldsymbol{H}_{mol}$, H_{mol}	Wiss molecular field
I	nuclear spin operator
$\boldsymbol{I}$	nuclear spin angular momentum
	light intensity
I	nuclear spin quantum number
	function of η
J	total angular momentum operator
$\boldsymbol{J}$	total angular momentum
J	quantum number of total angular momentum
	exchange integral
	spectral density
	power spectrum
J	the resonance integral or coupling factor
K	anisotropy constant
k	Boltzmann constant
	rate constant
L	orbital angular momentum operator
	nitary matrix
L	L-band
$\boldsymbol{L}$	orbital angular momentum
L	quantum number of orbital angular momentum
L	Lorentzian (function)
	Langevin function
l	azimutal quantum number
$\boldsymbol{M}$	magnetization
M	magnetization (M_x, M_y, M_z, M_0)
M_S	saturation magnetization
M_r	residual magnetization
$\boldsymbol{m}$	magnetic moment
$\boldsymbol{m}_{eff}$, m_{eff}	effective magnetic momnt
m_e	mass of electron
m_p	mass of proton
m_i ($i = l$, S, I)	quantum number
n	principal quantum number
Q^{i}_{ij}	McConnell proprotionality

$\boldsymbol{R}$	relaxation term
$\mathbf{S}$	spin operator (electron)
$\boldsymbol{S}$	spin angular momentum (electron)
S	spin quantum number (electron)
s	spin quantum number $s = 1/2$ (electron)
	saturation factor
Tr	trace
T_i ($i = x,y,z$)	triplet basis functions
T_1	spin–lattice relaxation time
T_2	spin–spin relaxation time
T_C	Curie temperature
T_N	Neel temperature
t	time
u	magnetization
v	magnetization
X	X-ray, X-band
z	number of the nearest neighbor or the interchain paths

Abbreviations

CT	charge-transfer
CW-ESR	continuous wave-electron magnetic resonance
DANO	di-*p*-anisyl nitroxide
DDQ	2,3-dichloro-5,6-dicyano-*p*-benzoquinone
DEER	double electrone electron resonance
DMPO	5,5-dimethylpyrroline-*N*-oxide
DPPH	diphenyl picryl hydrazyl
DQC	double quantum coherence
DTBNO	di-*t*-butyl nitroxide
ED-ESR	echo detected ESR
ELDOR	electron double resonance
ESR	electron spin resonance
ENDOR	electron nuclear double resonance
ESEEM	electron spin echo envelope modulation
FT-ESR	Fourier transform-electron spin resonance
hfcc	hyperfine coupling constant
hfs	hyperfrine splitting
HOMO	highest occupied molecular orbital
HTS	high temperature-series (expansion)
IN	imine nitroxide
LCAO	linear combination of atomic orbital
LUMO	lowest unoccupied molecular orbital
MD	molecular dynamics
MM	molecular mechanics

MO	molecular orbital
NMR	nuclear magnetic resonance
NMLP	nitroxide mediated leavingpolymerization
NR, NRO·	nitroxide radical
NNR, NNRO·	nitronyl nitroxide radical
PBN	phenyl *t*-butyl nitrone
POBN	α–(4-pyridyl-1-oxide)-*N*-*t*-butylnitrone
SDSL	site-directed spin-labeling
SO	super oxide
SOD	super oxide dismutase
SOMO	singly occupied molecular orbital
SQUID	superconducting quantum interference device
PEDRI	proton electron double resonance imaging instrumentation
PELDOR	pulse electron-electron double resonance
ROS	reactive oxygen species
SIFTER	single-frequency technique for refocusing
TANOL	2,2,6,6-tetramethylpiperidin-4-ol-1-oxyl
TEMPOL	2,2,6,6-tetramethylpiperidinyl-1-oxyl
TEMPO	2,2,6,6-tetramethylpiperidinyl-1-oxy
TPV	1,3,5-triphenylverdazyl
PROXYL	2,2,5,5-tetramethylpyrrolidinyl-1-oxy
TCNE	tetracyanoethylene
TCNQ	7,7,8,8-tetracyanoquinodimethane
$TCNQF_4$	2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane
TMM	trimethylenemethane
TTF	tetrathiafulvalene
	bis(ethylenedithio)tetrathiafulvalene
TMTSF	tetramethyltetrathiafulvalene
TRESR	time-resolved electron spin resonance

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