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Electron Spin Resonance Spectroscopy of Organic Radicals

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Contents

Preface

Several years ago, electron spin resonance (ESR) spectroscopy celebrated the 50th anniversary of its discovery in 1944. Its application to organic radicals [1] underwent rapid expansion in the following three decades, with many monographs being published between 1965 and 1978 [2–15]. Among them, a booklet by one of us, entitled *High-Resolution ESR Spectroscopy* [6], concerned the multiline hyperfine patterns of organic radicals in solution. The radicals discussed were mostly ions readily generated by reduction or oxidation of aromatic compounds. This limitation permitted the number of pages to be kept low, and the comprehensible treatment made the booklet attractive to researchers with a background in organic chemistry. Suggestions for writing a second, updated version have been made repeatedly since then, but for various reasons, they were not implemented. Only recently, after the author's retirement in 1997, was such a project envisaged and, two years later, also tackled. It soon became obvious that supplementing the booklet with a few paragraphs would not suffice to account for the important developments in the field and, particularly, for the enormous amount of data accumulated in the literature during the last third of the 20th century. Thus, an almost completely new and more comprehensive volume had to be written, but we have tried to preserve the lucidity of its modest forerunner.

The term ESR has been retained throughout, even though the more extensive term electron paramagnetic resonance (EPR) has been recommended. As argued in Chapt. 2.1, this is because the magnetism of organic radicals is predominantly due to the electron spin. Also retained has been a division of the contents into a General Part A, serving as an introduction to the field, and a Special Part B, in which organic radicals are classified and characterized by their hyperfine data.

The most important topics added to the first version are as follows.

(1) Organic π radicals, both charged and neutral, as well as σ radicals, have been fully dealt with. (2) Biradicals and triplet molecules have also received consideration. (3) More attention has been given to g_e factors of radicals. (4) The origin and consequences of g_e and hyperfine anisotropies have been described (thus the epithet ''high-resolution'' is no longer appropriate). (5) New methods for generation of radicals have been introduced, in particular those producing radical cations from compounds with higher ionization energy, either by more efficient reagents in solution or by X- or γ-irradiation in solid matrices. (6) Multiresonance methods

have been described, especially electron-nuclear double resonance (ENDOR) spectroscopy [12, 15, 16] and its physical fundamentals. (7) Modern quantum-chemical procedures for calculation of spin distribution in radicals, going beyond the π-electron models, have been briefly presented and their results for particular radicals are quoted. However, the theories underlying these procedures are outside the scope of this monograph; the pertinent computer programs are readily available and can easily be handled by experimentalists.

Several areas in the field, which are less relevant to ESR spectroscopy of organic radicals and thus have not been dealt with, are listed below.

(1) Paramagnetic species in physics and biology, like color centers in crystals and radicals produced by high-energy irradiation of biological material. (2) Chemistry of radicals as such, although we have indicated throughout how radicals are generated and, in many cases, into which secondary paramagnetic species they convert. (3) Complexes of organic ligands with transition metals, because their structure strongly differs from that of organic radicals and their hyperfine interactions are dominated by those with the nuclei of heavy atoms. (4) Instrument conditions other than those at constant waves (CW), namely the pulsed ESR and ENDOR techniques.

A book illuminating the achievements in the ESR field appeared in 1997 [17]. Data relevant to radicals (g_e factors and hyperfine-coupling constants) have been compiled in the Landolt–Börnstein Tables since 1965 [18], and publications on ESR spectroscopy have been reviewed in Chemical Society Special Reports since 1973 [19].

Abbreviations and Symbols

ESR	electron spin resonance
EPR	electron paramagnetic resonance
ENDOR	electron-nuclear double resonance
ELDOR	electron-electron double resonance
TRIPLE	electron-nuclear-nuclear triple resonance
NMR	nuclear magnetic resonance
MW	microwaves
RF	radio frequency
SLR	spin-lattice relaxation
SSR	spin-spin relaxation
ZFS	zero-field splitting
AO	atomic orbital
LCAO	linear combination of AOs
MO	molecular orbital
SOMO	singly occupied MO
HOMO	highest occupied MO
LUMO	lowest occupied MO
NHOMO	next highest occupied MO
NLUMO	next lowest occupied MO
NBMO	nonbonding MO
IE	ionization energy
EA	electron affinity
UHF	unrestricted Hartree-Fock
DODS	different orbitals for different spins
INDO	intermediate neglect of differential overlap
MNDO	modified neglect of differential overlap
AM1	Austin model 1 (reparametrized version of MNDO)
DFT	density functional theory
ACN	acetonitrile
DME	1,2-dimethoxyethane

DEE	diethylether
DMF	N,N-dimethylformamide
DMSO	dimethylsulfoxide
MTHF	2-methyltetrahydrofuran
TFA	trifluoroacetic acid
THF	tetrahydrofuran
Alk	alkali-metal atom
COT	cyclooctatetraene
DABCO	1,4-diazabicyclo[2.2.2]octane
DDQ	2,3-dichloro-5,6-dicyano-p-benzoquinone
DPPH	2,2-diphenyl-1-picrylhydrazyl
TCNE	tetracyanoethene
TCNQ	7,7,8,8-tetracyanobenzo-1,4-quinodimethane
TEMPO	2,2,6,6-tetramethyl-4-oxopiperidin-1-oxyl
TME	tetramethyleneethane
TMM	trimethylenemethane
TTF	1,4,5,8-tetrahydro-1,4,5,8-tetrathiafulvalene
e	elementary charge
m_e	(rest) mass of electron
m_p	(rest) mass of proton
A	absorption intensity of ESR line
$\vec{\mathbf{B}}$	external magnetic field
B	strength of magnetic field $\bar{\mathbf{B}}$
ΔB	line-width in mT
$\Delta B_{1/2}$	line-width at half-height
dA/dB	first derivative of A with respect to B
ΔB_{pp}	peak-to-peak-distance in dA/dB
v	frequency
$\omega = 2\pi v$	circular frequency
v_e	resonance frequency of electron
v_n	resonance frequency of nucleus
Δv	line-width in MHz
T	absolute temperature in K
t	time
Δt	lifetime of spin state
T_{1e}	SLR time of electron
T_{2e}	SSR time of electron
T_{1n}	SLR time of nucleus
T_x	SLR cross-relaxation time
τ	lifetime of an individual form of radical

τ_r	rotational correlation time
P	transition probability
η	viscosity of the solvent
h	Planck constant
$\hbar$	$h/2\pi$
k	Boltzmann constant
μ_o	permeability of vacuum
$\vec{\mathbf{S}}$	electron-spin vector
S_x, S_y, S_z	components of $\vec{\mathbf{S}}$
S	electron-spin quantum number
M_S	magnetic electron-spin quantum number
α	spin function for $M_S = +1/2$ (spin up)
β	spin function for $M_S = -1/2$ (spin down)
$\vec{\boldsymbol{\mu}}_e$	magnetic moment of electron
$\mu_{e,x}$, $\mu_{e,y}$, $\mu_{e,z}$	components of $\vec{\boldsymbol{\mu}}_e$
g_e	g factor of electron
μ_B	Bohr magneton
γ_e	gyromagnetic ratio of electron
$\vec{\mathbf{I}}$	nuclear spin vector
I	nuclear spin quantum number
M_I	magnetic nuclear spin quantum number
I_s	spin quantum number of a subset of equivalent nuclei
$\vec{\boldsymbol{\mu}}_n$	magnetic moment of nucleus
$\mu_{n,x}$, $\mu_{n,y}$, $\mu_{n,z}$	components of $\vec{\boldsymbol{\mu}}_n$
g_n	g factor of nucleus
μ_N	nuclear magneton
γ_n	gyromagnetic ratio of nucleus
T_x, T_y, T_z	components of triplet spin state
T_{+1}, T_0, T_{-1}	components of triplet spin state in a relatively strong field $\vec{\mathbf{B}}$
$\mathbf{D}$	ZFS tensor
D_x, D_y, D_z	principal values of $\mathbf{D}$
D and E	ZFS parameters in cm^{-1}
D' and E'	ZFS parameters in mT
$\vec{\mathbf{r}}$	vector joining $\vec{\boldsymbol{\mu}}_e$ and $\vec{\boldsymbol{\mu}}_n$ or $\vec{\mathbf{S}}$ and $\vec{\mathbf{I}}$
r	length of $\vec{\mathbf{r}}$
φ	angle between $\vec{\mathbf{r}}$ and $\vec{\mathbf{B}}$ in a relatively strong field $\vec{\mathbf{B}}$
J	exchange integral over two SOMOs

E_{hf}	energy of hyperfine interaction
E_{dip}	energy of dipolar hyperfine interaction
E_{Fc}	energy of Fermi-contact term
δ_{Fc}	NMR shift due to Fermi-contact term
$\rho(x, y, z)$	electron density
$\rho_S(x, y, z)$	spin density
ρ_X^ψ	spin population in an orbital ψ (AO or MO) centered at the nucleus X
ρ_μ^π	π-spin population at π-center μ
ψ_j	π-MO
ϕ_μ	p_z-AO at π-center μ
$c_{j,\mu}$	LCAO coefficient at center μ for ψ_j
X	nucleus or the atom pertinent it
$X(\alpha), X(\beta), X(\gamma), X(\delta), X(\varepsilon), \ldots$	X separated from the spin-bearing center (usually π-center) by $1, 2, 3, 4, 5, \ldots$ sp^3-hybridized atoms
a_X	isotropic hyperfine-coupling constant of X in mT
a_X'	isotropic hyperfine-coupling constant of X in MHz
a_{X_μ}	isotropic hyperfine-coupling constant of X in or at π-center μ in mT
a_{X_μ}'	isotropic hyperfine-coupling constant of X in or at π-center μ in MHz
$\mathbf{A}_X$	hyperfine tensor of X
$A_{X,x}, A_{X,y}, A_{X,z}$	principal values of $\mathbf{A}_X$ in mT
$A_{X,x}', A_{X,y}', A_{X,z}'$	principal values of $\mathbf{A}_X$ in MHz
$A_{H\parallel}, A_{H\perp}$	principal values of an axial tensor $\mathbf{A}_X$ in mT
$A_{H\parallel}', A_{H\perp}'$	principal values of an axial tensor $\mathbf{A}_X$ in MHz
$\mathbf{A}_{X,dip}$	(traceless) hyperfine-anisotropy tensor of X
$2B_{X,dip}, -B_{X,dip}$	principal values of an axial tensor $\mathbf{A}_{X,dip}$ in mT
$2B_{X,dip}', -B_{X,dip}'$	principal values of an axial tensor $\mathbf{A}_{X,dip}$ in MHz
$\mathbf{G}_e$	tensor of the g_e factor
$g_{e,x}, g_{e,y}, g_{e,z}$	principal values of $\mathbf{G}_e$
$g_{e\parallel}, g_{e\perp}$	principal values of an axial $\mathbf{G}_e$ tensor
Δg_e	$g_{e\parallel} - g_{e\perp} = g_{e,z} - 1/2(g_{e,x} + g_{e,y})$
$\mathbf{G}_{e,aniso}$	(traceless) tensor with anisotropic contributions to g_e as principal values
$Q_H^{X_\mu H_\mu}$	π,σ-spin polarization parameter for α-protons
$B_H^{X_{\mu'} H_{\mu'}}$	π,σ-spin delocalization parameter for β-protons
$Q_X, Q_X^{X_\mu X_\nu}, Q_X^{X_\nu X_\mu}$	π,σ-spin polarization parameters for nuclei X other than protons
S_C	π-1s spin polarization parameter for C

θ — dihedral angle between p_z-axis at the spin-bearing center and direction of C–H(β) bond of an alkyl substituent, in particular, and of X(α)–X(β), in general.

U, V, W — parameters for anisotropy contributions to ΔB in solution

A
General Part

Part A, comprising Chapters 1.1 through 6.7, is an introduction to electron spin resonance (ESR) spectroscopy of organic radicals. It is amply garnished with examples illustrating how ESR spectra are obtained and what information they provide on the structure of these paramagnetic species. A large number of cited references and most of the illustrating examples have been taken from our work, because we are best familiar with them. This selection has been made by convenience and it does not claim to be guided by criteria of quality.

1
Physical Fundamentals of Electron Spin Resonance

1.1
Spin and Magnetic Moment of Electron

Spin is an intrinsic, nonclassical, orbital angular momentum. If one considers electron spin to be a kind of motion about an axis of the electron, an analogy may be drawn between an atom (microcosmos) and the solar system (macrocosmos), as illustrated in Figure 1.1.

The concept of spin was suggested by Uhlenbeck and Goudsmit in 1925 [17a, 20] to account for the splitting of lines in the electronic spectra of alkali-metal atoms in a magnetic field. Such splitting, known as the *Zeeman effect*, could not arise from an orbital angular momentum, which is zero for electrons in the s orbitals of an alkali-metal atom. Spin functions were introduced theoretically in 1926 by Pauli, as a complement of spatial functions [21]. Later, Dirac [22] showed that spin emerges without additional postulates from a relativistic treatment of quantum mechanics.

Pauli's procedure is generally followed, according to which a spin quantum number $S = 1/2$ is assigned to an electron. In the presence of a strong external magnetic field $\vec{\mathbf{B}}$, a second (magnetic) quantum number $M_S = +1/2$ or $-1/2$ becomes effective, and the functions associated with M_S are denoted α and β, respectively. The spin can then be represented by a vector $\vec{\mathbf{S}}$ precessing about $\vec{\mathbf{B}}$ in the z direction (Figure 1.2). The length of this vector is $|\vec{\mathbf{S}}| = \hbar\sqrt{S(S+1)} = \hbar\sqrt{3}/2$, where $\hbar = h/2\pi$ and $h = 6.6262 \cdot 10^{-34}$ J·s is Planck's constant. The component S_z in the z direction is $\hbar M_S = +\hbar/2$ or $-\hbar/2$, with the former
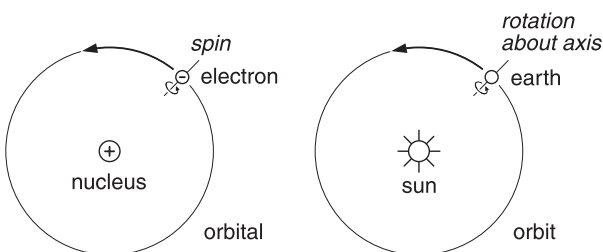

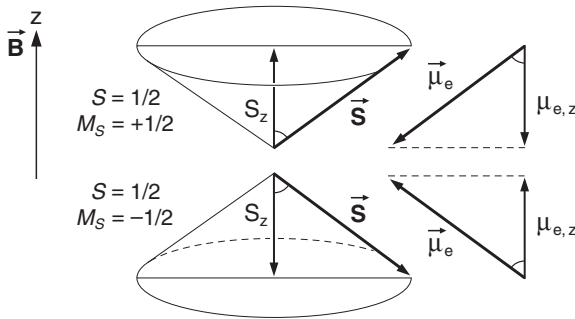**Fig. 1.1.**   Analogy between an atom and the solar system.

Fig. 1.2. Precession of the spin vector $\vec{S}$ about the magnetic field $\vec{B}$ in the z direction.

being parallel and the latter antiparallel to the z direction. The spin with $M_S = +1/2$ is also denoted spin up (↑) and α, and its counterpart with $M_S = -1/2$ is named spin down (↓) and β. While precessing about $\vec{B}$, the vector $\vec{S}$ traces a conic area with a half-opening angle of $\arccos(1/\sqrt{3}) = 54.73°$. The components S_x and S_y, perpendicular to the z direction of $\vec{B}$, cannot be determined individually; however, the sum of their squares, $S_x^2 + S_y^2 = |\vec{S}|^2 - S_z^2 = \hbar[S(S+1) - M_S^2] = \hbar[3/4 - 1/4] = \hbar/2$ is an observable quantity.

Due to its spin (classically, a rotating charge), an electron possesses a *magnetic moment* $\vec{\mu}_e$ which is proportional to $\vec{S}$ (Figure 1.2).

$$\vec{\mu}_e = [g_e(-e)/(2m_e)]\vec{S} \tag{1.1}$$

with $|\vec{\mu}_e| = [g_e e/(2m_e)]\hbar\sqrt{S(S+1)}$ and $\mu_{e,z} = [g_e(-e)/(2m_e)]\hbar M_S$. Here, g_e is the (dimensionless) *g factor* of the electron, which is 2.0023 for a free electron (0.0023 is the relativistic correction), $e = 1.6022 \cdot 10^{-19}$ C is the elementary charge, and $m_e = 9.1096 \cdot 10^{-31}$ kg is the rest mass of the electron. Setting $\hbar e/(2m_e) = \mu_B = 9.2741 \cdot 10^{-24}$ A·m^2 or J·T^{-1}, where μ_B is the *Bohr magneton*, and T = Tesla = V·s·m^2 is the unit of magnetic field $\vec{B}$, Eq. 1.1 becomes

$$\vec{\mu}_e = -[g_e\mu_B/\hbar]\vec{S} \tag{1.2}$$

with $|\vec{\mu}_e| = g_e\mu_B\sqrt{S(S+1)} = g_e\mu_B\sqrt{3}/2$ and $\mu_{e,z} = -g_e\mu_B M_S = -g_e\mu_B(\pm 1/2)$. As $g_e \approx 2$, $|\vec{\mu}_e| \approx \mu_B\sqrt{3}$ and $\mu_{e,z} \approx \mp\mu_B$. Due to the negative charge of the electron, the direction of $\vec{\mu}_e$ is opposite to that of $\vec{S}$ (Figure 1.2).

1.2
Zeeman Splitting and Resonance Condition

By virtue of its magnetic moment $\vec{\mu}_e$, the electron interacts with the external magnetic field $\vec{B}$, the interaction energy E being equal to the negative value of the scalar
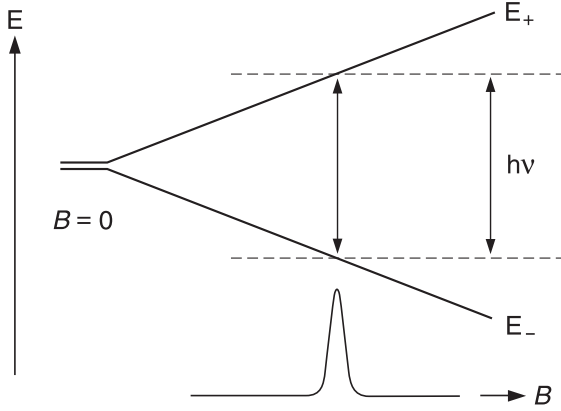
Fig. 1.3. Electron-Zeeman splitting as a function of the
strength, *B*, of the magnetic field and the resonance condition.

product of $\vec{\mu}_e$ and $\vec{B}$. Accordingly, this energy is

$$E = -\vec{\mu}_e \cdot \vec{B} = -\mu_{e,z}B = -(-g_e\mu_B M_S)B = +g_e\mu_B M_S B \tag{1.3}$$

where $|\vec{B}| = B$ the field strength, and $\mu_{e,z} = -g_e\mu_B M_S$. Therefore, E is different for
the two sorts of spin (Figure 1.3), namely:

$$E_+ = (+1/2)g_e\mu_B B \quad \text{for } M_S = +1/2 \quad \text{(spin up; } \alpha\text{)}$$
$$E_- = (-1/2)g_e\mu_B B \quad \text{for } M_S = -1/2 \quad \text{(spin down; } \beta\text{)} \tag{1.4}$$

The difference $E_+ - E_- = g_e\mu_B B$ is the electron-Zeeman splitting, which is pro-
portional to the strength, *B*, of the applied external magnetic field $\vec{B}$ (Figure 1.3).
Transitions $E_+ \leftrightarrows E_-$ between the two levels, i.e., spin inversions $\alpha \leftrightarrows \beta$, comply
with the selection rule $\Delta M_S = \pm 1$. These transitions can be induced by electro-
magnetic radiation hν, provided that

(i) the direction of the magnetic field associated with this radiation is perpen-
dicular to that (z) of the external magnetic field $\vec{B}$, i.e., it lies in the xy plane
(Figure 1.2), and
(ii) the energy of the radiation is equal to that of the *Zeeman splitting*

$$h\nu = E_+ - E_- = g_e\mu_B B \tag{1.5}$$

a relation known as the *resonance condition* (Figure 1.3). This condition can be
expressed as

$$\nu = g_e(\mu_B/h)B = \gamma_e B \quad \text{or} \quad \omega = g_e(\mu_B/\hbar)B = 2\pi\gamma_e B \tag{1.6}$$

where v (in $Hz = s^{-1}$) is the frequency of the electromagnetic radiation, and $\omega = 2\pi v$ is the circular frequency, which is also the frequency of the spin $\vec{S}$ precessing about $\vec{B}$ (the *Larmor frequency*) at resonance. The conversion factor of the frequency v into the field strength B, $\gamma_e = v/B = g_e \mu_B/h$, is called the *gyromagnetic* ratio of the electron. For $g_e = 2.0023$, $\gamma_e = 2.8024 \cdot 10^{10}$ Hz/T = 28.024 MHz/mT.

To satisfy the resonance condition, one can vary v or B or both. For technical reasons, the frequency v is kept constant and the field strength B is varied to bring it to the value at which the resonance condition is fulfilled. One generally uses the microwave (MW) X band with a frequency v of ca. 9500 MHz, which requires a field strength B of ca 340 mT.

1.3
Spin-lattice Relaxation

Besides the resonance condition, other prerequisites must be met for a successful electron spin resonance experiment. To observe an ESR signal, a single electron is not sufficient, but many of them (an *ensemble*) are needed. Also, the electrons should not be isolated but must be embedded in a suitable environment (a *lattice*), which is usually provided by atoms and molecules.

The numbers of electrons in the two Zeeman levels, E_+ and E_-, are their *populations* n_+ and n_-, respectively. According to the Boltzmann distribution law, the ratio of these populations is

$$n_+/n_- = \exp[-(E_+ - E_-)/(kT)] = \exp[-(g_e \mu_B B)/(kT)] \tag{1.7}$$

where $k = 1.3806 \cdot 10^{-23}$ J·K^{-1} is the Boltzmann constant, and T is the absolute temperature in K. In the absence of an external magnetic field ($B = 0$), n_+ is equal to n_-, but for $B > 0$, n_- is larger than n_+, i.e., there is an excess, $\Delta n = n_- - n_+$, of spins in the lower level E_- relative to the higher level E_+. To bring about this excess, some "hot" spins in E_+ ($M_S = +1/2$; spin up; α) must be converted into spins in E_- ($M_S = -1/2$; spin down; β). Such a "cooling" process, leading to magnetization, requires energy transfer from the spin ensemble to the lattice and is effected by *spin-lattice relaxation* (SLR). The excess Δn_m, at full magnetization at B, is

$$\Delta n_m \approx (n/2)(g_e \mu_B B)/(kT) \tag{1.8}$$

where $n = n_+ + n_-$ is the total number of spins in the ensemble. This excess is only slight: for $g_e = 2$, $B = 340$ mT, and $T = 298$ K, it amounts to merely 0.00077n. However, because the probability for an $E_+ \rightarrow E_-$ and an $E_- \rightarrow E_+$ transition is the same, it is due to an excess of this size that the radiation hv gives rise to net ESR absorption.

When the magnetic field is switched on, Δn should increase from 0 to Δn_m as a function of time t (Curve ①, Figure 1.4):
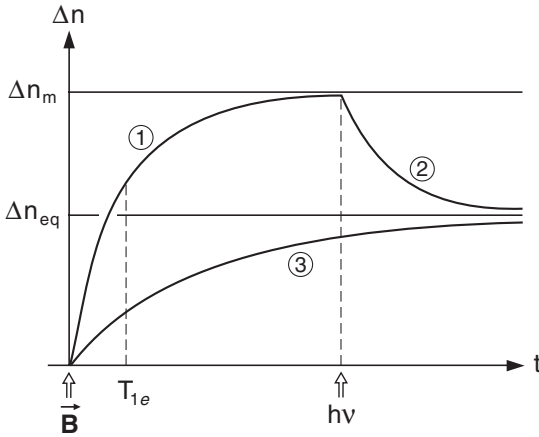
Fig. 1.4. Population excess, $\Delta n = n_- - n_+$ as a function of
time t. Curve ①, magnetization upon switching on $\vec{\mathbf{B}}$; curve ②,
partial decay of magnetization as a consequence of starting hν;
curve ③, magnetization upon simultaneous application of $\vec{\mathbf{B}}$
and hν.

$$\Delta n = \Delta n_m (1 - \exp[-t/T_{1e}]) \tag{1.9}$$

At $t = 0$ (switching on of $\vec{\mathbf{B}}$), $\Delta n = 0$, for $t \to \infty$, $\Delta n \to \Delta n_m$, and for $t = T_{1e}$,
$\Delta n = \Delta n_m (1 - \exp[-1]) \approx \Delta n_m (2/3)$. T_{1e} is called the *SLR time* of an electron, in
which the number of hot spins drops to 1/e or to ca 1/3. A short (or long) T_{1e}
means an efficient (or inefficient) SLR. This relaxation provides not only the means
for magnetization in the field $\vec{\mathbf{B}}$ but it also takes care that Δn does not vanish upon
continuous radiation hν. When hν is applied, and if SLR was ineffective, the pop-
ulations n_+ and n_- would equalize, with Δn decreasing from Δn_m to 0. This
is because the number of transitions $E_- \to E_+$ exceeds that of $E_+ \to E_-$. The
decrease of Δn, known as *saturation*, follows the equation

$$\Delta n = \Delta n_m \exp(-2Pt) \tag{1.10}$$

where P is the transition probability, common to $E_- \to E_+$ and $E_+ \to E_-$. At $t = 0$
(start of hν in $\vec{\mathbf{B}}$), $\Delta n = \Delta n_m$, and for $t \to \infty$, $\Delta n \to 0$.

Fortunately, SLR counteracts this effect and, consequently, equilibrium is
achieved at $0 < \Delta n_{eq} < \Delta n_m$ (Curves ② and ③, Figure 1.4):

$$\Delta n_{eq} = \Delta n_m / (1 + 2PT_{1e}) \tag{1.11}$$

The denominator $1 + 2PT_{1e}$, referred to as the saturation term, is large when P is
high and/or T_{1e} is long and small when P is low and/or T_{1e} is short.

The most important mechanism of SLR is *spin-orbit coupling*, which is substan-
tial for heavy atoms. For organic radicals lacking such atoms, SLR is not very effi-

cient and T_{1e} is rather long. Therefore, to keep the saturation term PT_{1e} as small as possible, P must be relatively low, which is achieved by attenuating the intensity of $h\nu$. However because the ESR absorption is proportional to both P and Δn_{eq}, i.e. to $P/(1 + 2PT_{1e})$, the attenuation should be carried on until the P value is optimal for observing a strong signal. Such P value is not the same for different samples investigated: the shorter (or longer) T_{1e} is, the larger (or smaller) it is and the higher (or lower) is the allowed intensity of $h\nu$. T_{1e} can be determined by saturation experiments, in which the term PT_{1e} is measured as a function of the applied intensity of $h\nu$.

1.4
Line-width and Line-form

The Heisenberg uncertainty relation, $\Delta E \cdot \Delta t \approx \hbar$, can be expressed by an equivalent formula:

$$\Delta\nu \cdot \Delta t = \gamma_e \Delta B \cdot \Delta t \approx 1/(2\pi) \tag{1.12}$$

where $\Delta\nu$ ($=\gamma_e\Delta B$) (in Hz) or ΔB (in mT) stands for the width of the ESR signal, and Δt (in s) is the lifetime of a spin state. A long- (or short-) lived state thus gives thus rise to a narrow (or broad) ESR signal.

The lifetime, Δt, of the spin state α ($M_S = +1/2$; spin up) or β ($M_S = -1/2$; spin down) is determined by the relaxation times T_{1e} and T_{2e}:

$$1/\Delta t \approx (1/T_{1e}) + (1/T_{2e}) \tag{1.13}$$

where T_{1e} is the spin-lattice relaxation (SLR) time, introduced in Chapt. 1.3, and T_{2e} is the *spin–spin-relaxation* (SSR) *time* of electron. Whereas SLR governs energy exchange between the spin ensemble and the environment (lattice), SSR comprises interactions within the ensemble itself without such an exchange. For instance, two radicals, 1 and 2, may interchange the different states of their electron spins (''flip-flop''), so that their total energy is not changed, but, nevertheless, the lifetime of an individual spin is reduced:

$$\text{Radical} \quad \begin{pmatrix} 1 & 2 \\ \alpha & \beta \end{pmatrix} \rightarrow \begin{pmatrix} 1 & 2 \\ \beta & \alpha \end{pmatrix}$$
$$\text{Spin}$$

Such a phenomenon, referred to as *Heisenberg exchange*, is particularly effective when the spin-bearing orbitals of the radicals overlap, which occurs with high radical concentrations. As mentioned above, T_{1e} is long for organic radicals without heavy atoms (10^{-3} to 10^{-1} s). Because T_{2e} is much shorter (10^{-5} to 10^{-7} s), the relations $T_{1e} \gg T_{2e}$ and $1/T_{1e} \ll 1/T_{2e}$ generally hold, leading to
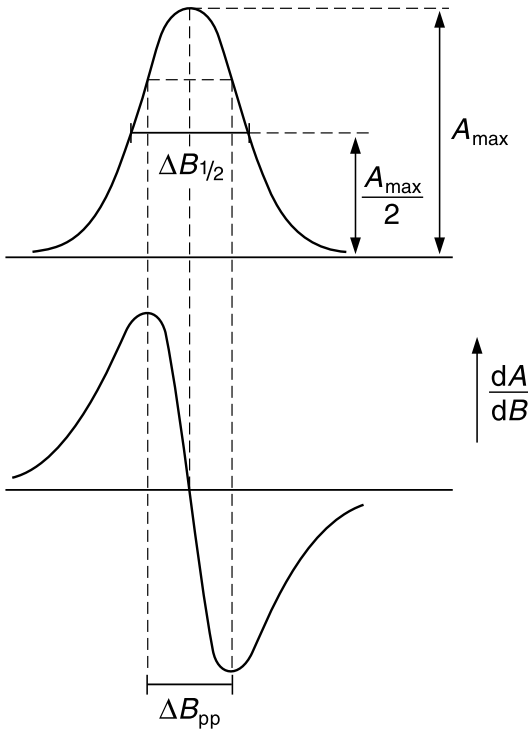
$$1/\Delta t \approx 1/T_{2e} \tag{1.14}$$

Fig. 1.5. ESR absorption A and its first derivative, dA/dB, as a function of the strength, B, of the magnetic field.

Hence, according to the uncertainty principle, the line-width becomes

$$\Delta v = \gamma_e \Delta B \propto 1/\Delta t \approx 1/T_{2e} \tag{1.15}$$

with $\Delta v \approx 10^5$ to 10^7 Hz and ΔB lies roughly in the range between 0.001 and 0.1 mT. Thus, T_{2e} can be determined from the measurements of the line-width ΔB.

The ESR signal is usually recorded as the first derivative, dA/dB, of the absorption A with respect to B as a function of B (Figure 1.5). The form of A can be approximated by a *Gaussian* or a *Lorentzian* curve or by an appropriate mixture of both, in which T_{2e} is multiplied by a function of T_{1e}^2, with T_{2e}^2 either in the exponent (Gaussian) or in the denominator (Lorentzian). The characteristic values are A_{max}, the maximum of A, and $\Delta B_{1/2}$, the peak width at its half-height ($A_{max}/2$), and ΔB_{pp}, the peak-to-peak distance of the derivative curve dA/dB (Figure 1.5). For the Gaussian, $A_{max} = \gamma_e 2T_{2e}$, with $\Delta B_{1/2} \approx 0.47/(\gamma_e T_{2e})$ and $\Delta B_{pp} \approx 0.85\Delta B_{1/2} \approx 0.40/(\gamma_e T_{2e})$, and for the Lorentzian, $A_{max} = \gamma_e 2T_{2e}$, with $\Delta B_{1/2} \approx 0.32/(\gamma_e T_{2e})$ and $\Delta B_{pp} \approx 0.58\Delta B_{1/2} \approx 0.18(\gamma_e T_{2e})$. The bell-like form of the Gaussian curve thus has a broader waist and shorter tails than its Lorentzian counterpart.

2
Paramagnetic Organic Species and Their Generation

2.1
Spin Multiplicity

Radicals are a special class of *paramagnetic* molecules [17b], i.e., those which are amenable to ESR spectroscopy. Although *diamagnetism* is a general property of matter, *paramagnetism* is diagnostic of molecules with an overall nonzero magnetic moment of their electrons. In such molecules, the paramagnetism masks the diamagnetism, because the contribution of the former is two orders of magnitude larger than that of the latter. In atoms, magnetic moments are due to the electron spins described in Chapt. 1.1, as well as to nonzero orbital angular momenta characteristic of electrons in other than the spherically shaped s orbitals. However, in molecules generally, and in organic molecules particularly, the orbital angular momenta are essentially ineffective ("quenched"), although they can slightly alter the g_e factor via spin-orbit coupling. The paramagnetism of organic molecules thus arises almost entirely from the electron spins.

When speaking about magnetic resonance of such molecules, one is, therefore, justified in using the name *electron spin resonance* (ESR) instead of more general expression *electron paramagnetic resonance* (EPR). Because organic molecules contain many electrons, the total spin function is derived from contributions by all electrons. These contributions cancel for most electrons (which occupy orbitals pairwise and have opposite spins). Thus, only electrons with unpaired spins in the singly occupied, usually uppermost, orbitals are relevant to the total spin function. The spin-quantum number S then becomes a positive algebraic sum of the corresponding numbers, $1/2$, of the unpaired electrons; and the spin multiplicity, $2S + 1$, which is even (or odd) for an odd (or even) number of electrons, represents the multitude of the magnetic spin-quantum numbers, $M_S = S, S - 1, \ldots -S$, associated with S. A single unpaired electron thus gives rise to a *doublet*, because $2S + 1 = 2$ for $S = 1/2$ and $M_S = +1/2$ or $-1/2$. Two unpaired electrons have either $S = (1/2) - (1/2) = 0$ or $S = (1/2) + (1/2) = 1$, i.e., they lead to a *singlet* with $2S + 1 = 1$ and $M_S = 0$ or to a *triplet* with $2S + 1 = 3$ and $M_S = +1, 0,$ or -1.

The pertinent singlet-spin function is

$$(1/\sqrt{2})(\alpha\beta - \beta\alpha) \quad \text{for } S = 0 \text{ and } M_S = 0 \tag{2.1}$$

and the analogous triplet functions are

$\alpha\alpha$ for $S = 1$ and $M_S = +1$

$(1/\sqrt{2})(\alpha\beta + \beta\alpha)$ for $S = 1$ and $M_S = 0$

$\beta\beta$ for $S = 1$ and $M_S = -1$ (2.2)

where the first and the second letters in $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, and $\beta\beta$ refer to the first and the second unpaired electron. The singlet function is *antisymmetric*, whereas the three components of the triplet are *symmetric* with respect to the exchange of the two electrons. Because the spin orbital, which is the product of the spin and the space (orbital) functions of electron, must be antisymmetric in this respect, the total function must be symmetric for the singlet and antisymmetric for the triplet.

The formalism introduced in Chapts. 1.1 and 1.2 holds for the spin vectors $\vec{\mathbf{S}}$ and magnetic moments $\vec{\boldsymbol{\mu}}_e$ and their interaction with $\vec{\mathbf{B}}$ for any multiplicity $2S + 1$. Thus, for a doublet with $S = 1/2$ and $M_S = +1/2$ or $-1/2$, the resulting values are essentially the same as those given in this chapters, and the illustration of $\vec{\mathbf{S}}$ precessing about $\vec{\mathbf{B}}$ (Figure 1.2) is also valid. For a singlet, with $S = M_S = 0$, the vectors $\vec{\mathbf{S}}$ and $\vec{\boldsymbol{\mu}}_e$ vanish, and so does the interaction of $\vec{\boldsymbol{\mu}}_e$ with $\vec{\mathbf{B}}$. On the other hand, for a triplet, with $S = 1$ and $M_S = +1, 0$, or -1, one obtains

$$|\vec{\mathbf{S}}| = \hbar\sqrt{2}, \quad S_z = +\hbar, 0, \text{ or } -\hbar; \quad |\vec{\boldsymbol{\mu}}_e| = g_e\mu_B\sqrt{2}; \quad \text{and}$$

$$\mu_{e,z} = g_e\mu_B M_S = +g_e\mu_B, 0, \text{ or } -g_e\mu_B \qquad (2.3)$$

As $g_e \approx 2$, $|\vec{\boldsymbol{\mu}}_e| \approx 2\mu_B\sqrt{2}$ and $\mu_{e,z} \approx +2\mu_B, 0$, or $-2\mu_B$. The interaction of $\vec{\boldsymbol{\mu}}_e$ with $\vec{\mathbf{B}}$ is

$$E = -\mu_{e,z}B = +g_e\mu_B M_S B = +g_e\mu_B B, 0, \text{ or } -g_e\mu_B B \qquad (2.4)$$

for $M_S = +1, 0$, or -1, respectively.

The precessions of the spin vectors $\vec{\mathbf{S}}$ of the singlet and the three components of the triplet in the magnetic field $\vec{\mathbf{B}}$ are shown in Figure 2.1.

According to the ESR-selection rule, $\Delta M_S = \pm 1$, transitions should be allowed between the energy levels with $M_S = +1$ and 0, as well as between those with $M_S = 0$ and -1 when the resonance condition, $h\nu = g_e\mu_B B$, is fulfilled for both kinds of transition. In fact, the transition scheme is more complicated, because of interaction between the spin vectors $\vec{\mathbf{S}}_1$ and $\vec{\mathbf{S}}_2$ of the unpaired electrons (Chapt. 2.4).

The spin multiplicities for any number of unpaired electrons in a molecule can be derived from a branching diagram (Figure 2.2). For example, three electrons yield one quartet and two doublets, and four electrons give rise to one quintet, three triplets, and one singlet. Clearly, singlets with $|\vec{\boldsymbol{\mu}}_e| = 0$ are, diamagnetic,
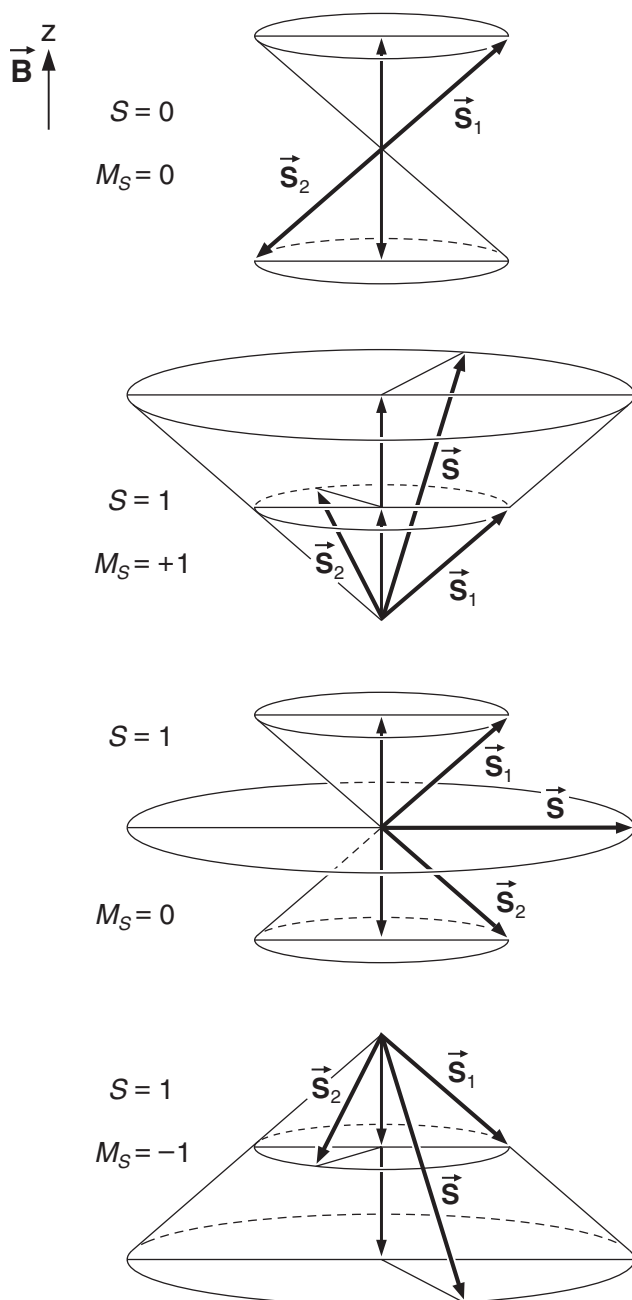
Fig. 2.1. Precession of the spin vector $\vec{S}$ about the magnetic field $\vec{B}$ in the z direction for the singlet (top) and the three components of the triplet.