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Spin Chemistry

Thanks to Prof. Peter Hore, Oxford

Lorentz Workshop Spin-Caloritronics

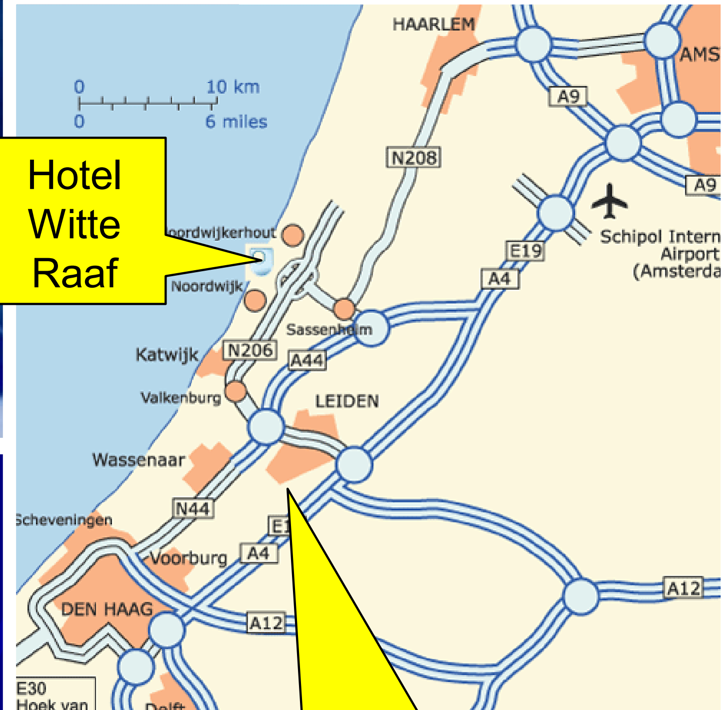
Leiden, 12 May 2011

SPIN CHEMISTRY MEETING 2011

The 12th International Symposium on Spin and Magnetic Field Effects in Chemistry and Related Phenomena

15-20 May 2011, Hotel Witte Raaf, Noordwijk, The Netherlands

http://scm2011.leidenuniv.nl



Hotel Witte Raaf

Lorentz-Center

Lorentz Workshop

SPIN-HYPERPOLARIZATION

Lorentz-Center, Leiden, scheduled for 30 Jan. - 3 Feb. 2012.

SPIN CHEMISTRY MEETING 2013

Badgastein, Austria

Updates, for example, at: http://www.cidnp.net/

Overview: Spin Chemistry

Effects of electron and nuclear spins **on the rates and yields of chemical processes**,

in particular those with **radical pairs** as reaction intermediates.

Overview: Spin Chemistry

Radical pair reactions

- **Spin states**
  - singlet (↑↓) & triplet (↑↑)

- **Formation**
  - bond homolysis: $A–B \rightarrow [A^{\bullet}\ B^{\bullet}]$
  - e⁻ transfer: $C + D \rightarrow [C^{\bullet+}\ D^{\bullet-}]$
  - H transfer: $E–H + F \rightarrow [E^{\bullet}\ F–H^{\bullet}]$

  - heat, light, ionizing irradiation, …
  - in liquid and solid states

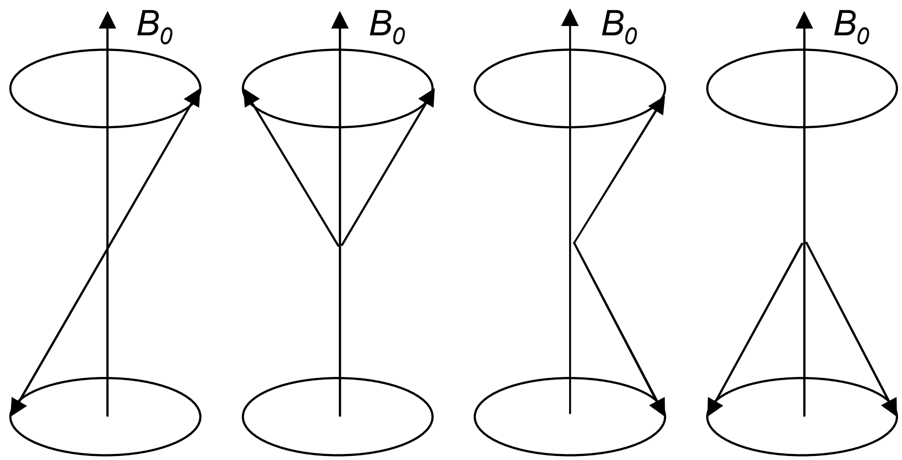
- **Spin-selective reactivity**
  - conservation of spin $^{S}C^{*} + D \rightarrow {}^{S}[C^{\bullet+}\ D^{\bullet-}]$ (Singlet-born RP)

    $^{T}[C^{\bullet+}\ D^{\bullet-}] \rightarrow {}^{T}C^{*} + D$ (Triplet-born RP)

Overview: Spin Chemistry

Four states in vector presentation

$R_1^\bullet$ + $R_2^\bullet$ pair: Vector model of electron spin states



Singlet S   Triplet T_+ Triplet T_0 Triplet T_-

Quantum states |j,m>

|1,1>	↑↑
|1,0>	**(↑↓ + ↓↑)/√2**
|1,1>	↓↓

} Three triplet states

|0,0>	**(↑↓ - ↓↑)/√2**

} One singlet state

Overview: Spin Chemistry

Radical pair interactions

- electron-nucleus: hyperfine interactions
  - ^{1}H, ^{14}N, ^{19}F, …
  - 1-100 MHz
  - anisotropic
- electron-electron: exchange & dipolar interactions
  - < hyperfine interactions when r_{ee} > ~1.5 nm
- electron-field: Zeeman interaction
  - 28 MHz per mT for $g \approx 2$
- $k_B T/h$: 6×10^6 MHz at 300 K

Overview: Spin Chemistry

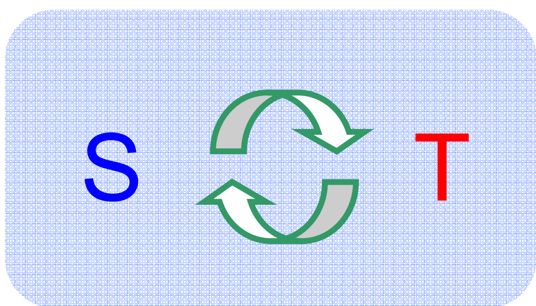
Radical pair properties

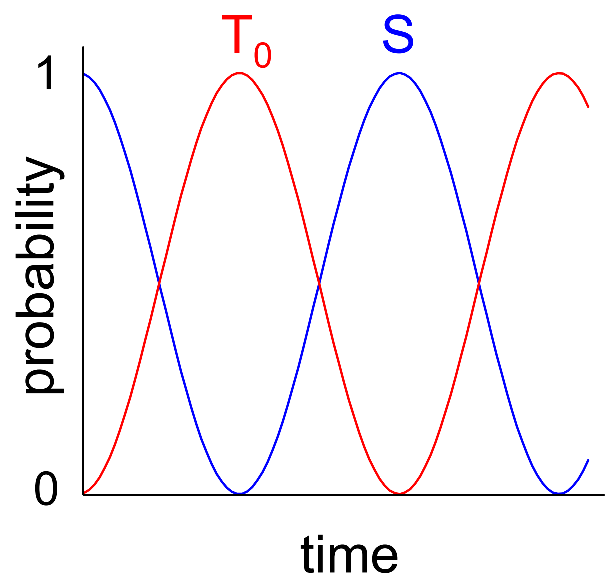
- lifetimes
  - typically 10 ns – 1 μs in solution
  - potentially unlimited in solids
- spin relaxation
  - typically 10 ns – 1 μs
- spin correlation
  - S and T are normally non-stationary states

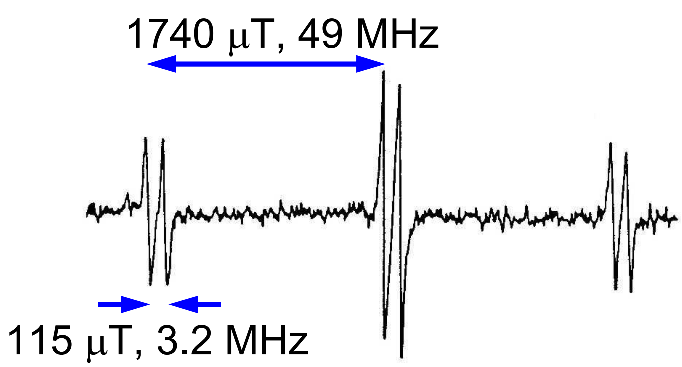
Overview: Spin Chemistry

Coherent singlet-triplet interconversion

- S and T states are not stationary states
- interconverted by weak magnetic interactions



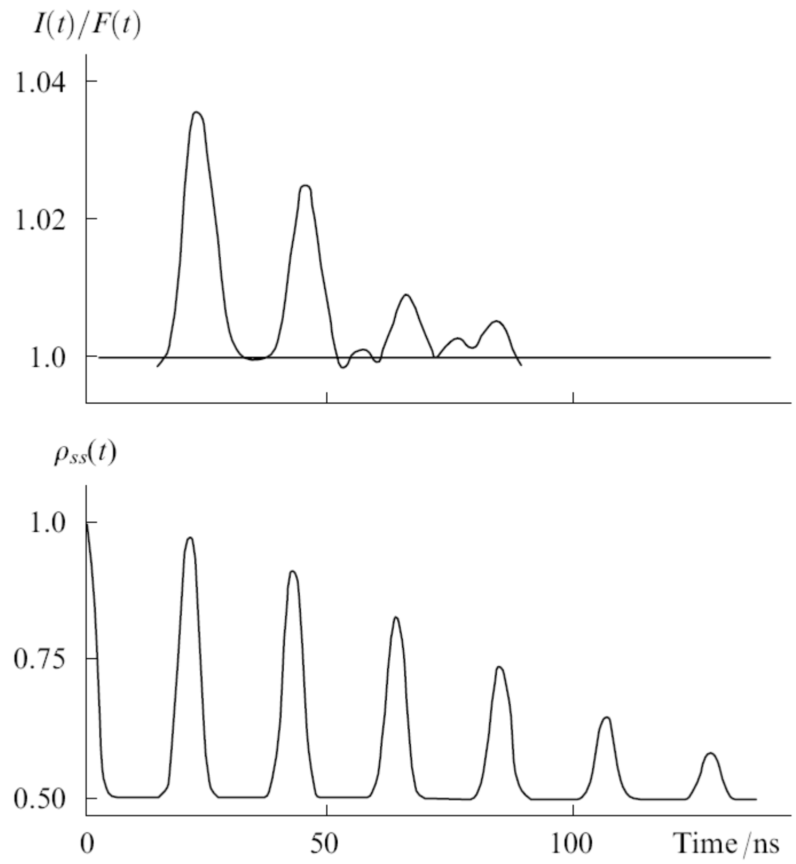




Overview: Spin Chemistry

Quantum beats by hyperfine interactions

[*p*-terphenyl-d_{14}]$^{\bullet+}$ + [tetramethylethylene]$^{\bullet-}$ in *trans*-decalin



0.33 T

$a = 45.5$ MHz

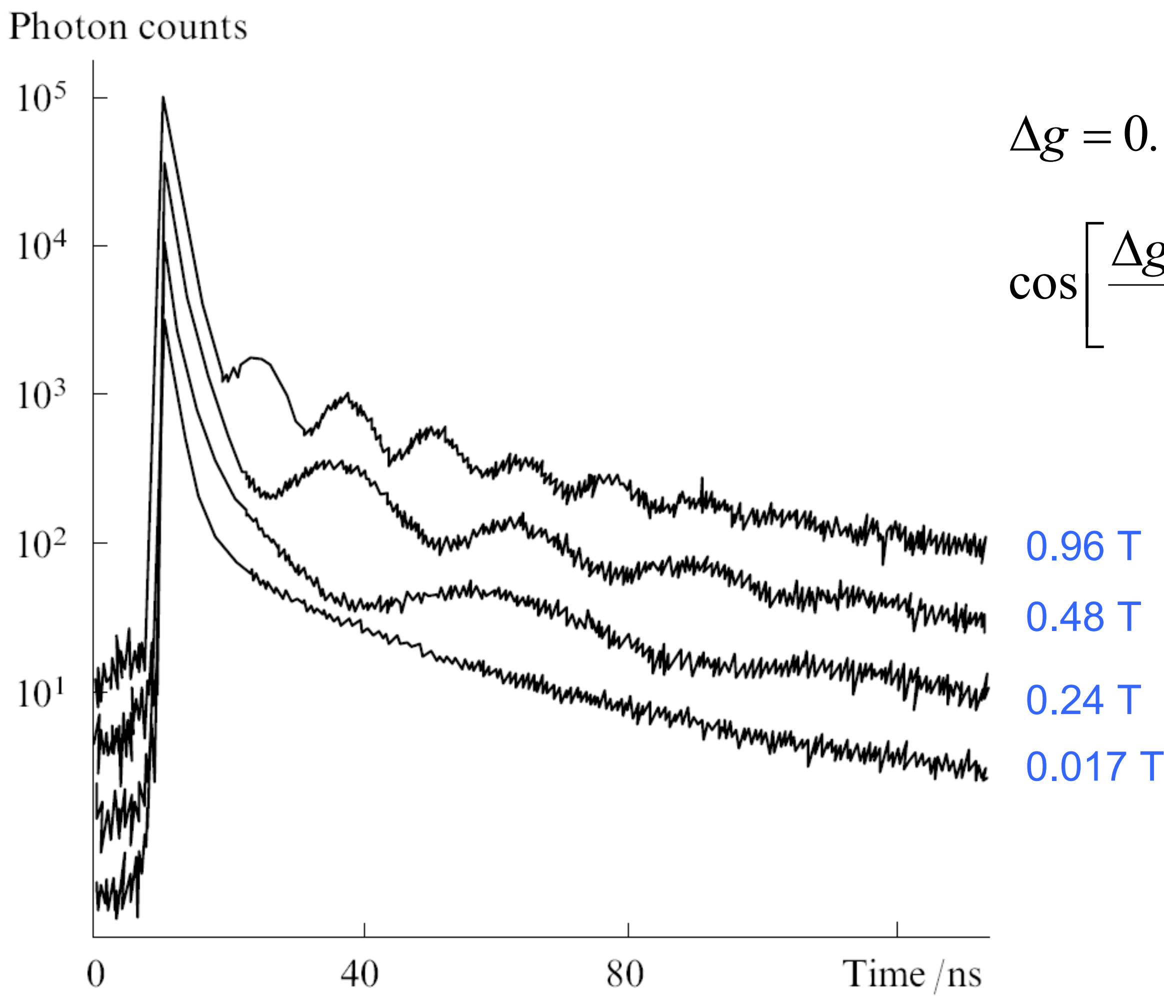
$\cos^{12}(\pi a t)$

Anisimov, Bizyaev, Lukzen, Grigoryants, Molin, *Chem. Phys. Lett.* (1983)

Overview: Spin Chemistry

Quantum beats by Zeeman interactions

$[p\text{-terphenyl-d}_{14}]^{\bullet+}$ + $[\text{diphenylsulphide-d}_{10}]^{\bullet-}$ in isooctane



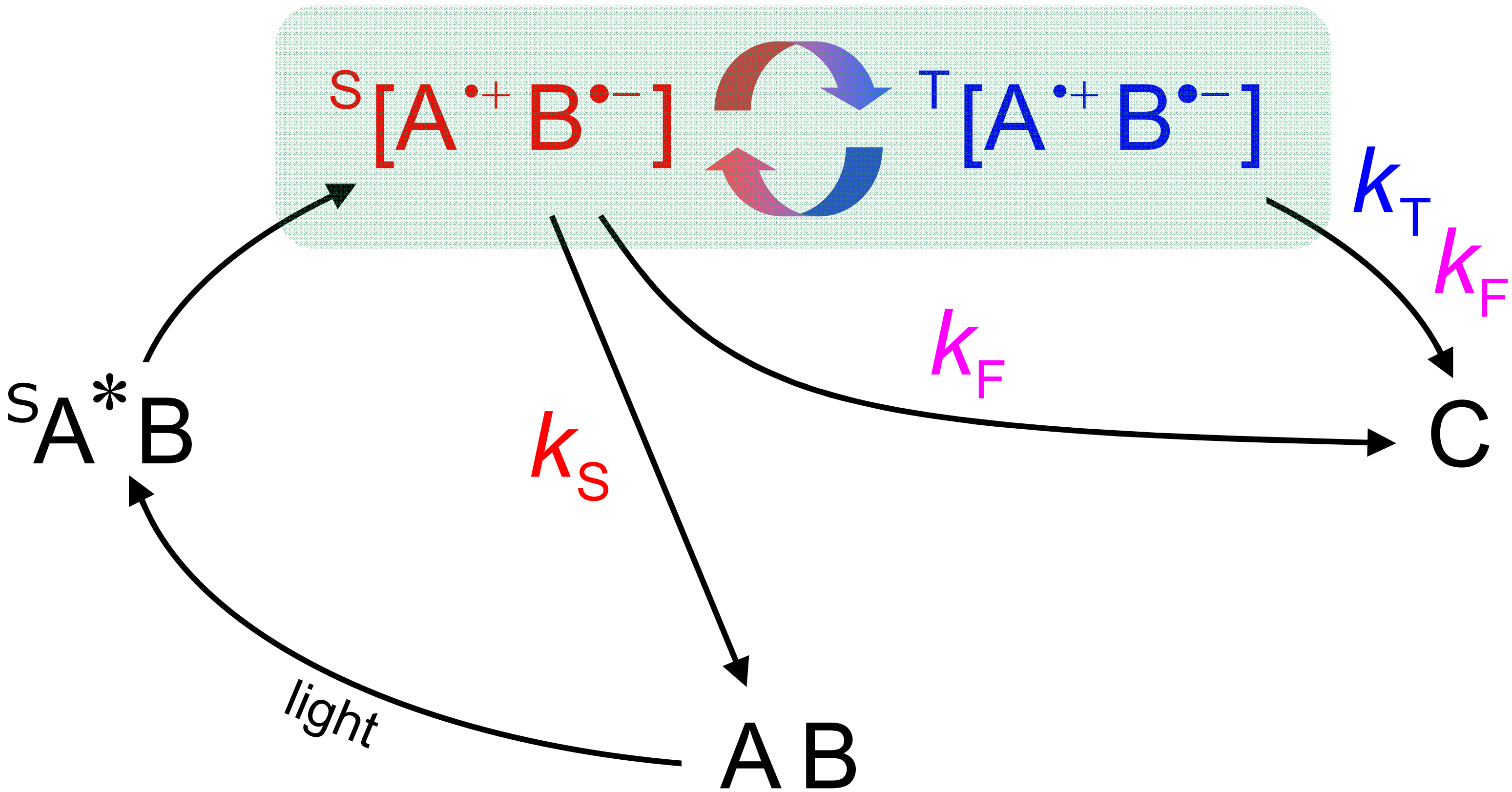
$$\Delta g = 0.0048$$

$$\cos\left[\frac{\Delta g \mu_B B}{\hbar} t\right]$$

Grigoryants, Tadjikov, Usov, Molin, *Chem. Phys. Lett.* (1995)

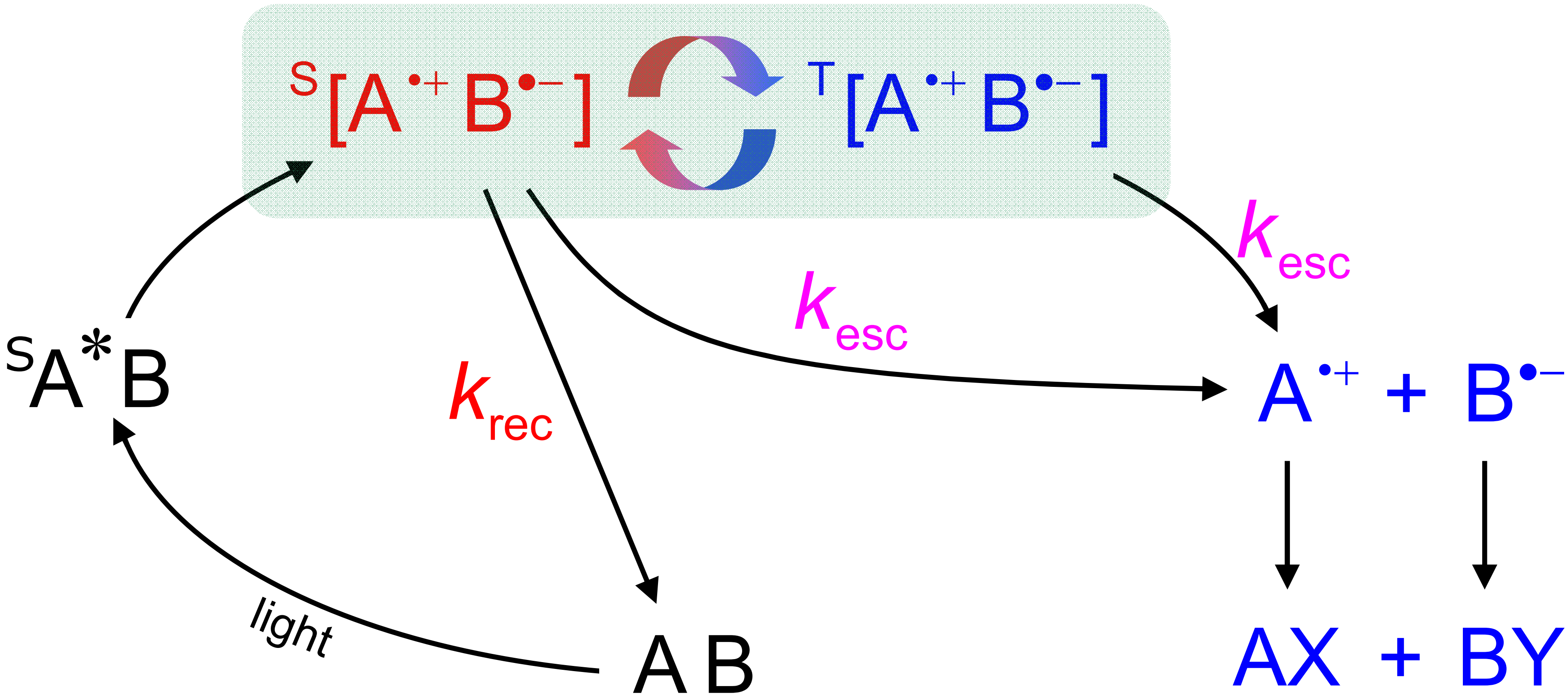
Overview: Spin Chemistry

Reaction dynamics in solid state



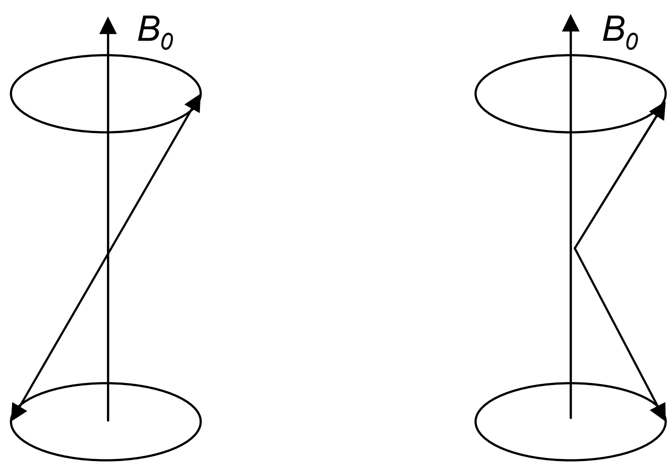
Overview: Spin Chemistry

Reaction dynamics in liquid state



Overview: Organic Spin Chemistry

Reaction dynamics in liquid state at high fields



Singlet S   Triplet T_0

Quantum mechanical ways for **ISC** **$S \rightarrow T_0$** :

1. **Δg** mechanism:

   difference in electron Larmor precession

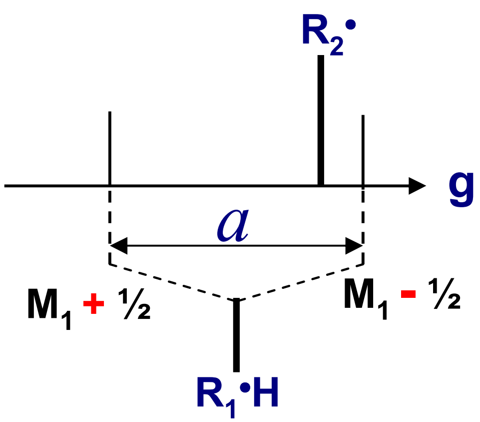
2. **hf** mechanism:

   hyperfine interaction unpaired e^-/nucleus

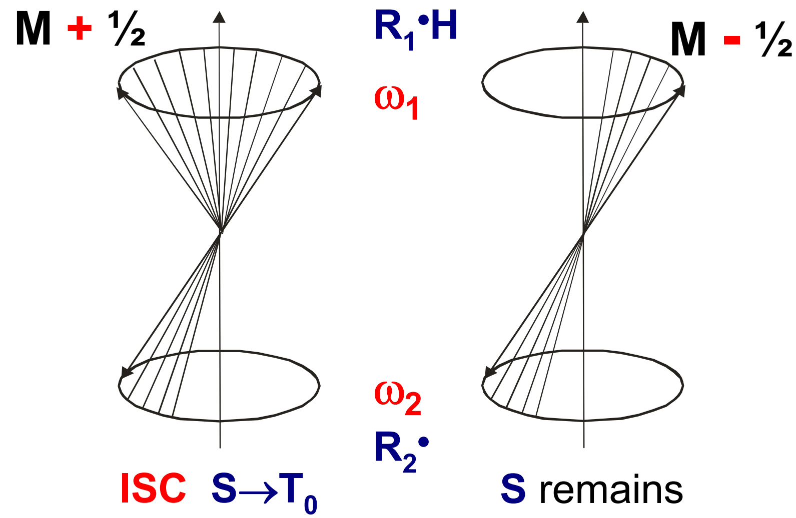
Overview: Spin Chemistry

Reaction dynamics in liquid state at high fields

EPR spectrum of **R_1•H + R_2•** pair:



hyperfine coupling constant *a*

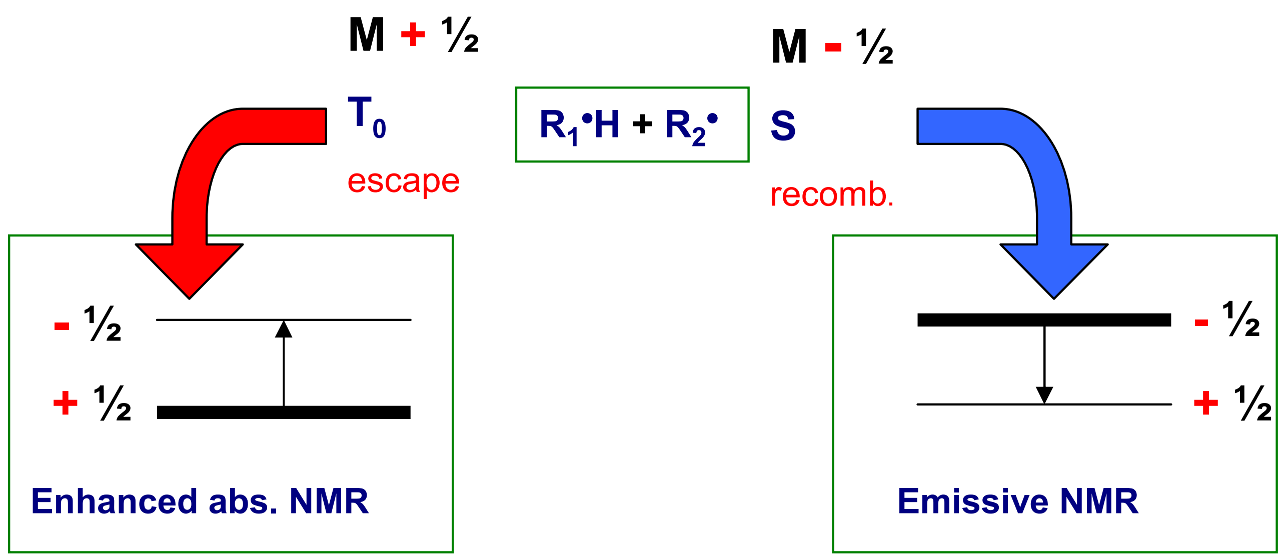


$$\Delta\omega = (g_1 - g_2)\frac{\beta B_0}{h} \pm \frac{1}{2} a_H$$

Nuclear spins control reaction path

Overview: Spin Chemistry

The classical Radical-Pair Mechanism (RPM)



- Reaction products **out of Boltzmann** equilibrium
- **Net polarization** observable by NMR, if

  1. different photo-products, or
  2. selective relaxation

Closs GL & Closs LE (1969) J Am Chem Soc 91: 4549-4550.

Kaptein R & Oosterhoff J L (1969) Chem Phys Lett 4: 195-197.

Overview: Spin Chemistry

Theoretical description

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\rho}(t) = -\mathrm{i}\left[\hat{H}(t), \hat{\rho}(t)\right]$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\left|\rho(t)\right) = -\left[\mathrm{i}\hat{\hat{H}} + \hat{\hat{K}} + \hat{\hat{R}} + \hat{\hat{W}}\right]\left|\rho(t)\right)$$

$\hat{\hat{H}}$ hyperfine, Zeeman, exchange, dipolar, quadrupolar … interactions

$\hat{\hat{K}}$ kinetics: formation, reaction, electron hopping, …

$\hat{\hat{R}}$ spin relaxation: usually *ad hoc* but also e.g. Redfield theory

$\hat{\hat{W}}$ motion: e.g. translational diffusion

$\left|\rho(t)\right)$ may include product states

Overview: Spin Chemistry

Four fields of spin effects in radical pairs

1. Electron spin polarization
2. Nuclear spin polarization
3. Magnetic field effect
4. Magnetic isotope effect

1 Electron spin polarization

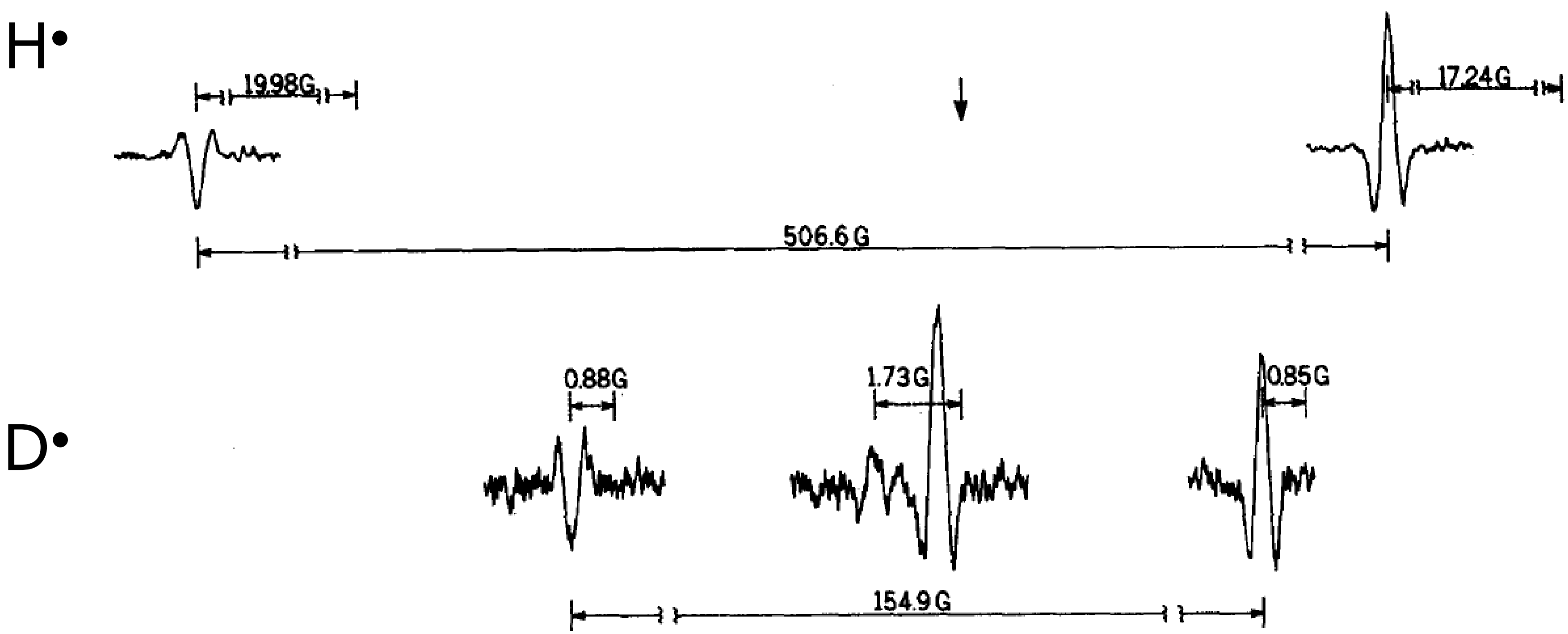
Chemically induced dynamic electron polarization (CIDEP)

- direct detection of radical pairs, free radicals, triplet states, … by (time-resolved) EPR spectroscopy
- usually X-band: ~0.3 T, ~9 GHz
- first observation 1963
- Radical Pair Mechanism (RPM), Triplet Mechanism (TM), Radical-Triplet Pair Mechanism, …
- identification and characterization of transient paramagnetic species
- study kinetics, dynamics, interactions, spin relaxation
- in liquid and solid state
- ESE, ESEEM, ENDOR, …

1 Electron spin polarization

CIDEP: First observation

2.8 MeV electron irradiation; liquid methane, −175 °C



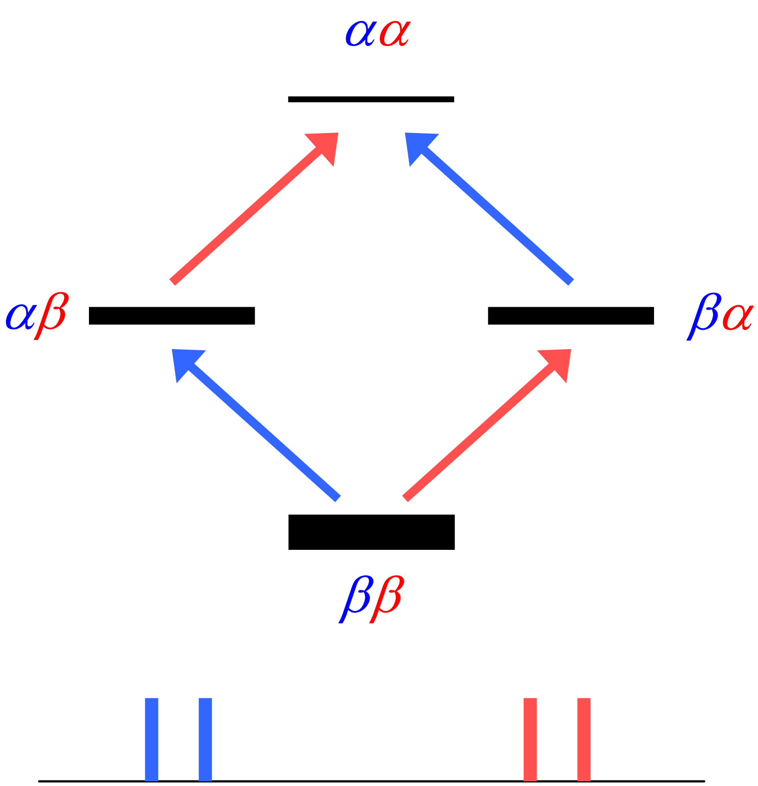
Fessenden & Schuler, *J. Chem. Phys.* (1963)

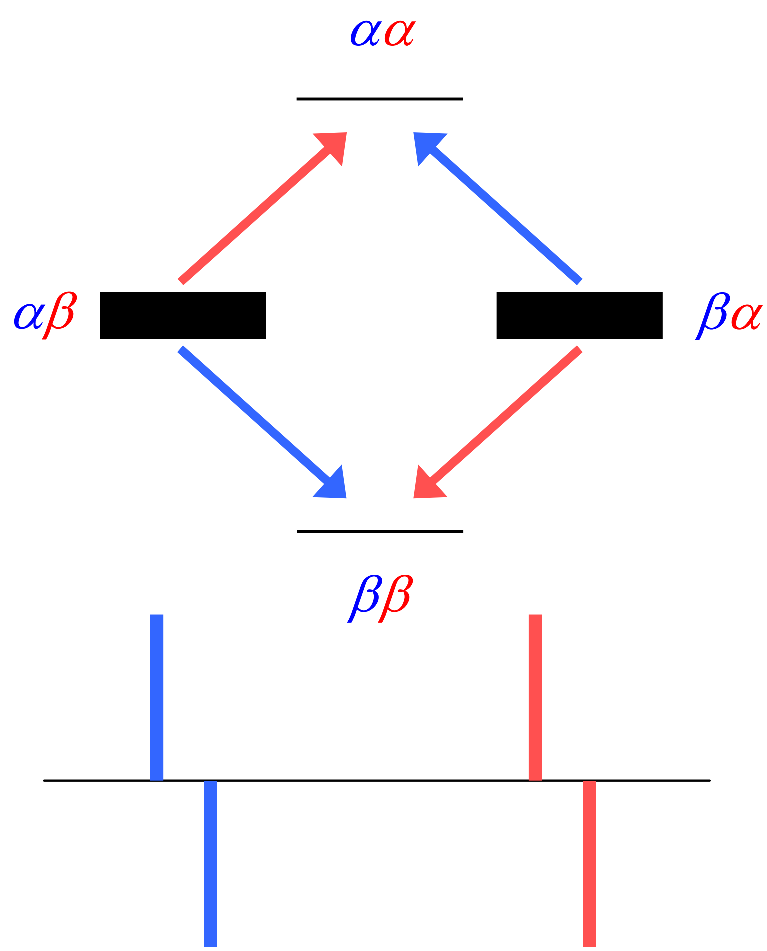
1 Electron spin polarization

Spin-correlated radical pair

$$\hat{\rho}(0) \propto \exp\left[-\hat{H} / k_{\mathrm{B}} T\right]$$

$$\hat{\rho}(0) = |S\rangle\langle S|; \quad |S\rangle = \tfrac{1}{\sqrt{2}}|\alpha\beta\rangle - \tfrac{1}{\sqrt{2}}|\beta\alpha\rangle$$





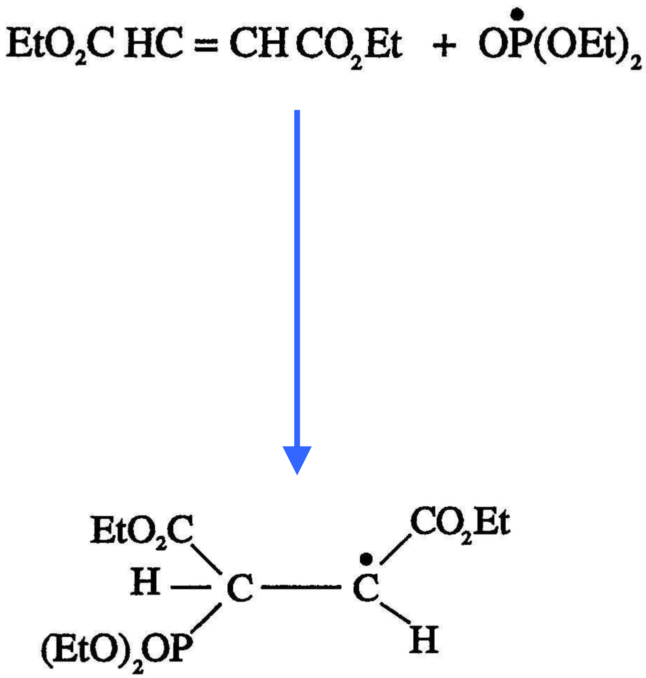
EPR

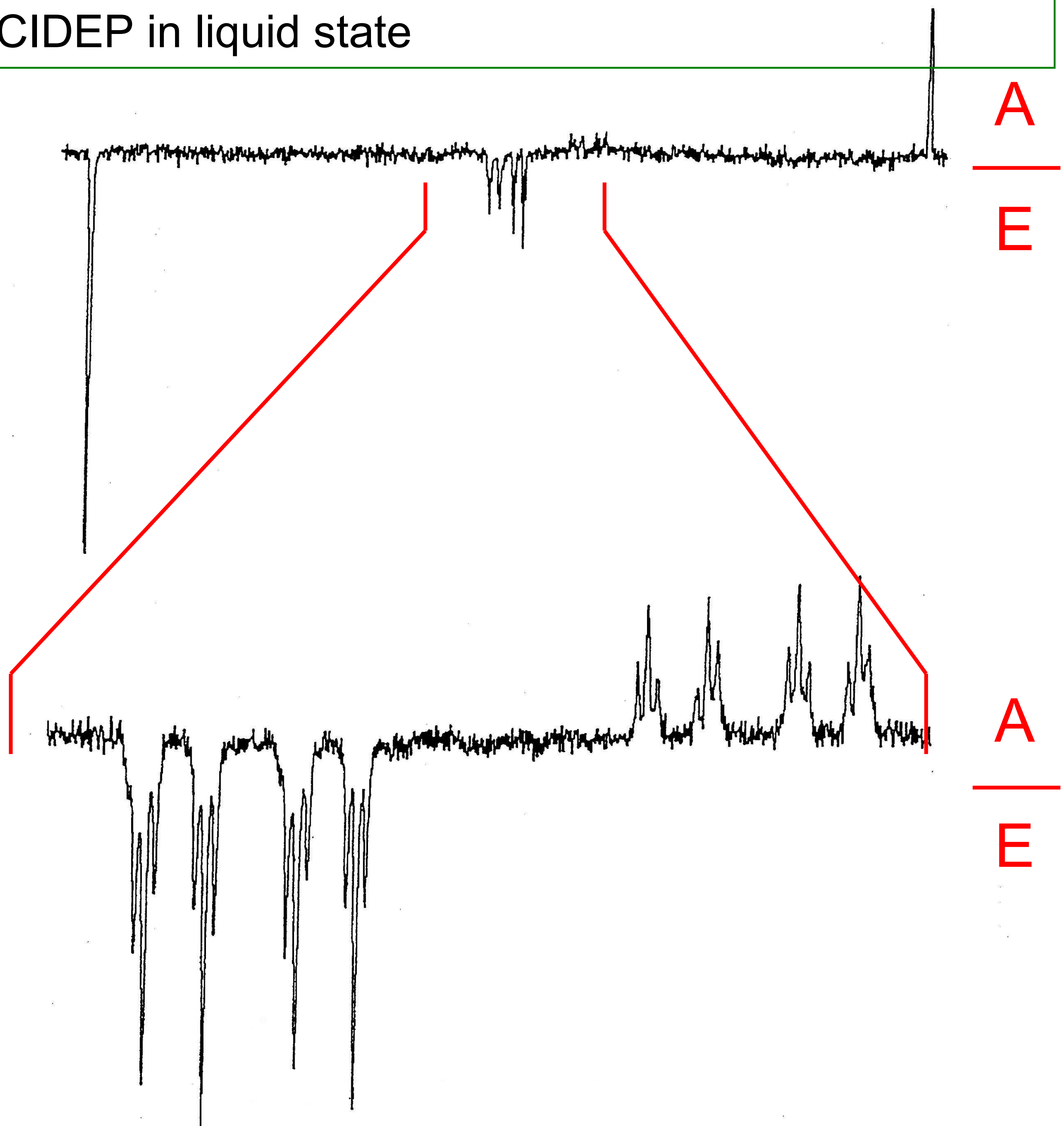
Equilibrium

Spin-polarized

1 Electron spin polarization

CIDEP in liquid state

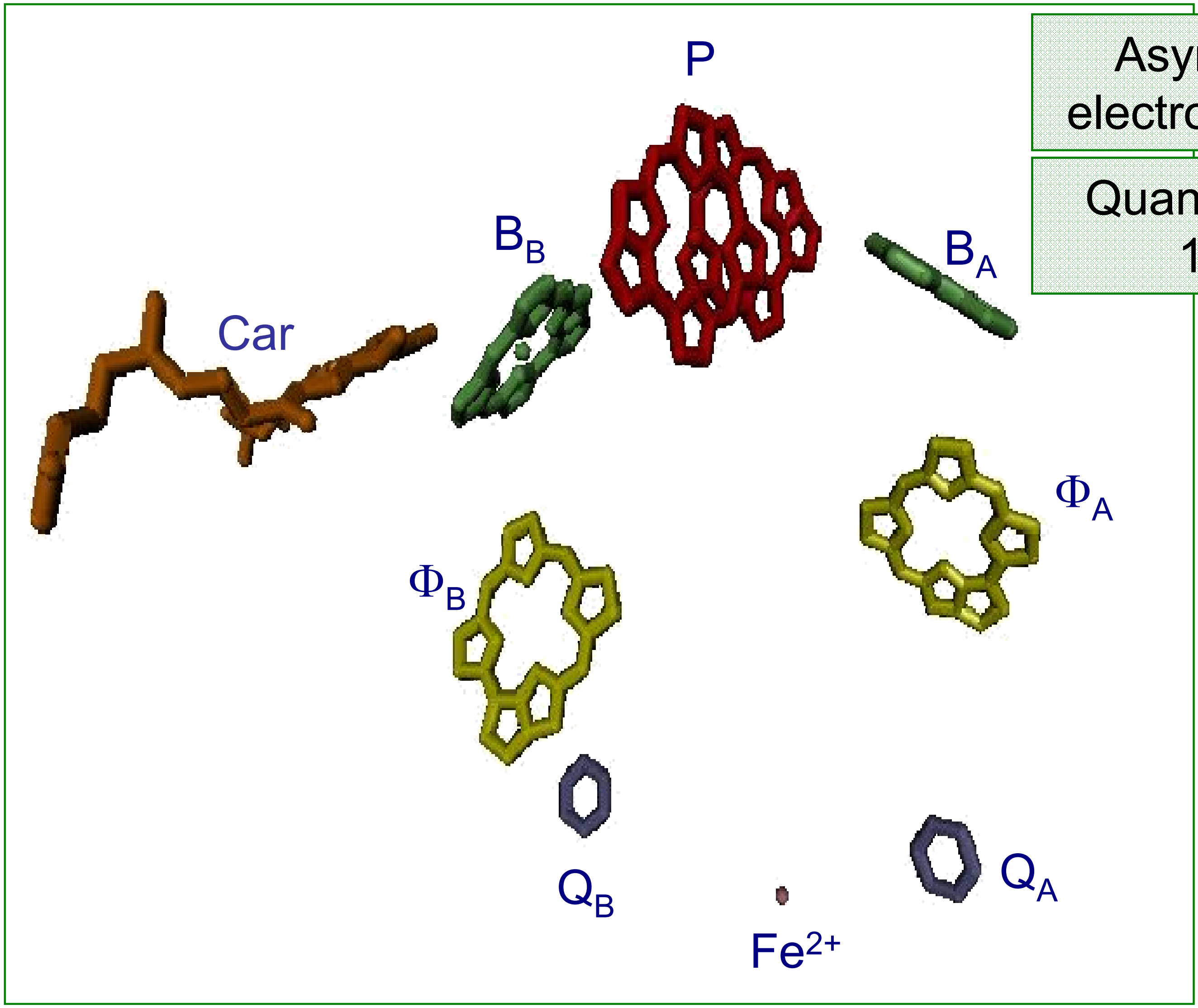




McLauchlan & Simpson, *J. Chem. Soc. Perkin Trans. II* (1990)

1 Electron spin polarization

The photosynthetic reaction center (RC) of *Rhodobacter sphaeroides*

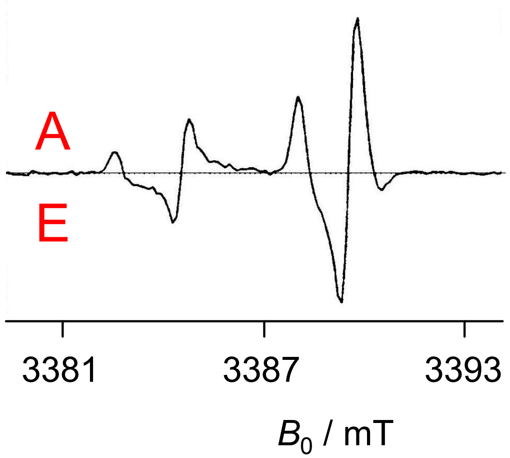


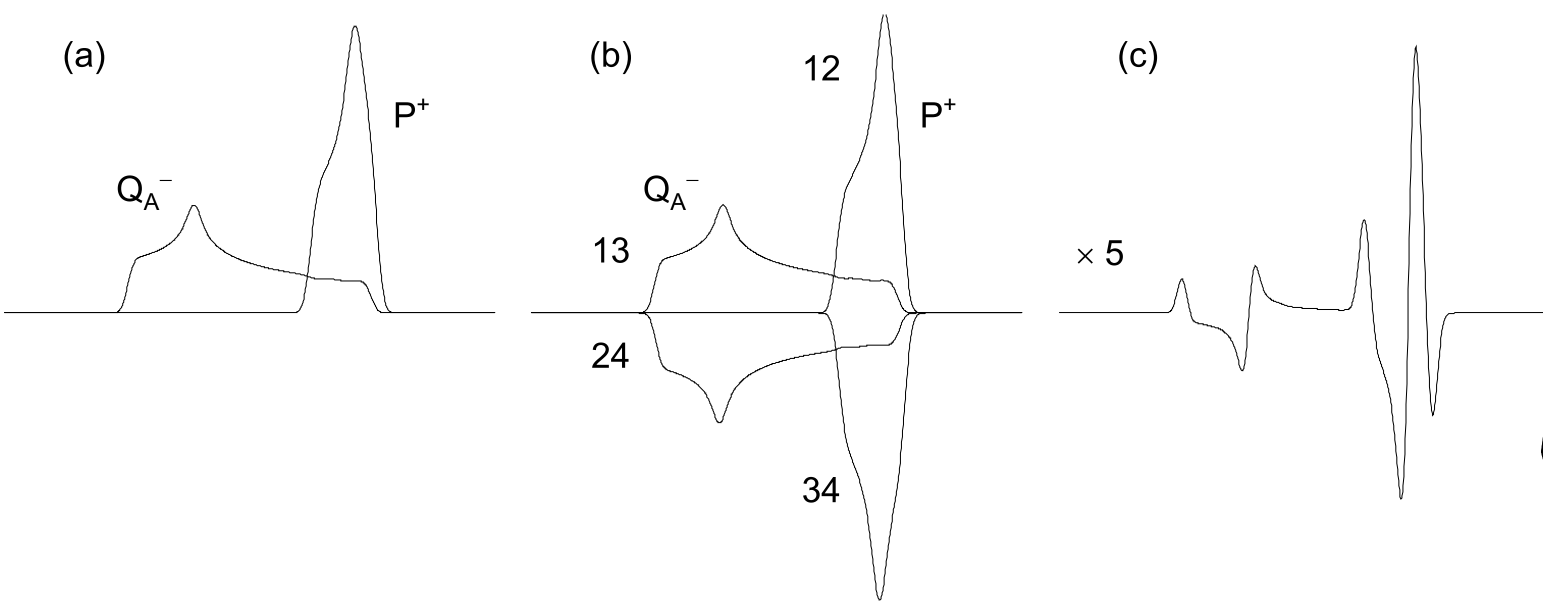
Asymmetric electron transfer

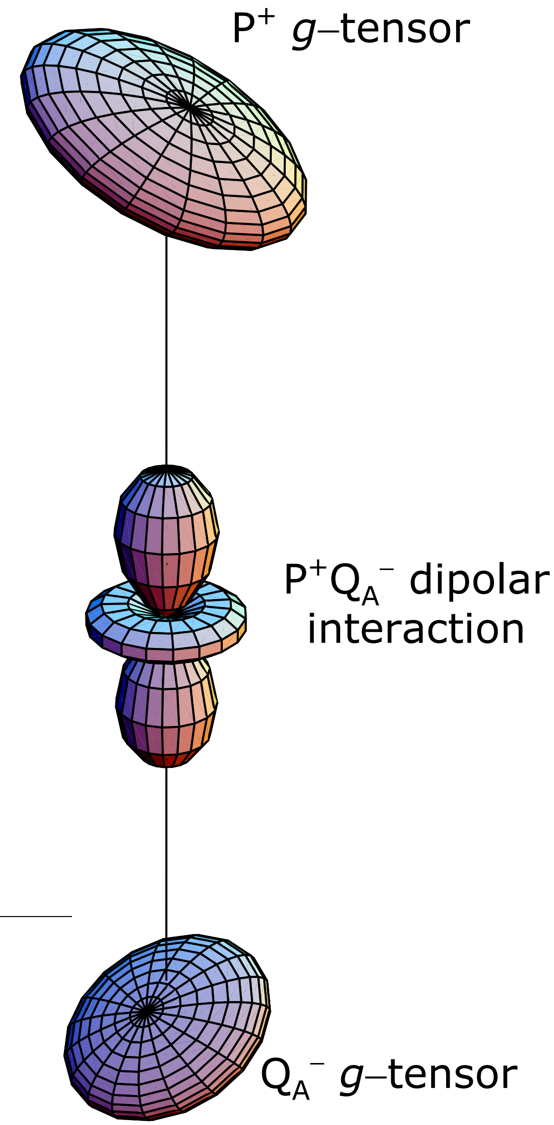
Quantum yield 100%

1 Electron spin polarization

Photosynthetic radical pairs







Prisner, van der Est, Bittl, Lubitz, Stehlik, Möbius

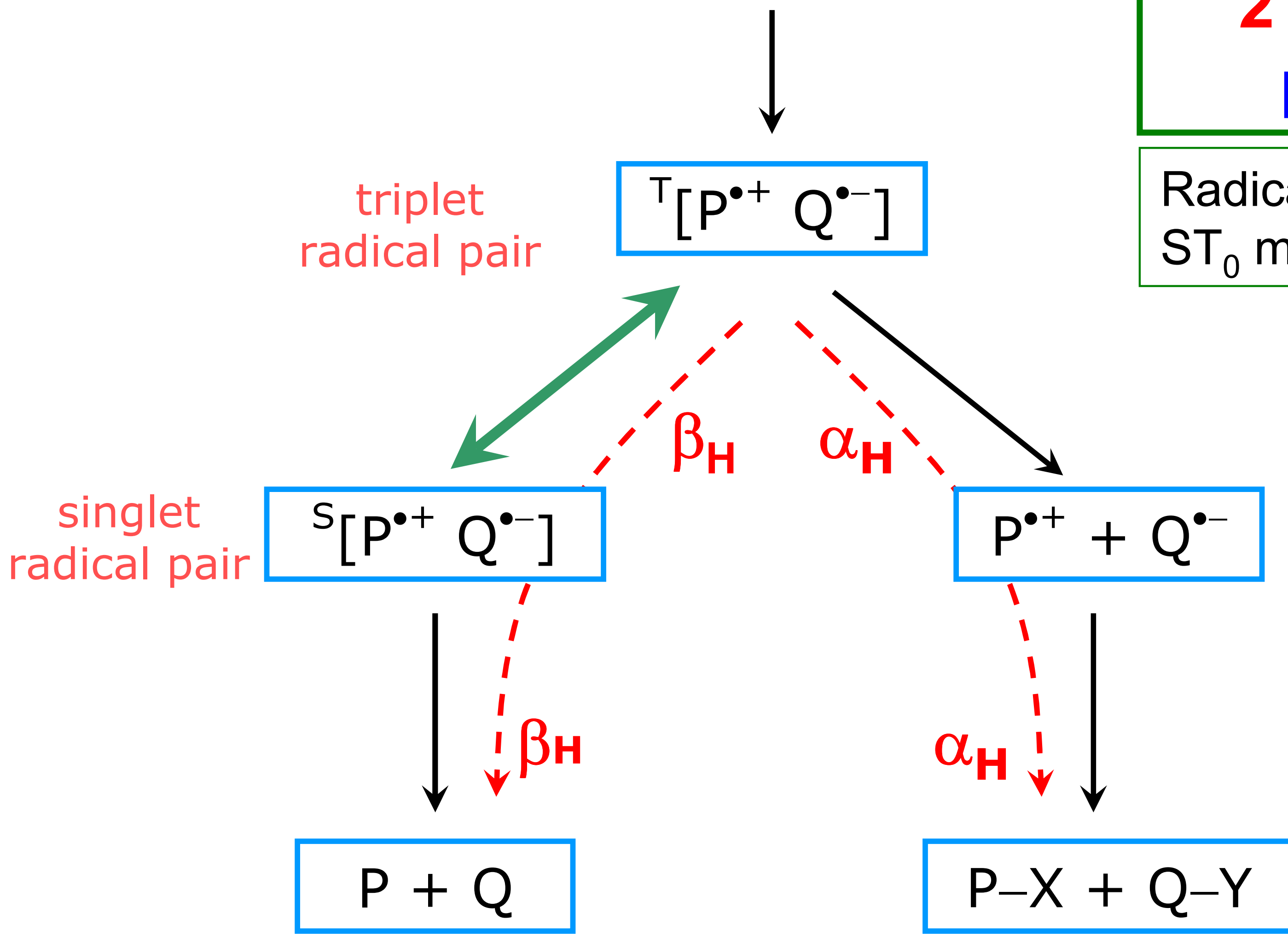
2 Nuclear spin polarization

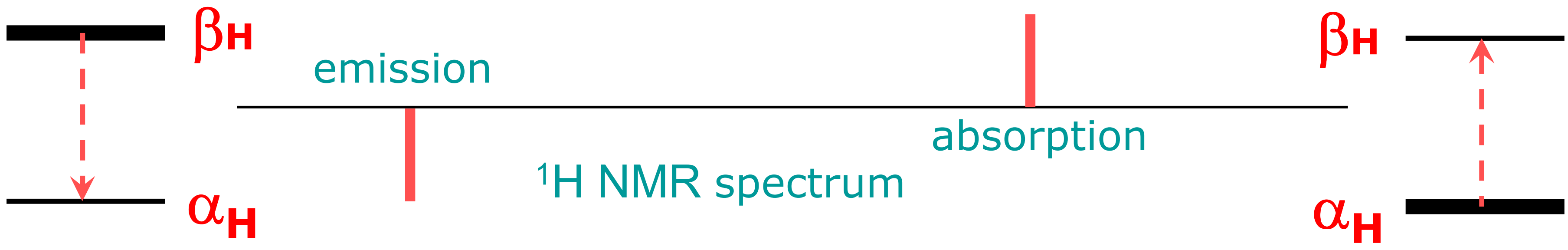
Chemically induced dynamic nuclear polarization (CIDNP)

- indirect detection of radical pairs, free radicals, triplet states … by (time-resolved) NMR spectroscopy
- mostly ^{1}H, but also ^{13}C, ^{15}N, ^{19}F, …
- first observation 1967 (Bargon & Fischer)
- Radical Pair Mechanism 1969 (Closs & Kaptein), spin relaxation, …
- identification and characterization of transient paramagnetic species
- study kinetics, dynamics, interactions, spin relaxation, protein structure
- mostly in liquid state

2 Nuclear spin polarization

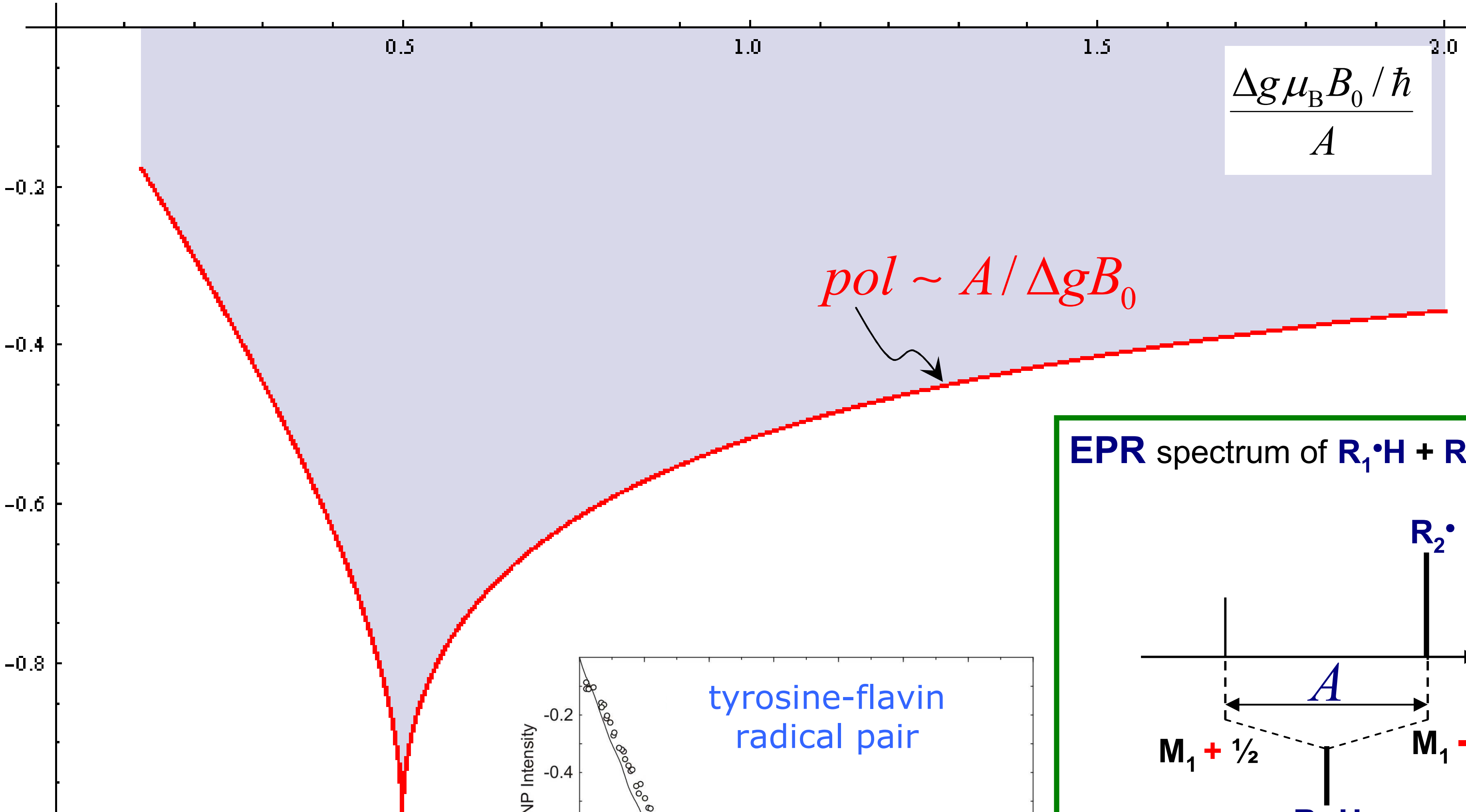
Radical Pair Mechanism
ST_0 mixing

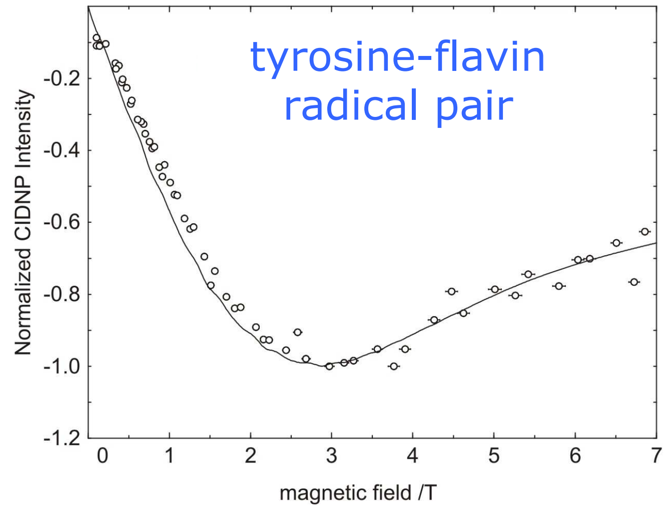




2 Nuclear spin polarization

Field dependence of CIDNP





Lyon *et al*. *Molec. Phys.* **100** (2002) 1261

EPR spectrum of $R_1{}^{\bullet}H$ + $R_2{}^{\bullet}$ pair:

$R_2{}^{\bullet}$

g

A

$M_1 + ½$

$M_1 - ½$

$R_1{}^{\bullet}H$

hyperfine coupling constant A

2 Nuclear spin polarization

Kaptein rules: Sign of CIDNP

$$\Gamma_{\mathrm{n}}(i) = \mu \cdot \varepsilon \cdot \Delta g \cdot A_i \qquad \begin{cases} +\mathrm{A} \\ -\mathrm{E} \end{cases} \qquad \text{net effect}$$

$$\mu \begin{cases} + \text{T precursor and F-pairs} \\ - \text{S precursor} \end{cases}$$

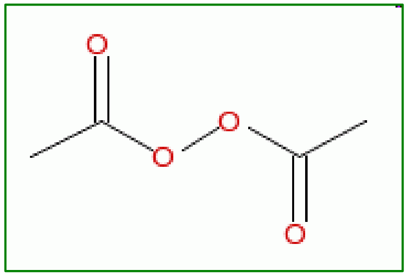
$$\varepsilon \begin{cases} + \text{recombination products} \\ - \text{escape products} \end{cases}$$

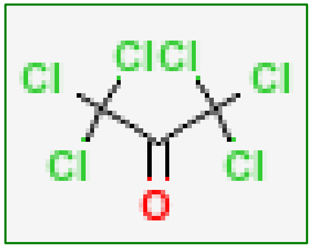
Kaptein, *Chem. Comm.* (1971) 732.

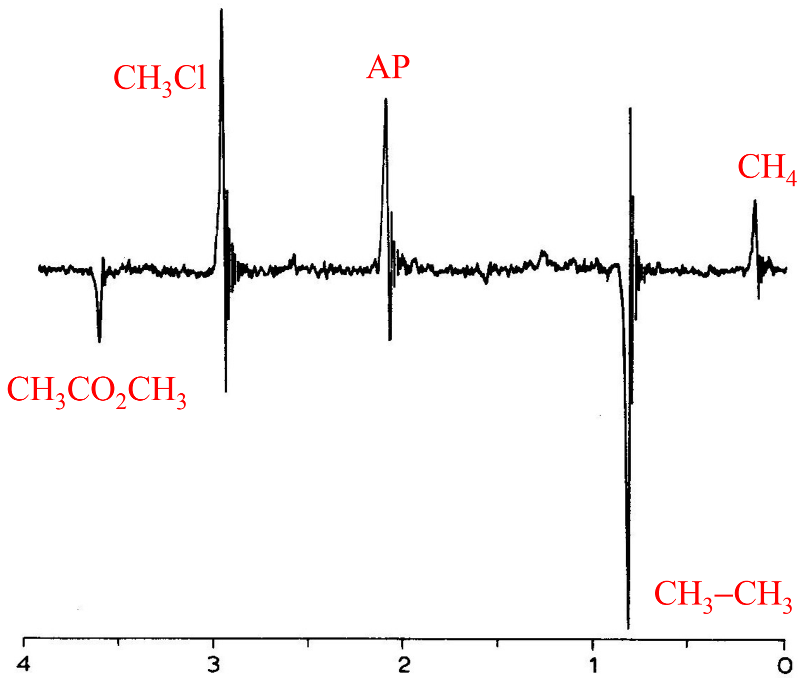
2 Nuclear spin polarization

CIDNP: Early observation

Thermal decomposition of acetyl peroxide (AP) in hexachloroacetone



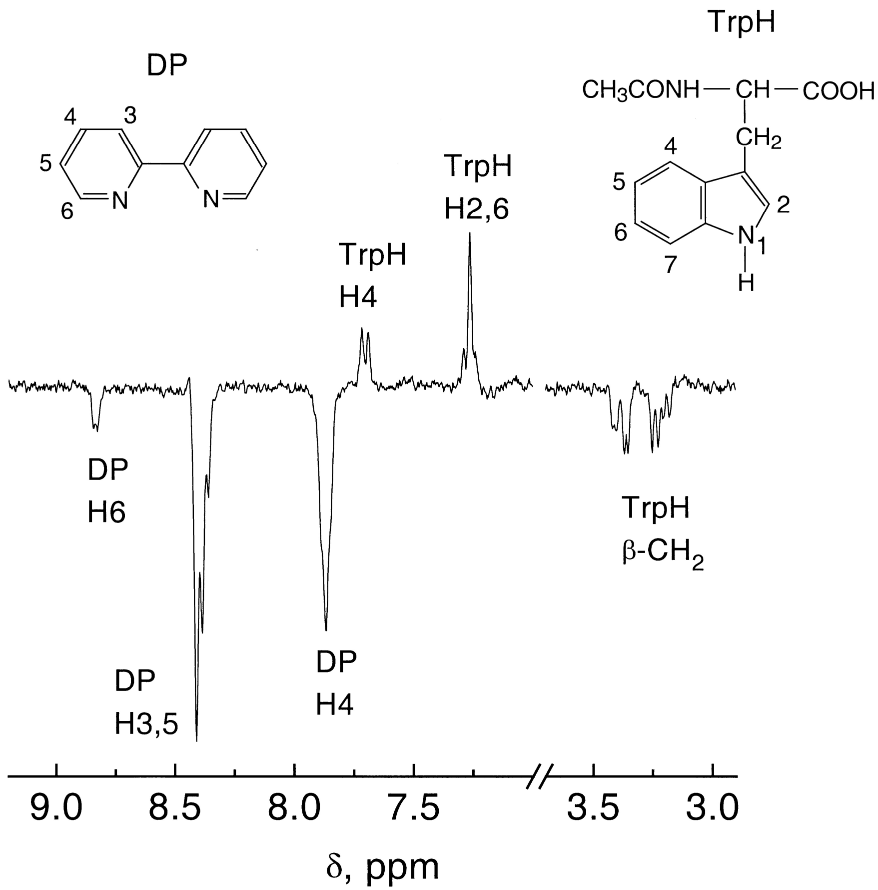


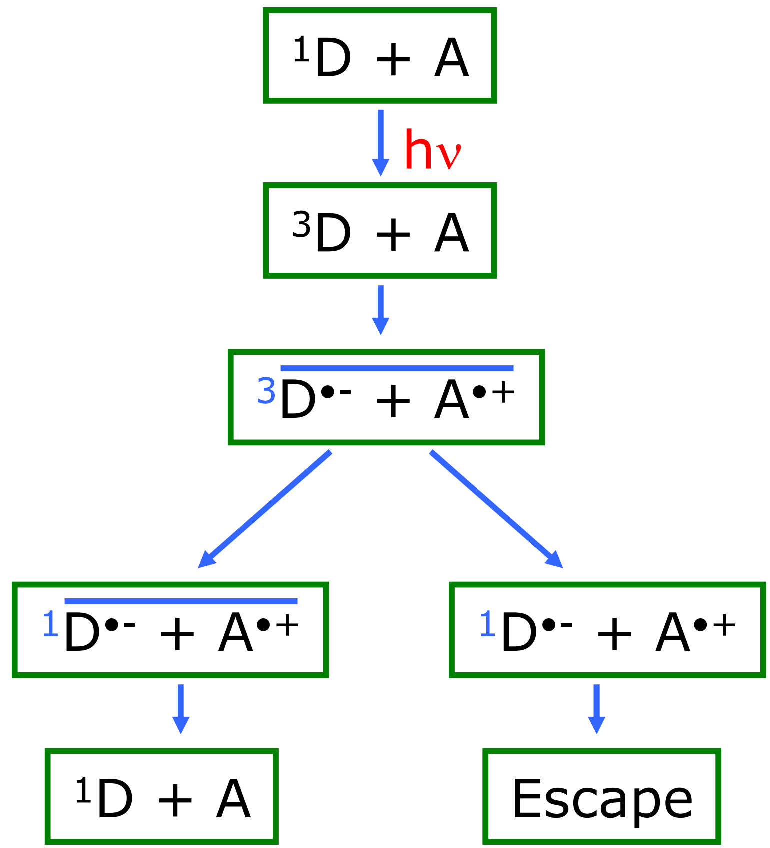


Kaptein, PhD thesis, Leiden University (1971)

2 Nuclear spin polarization

Chemically induced dynamic nuclear polarization (CIDNP)



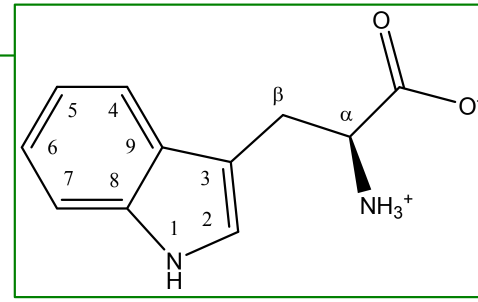


CIDNP spectrum, obtained during the irradiation of 4.4 10-4 M DP and 1.6 10-3 M TrpH solution.

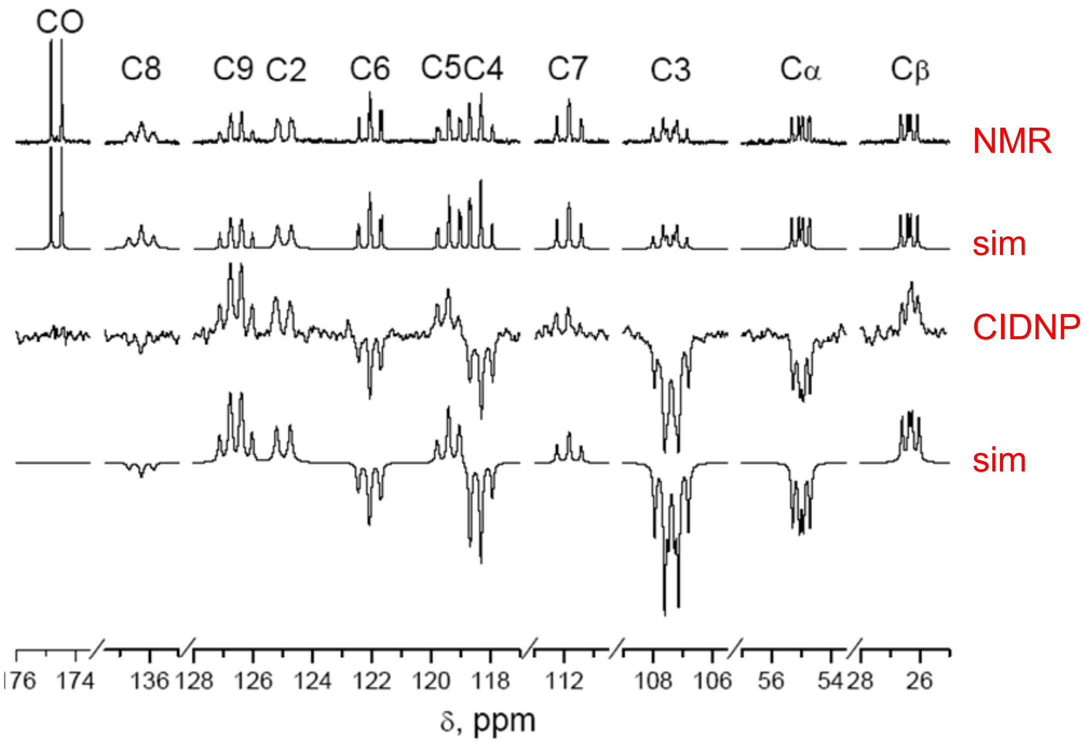
Yuri P. Tsentalovich; Olga B. Morozova; Alexandra V. Yurkovskaya; P. J. Hore; *J. Phys. Chem. A* **1999,** 103, 5362-5368.

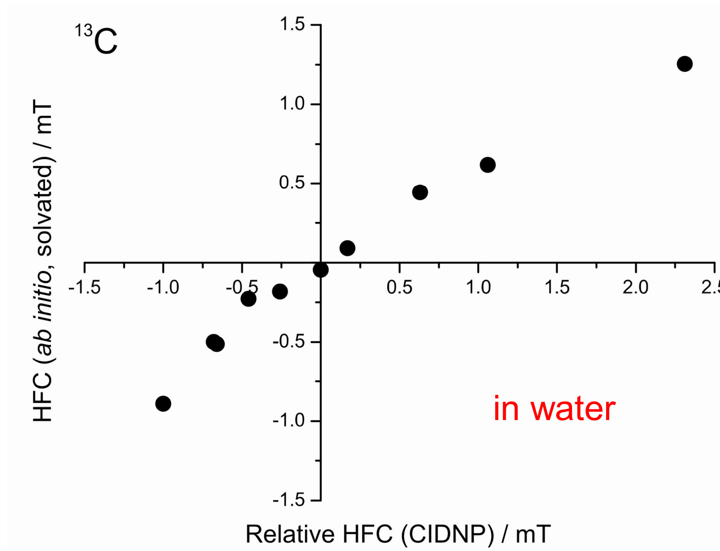
2 Nuclear spin polarization

^{13}C CIDNP on tryptophan



TrpH + ^{3}A → ^{3}[TrpH$^{•+}$ A$^{•−}$] ↔ ^{1}[TrpH$^{•+}$ A$^{•−}$] → TrpH + A

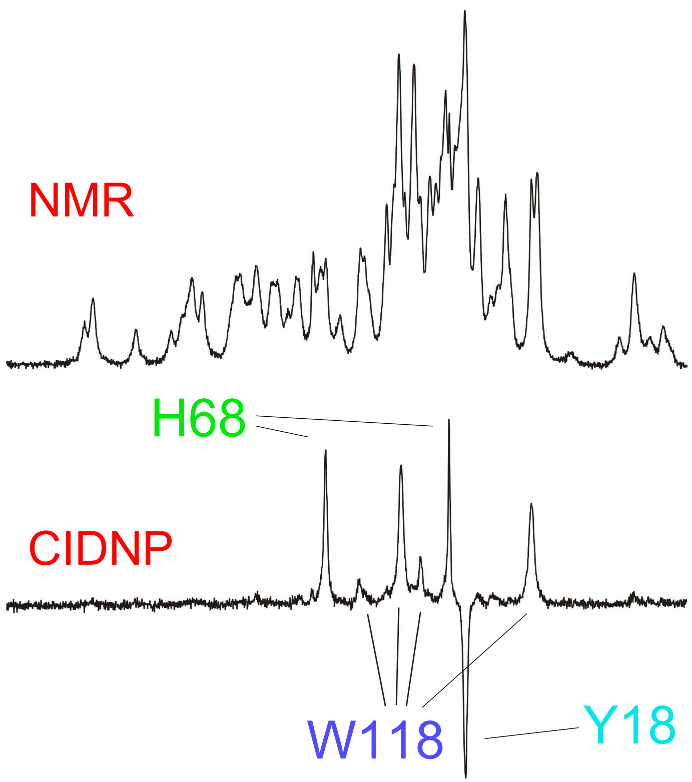


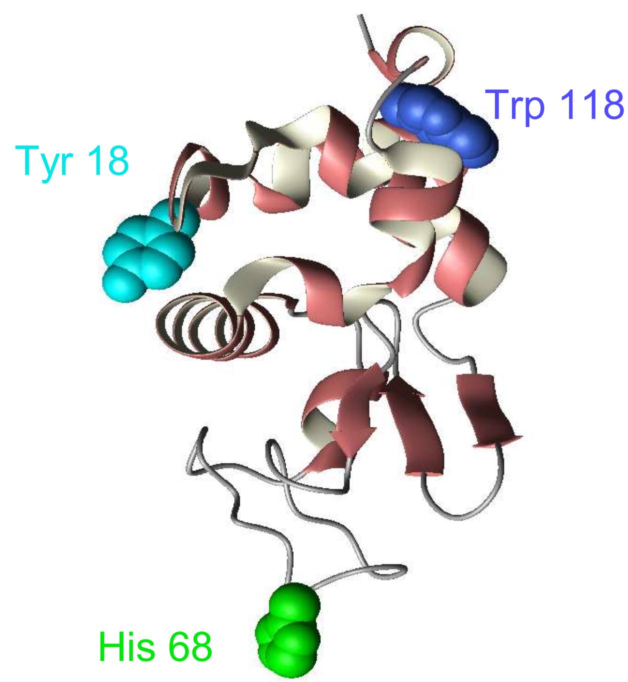


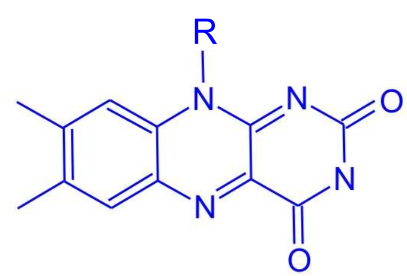
Kiryutin, Morozova, Kuhn, Yurkovskaya & Hore, *J. Phys. Chem. B* (2007)

2 Nuclear spin polarization

¹H photo-CIDNP on proteins







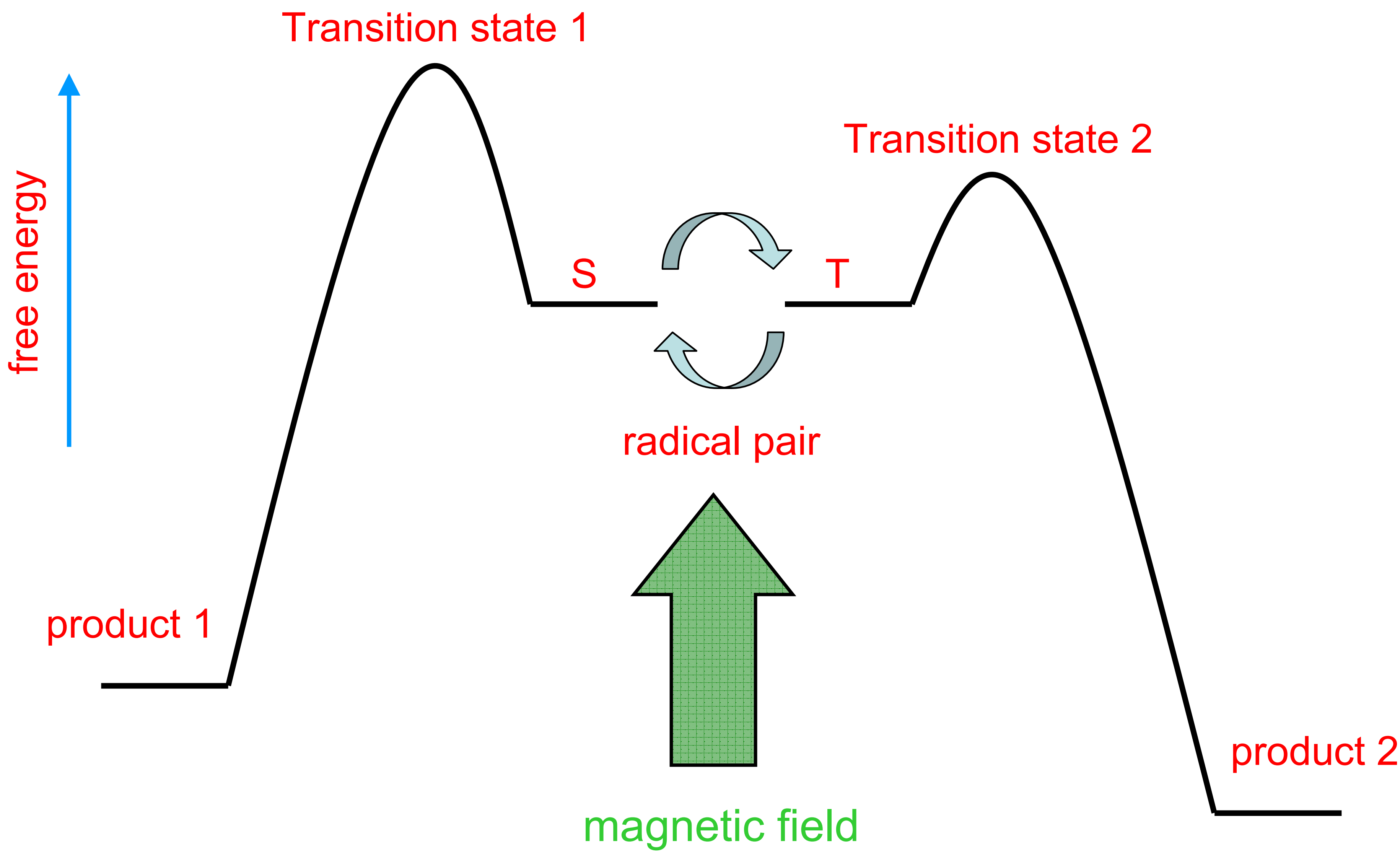
Mok, Nagashima, Day, Hore and Dobson, *PNAS* (2005)

Mok, Kuhn, Goez, Day, Lin, Andersen & Hore, *Nature* (2007)

3 Magnetic field effects

- static or time-dependent magnetic fields or both
- usually detect paramagnetic intermediates or reaction products by (time-resolved) optical spectroscopy
- first observation 1972
- < 50 μT to > 20 T
- mechanisms: hyperfine, Δ*g*, spin relaxation, …
- usually < 100% change in reaction yields, radical lifetimes, …
- study kinetics, dynamics, interactions, spin relaxation, …
- in liquid or solid states

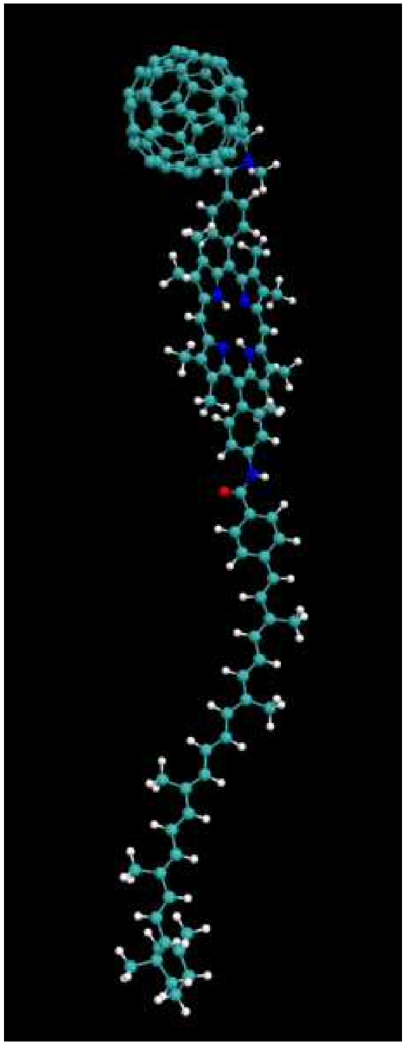
3 Radical pair magnetic field effects

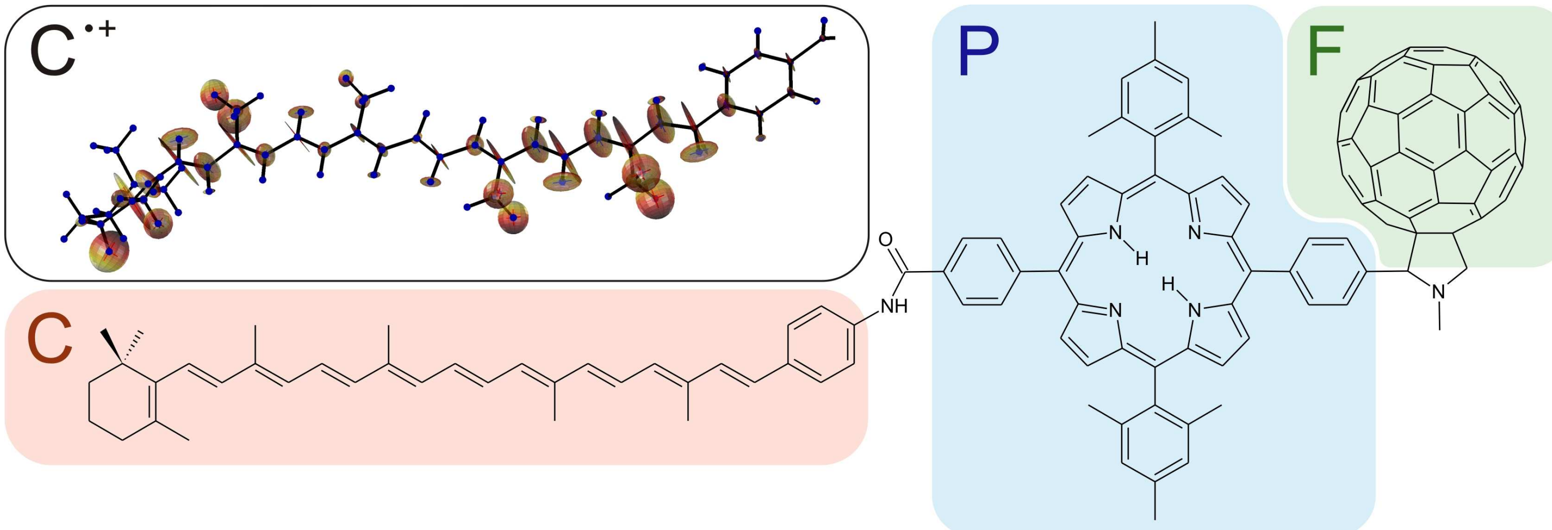


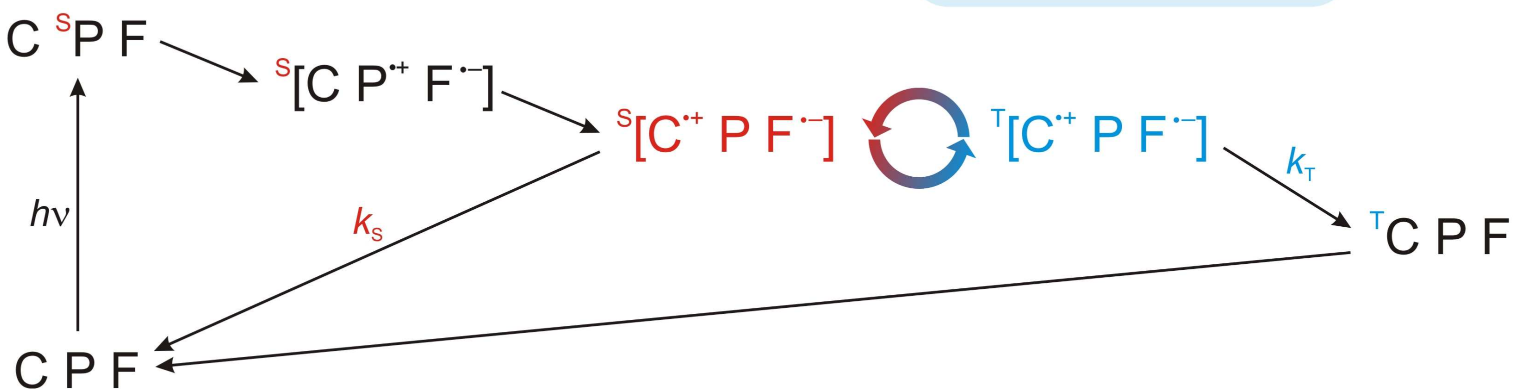
ΔE(magnetic field) << $k_B T$

3 Magnetic field effects

Carotenoid-porphyrin-fullerene triad



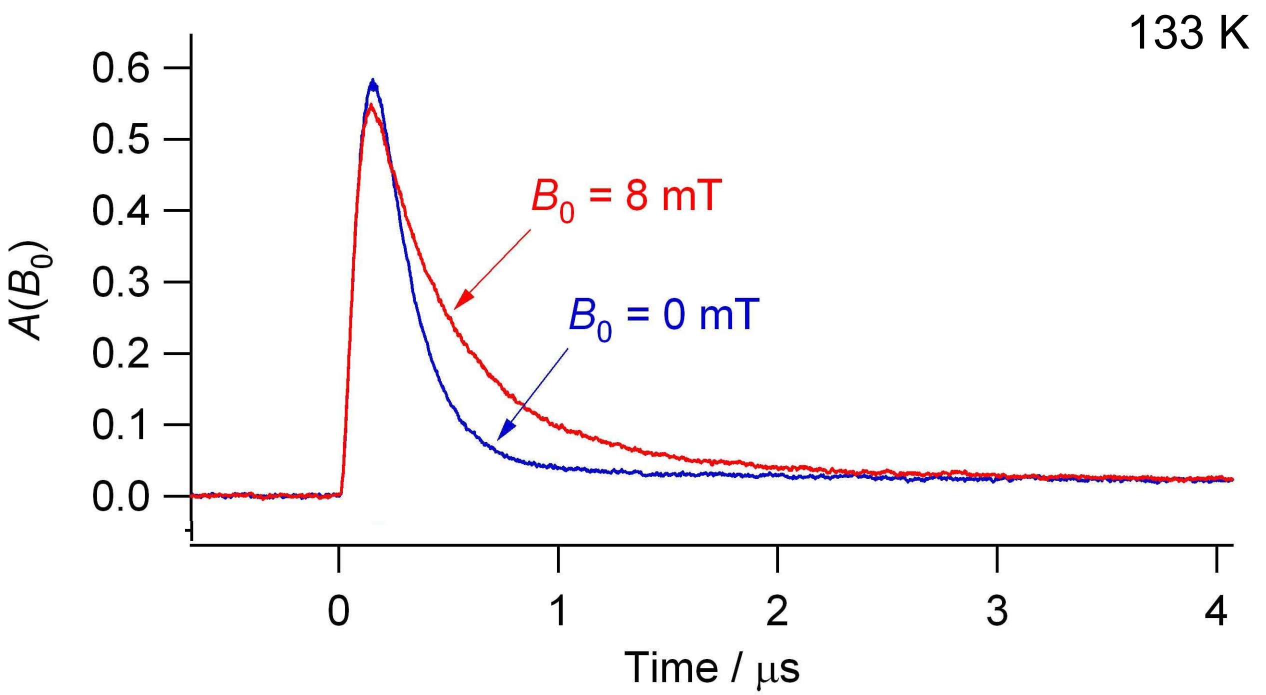




Maeda, Henbest, Cintolesi, Kuprov, Rodgers, Liddell, Gust, Timmel & Hore, *Nature* (2008)

3 Magnetic field effects

Carotenoid-porphyrin-fullerene triad

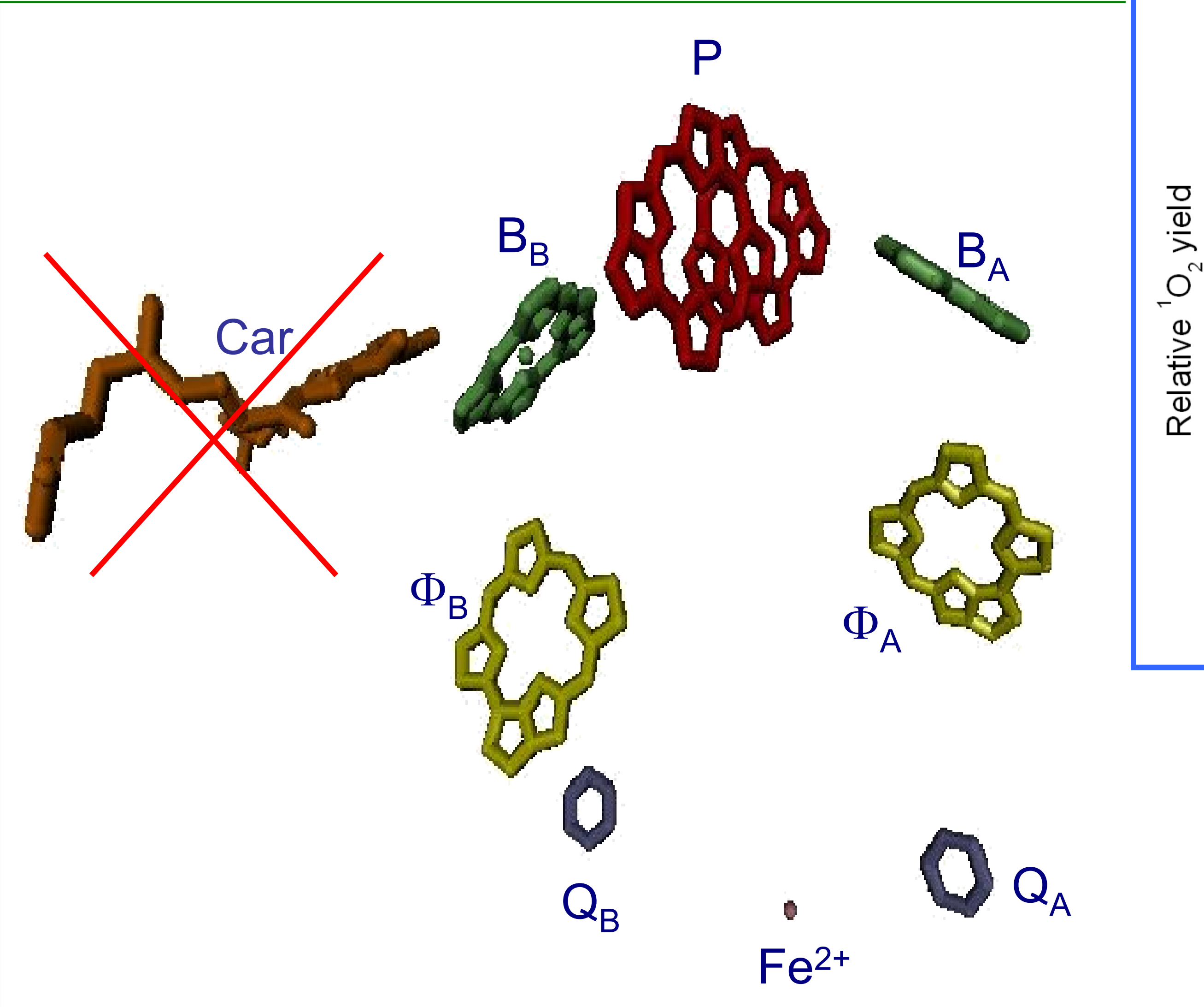


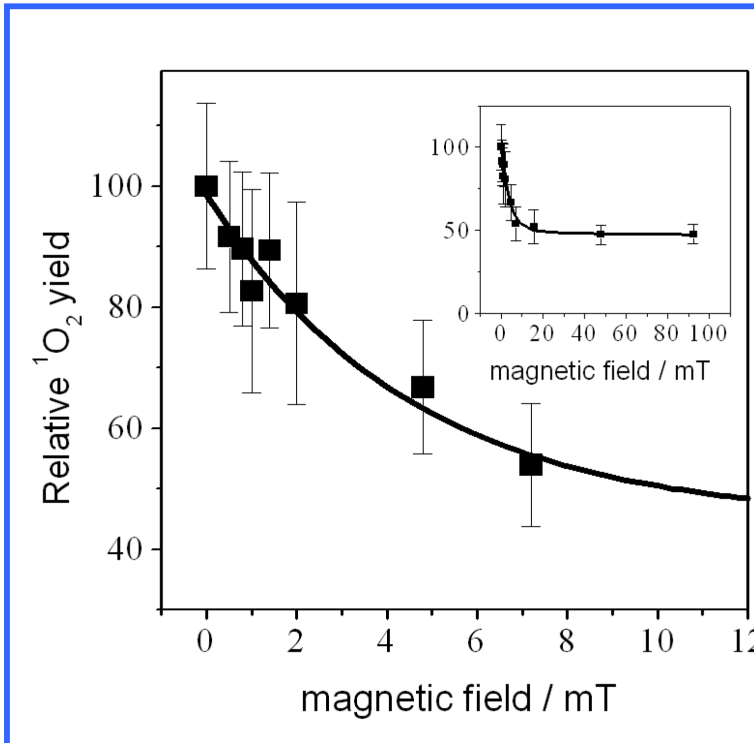
Lifetime of radical pair doubles (190 ns → 380 ns)
in a 8 mT magnetic field.

Maeda, Henbest, Cintolesi, Kuprov, Rodgers, Liddell, Gust, Timmel & Hore, *Nature* (2008)

3 Magnetic field effects

Singlet oxygen yield





Liu, Edge, Henbest, Timmel, Hore & Gast, *Chem. Comm.* (2005)

4 Magnetic isotope effects

- no magnetic field required
- first observation 1976
- distinct from mass isotope effect

Reviews:

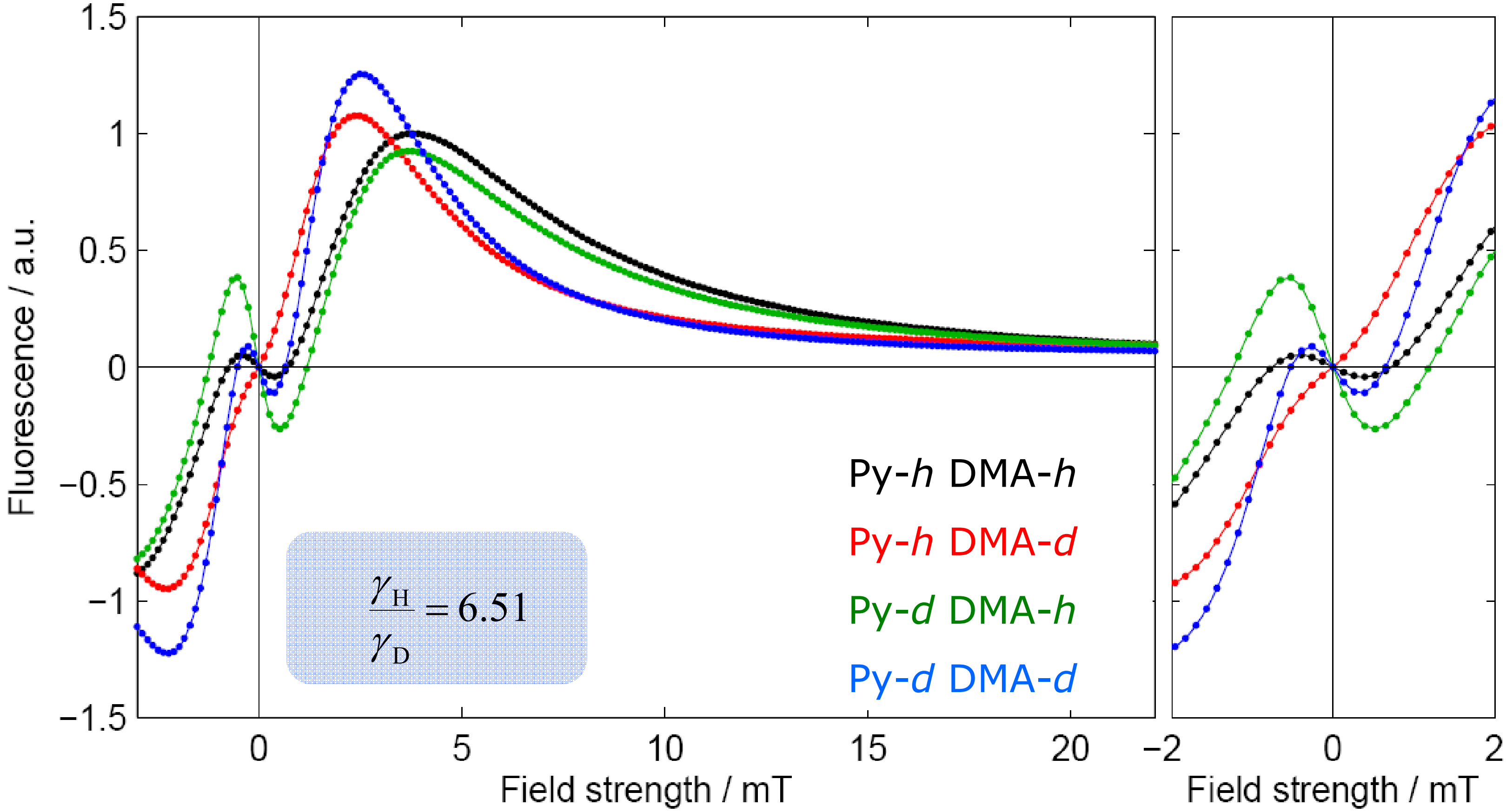
Anatoly L. Buchachenko (1995) Chem. Rev. 95, 2507-2528,

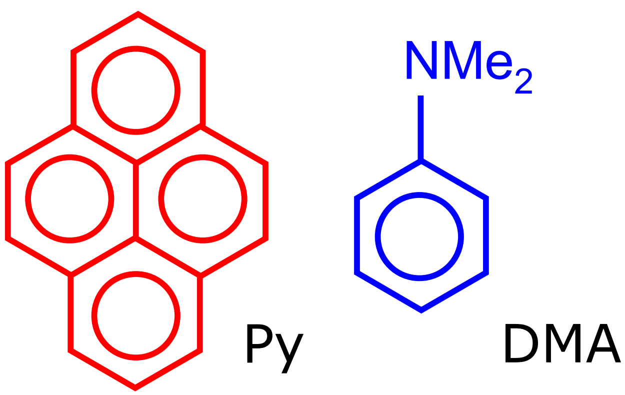
B. Brocklehurst (1997) Int. J. Radiat. Biol. 72, 587-597,

Anatoly L. Buchachenko (2001) J. Phys. Chem. A 105, 9995-10111.

4 Magnetic isotope effects

Magnetic field effects reaction yields





Magnetic responses of radical pairs are sensitive to deuteration

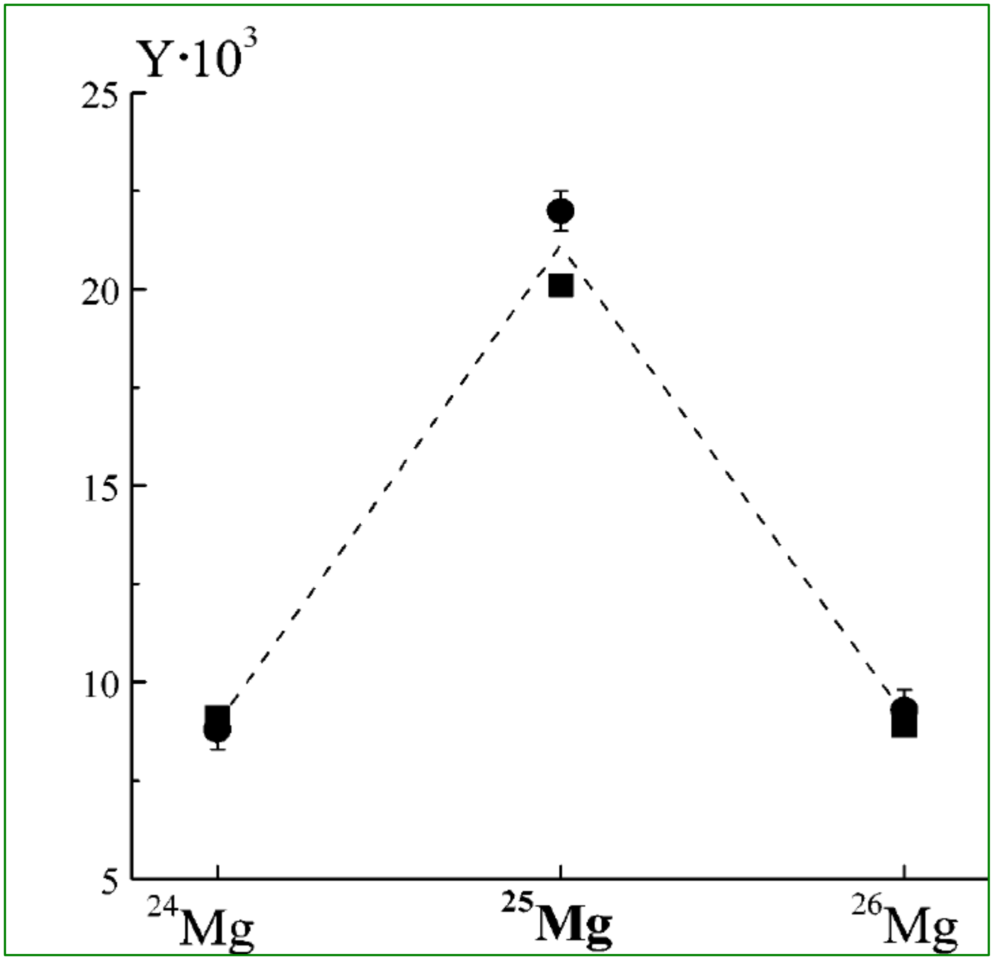
Rodgers, Norman, Henbest, Timmel & Hore, *JACS* (2007)

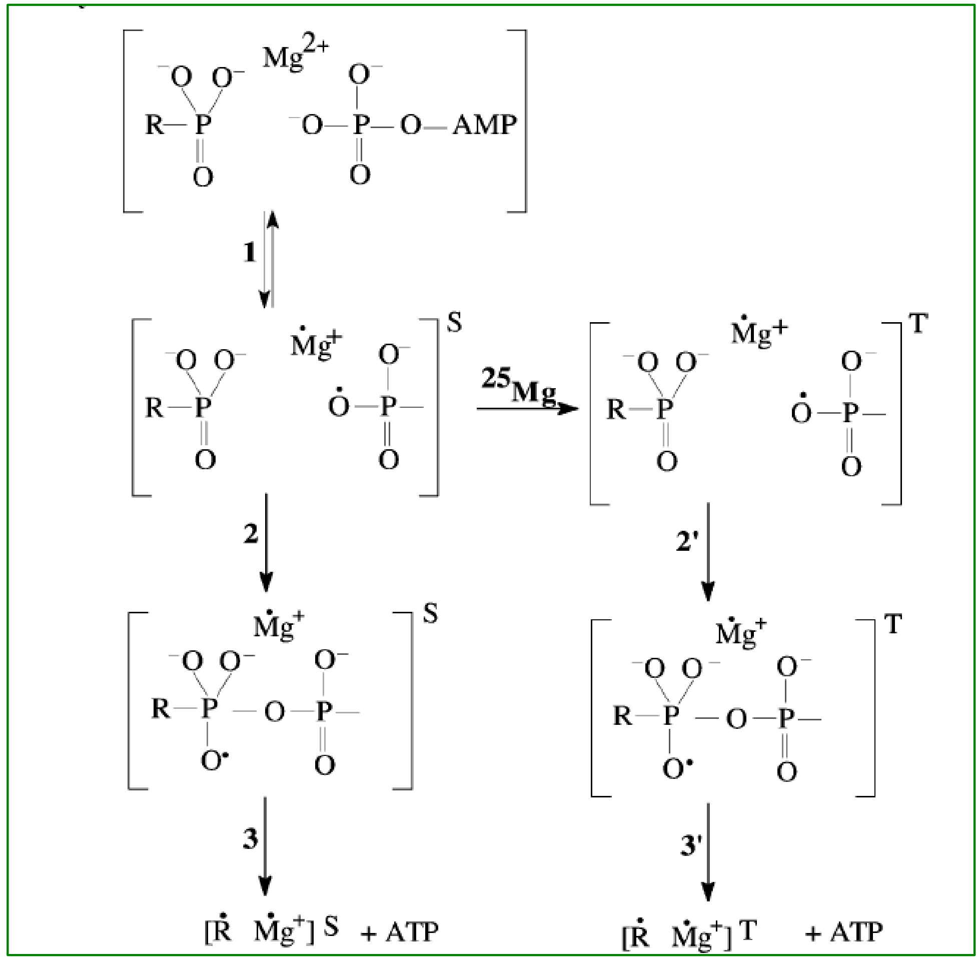
4 Magnetic isotope effects

Magnesium MIE

Rate of ATP synthesis by mitochondrial phosphocreatine kinase

^{24}Mg (I = 0); ^{25}Mg (I = 5/2); ^{26}Mg (I = 0)





Buchachenko, Kouznetsov, Breslavskaya & Orlova, *J. Phys. Chem. B* (2008)

Overview: Spin Chemistry

Two hot fields

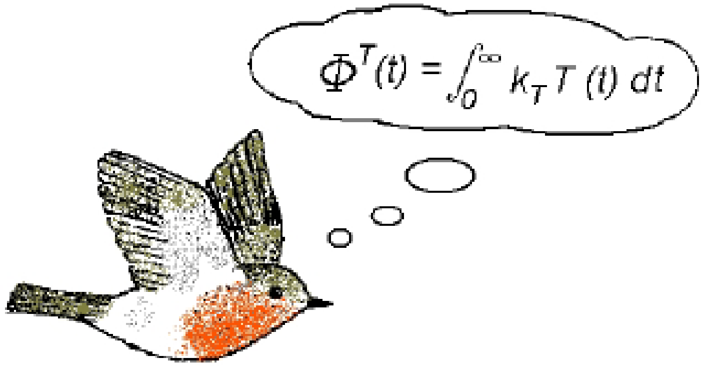
1 Bird orientation

2 Natural photosynthesis

1 Cryptochrome as magnetoreceptor?

Migratory birds seem to have up to three systems for orientation:
1. Blue-green light-dependent compass in the right eye.
2. Magnetite-based receptors in the upper beak.
3. Orientation on sun and stars.

It has been postulated that the primary process underlying magnetoreception of compass information in birds is a *radical pair mechanism*: **Cryptochromes are discussed as molecules forming the radical pairs.**



Möller, A., Sagasser, S., Wiltschko, W. & Schierwater, B. (2004): *Naturwissenschaften* 91, 585-588
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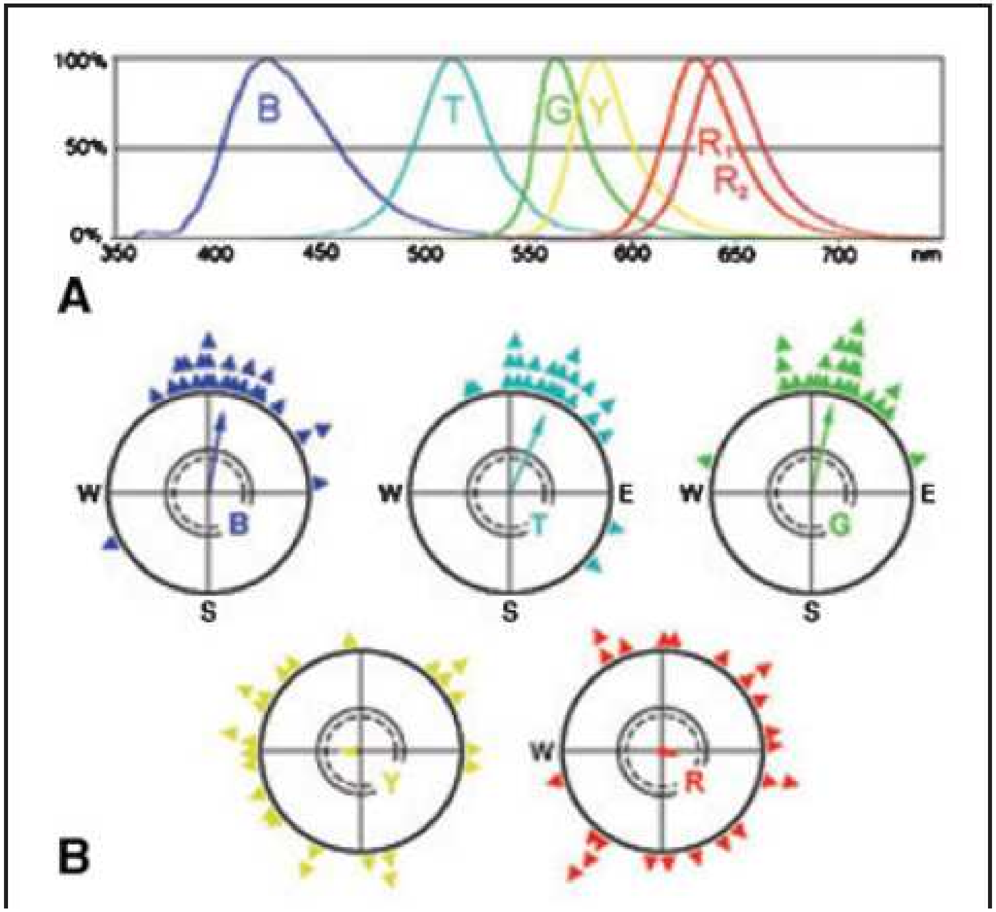
1 Cryptochrome as magnetoreceptor?



Blue-green light-dependent orientation of migratory birds.

European robin

Orientation behavior of birds under monochromatic lights produced by light-emitting diodes (LEDs) of various wavelengths with the peakwavelength indicated.
A: Spectra of the LEDs producing the test lights.
B: Orientation of European robins in spring.
Wiltschko, R., Wiltschko, W. (2006) Magnetoreception, *BioEssays* 28, 157-68.

1 Cryptochrome as magnetoreceptor?

Fluctuating magnetic field can disturb bird orientation

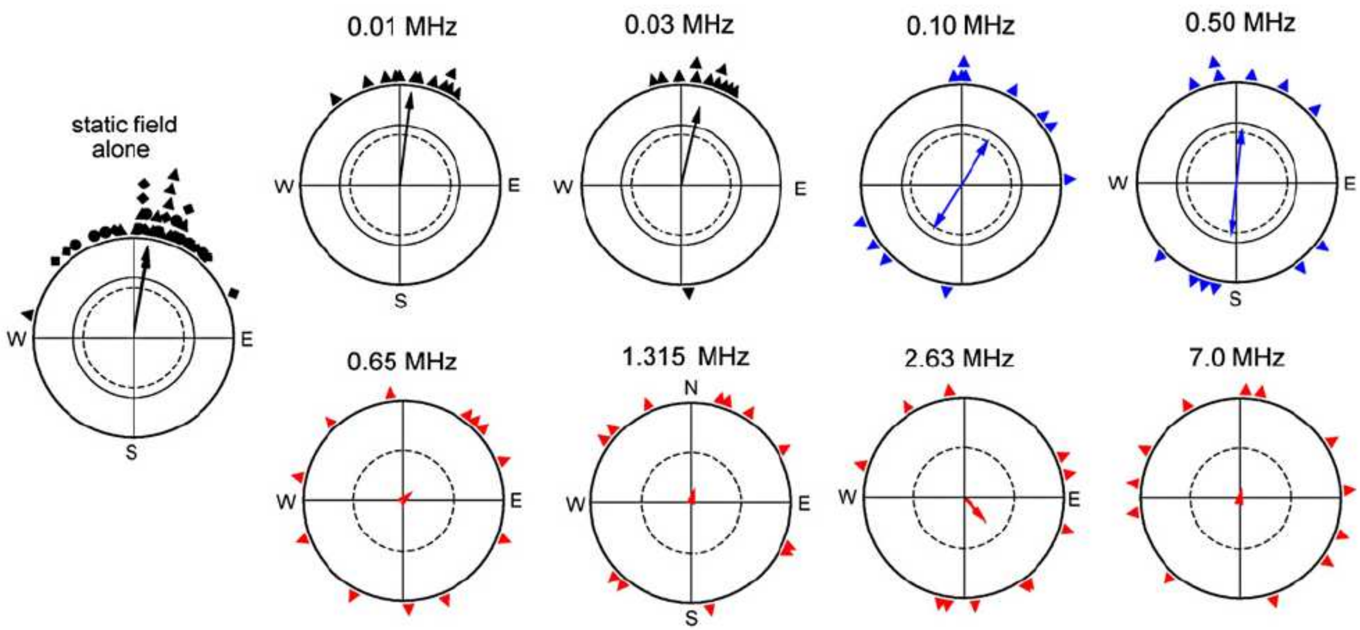


FIGURE 2 Orientation behavior of European robins in the local geomagnetic field: effects of added 480 nT oscillating fields of various frequencies. The symbols at the periphery of the circles mark the mean headings of the test birds based on three recordings each; the arrows represent the corresponding mean vectors. For the static field, the data from different years are given by different symbols; the three mean vectors almost coincide. The two inner circles are the 5% (*dotted*) and 1% significance limits of the Rayleigh test (17).

1 Cryptochrome as magnetoreceptor?

A **Radical Pair Mechanism** may indicate magnetic directions for birds.

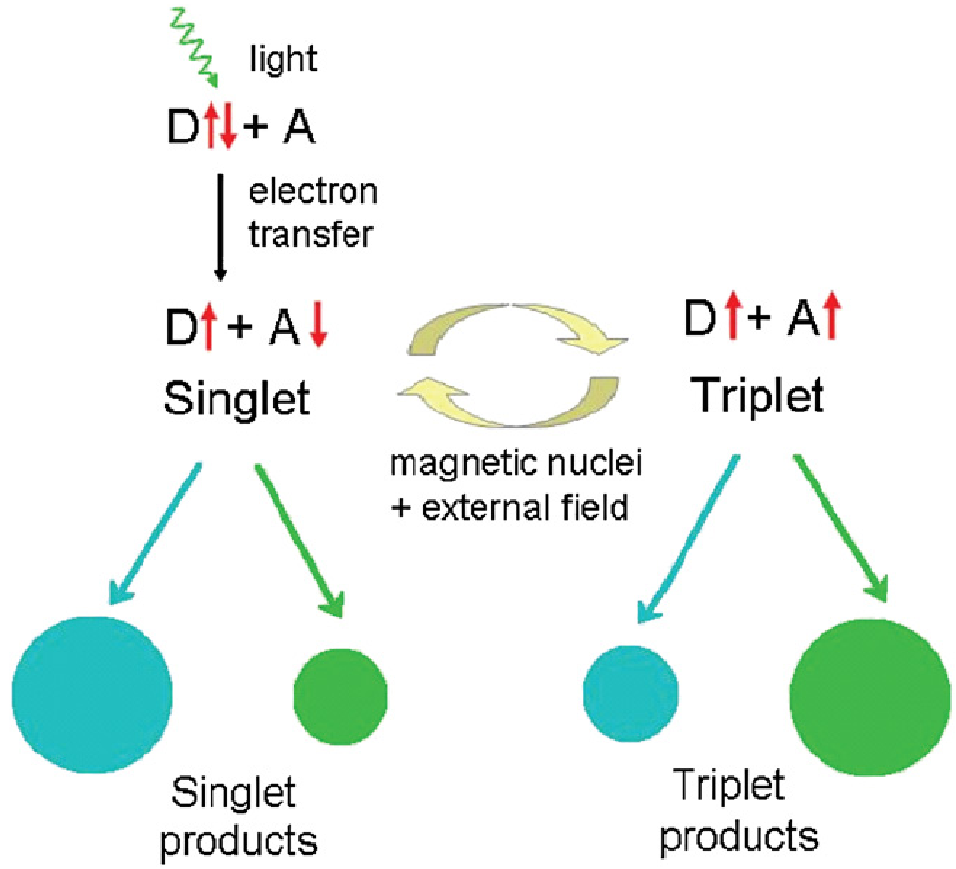
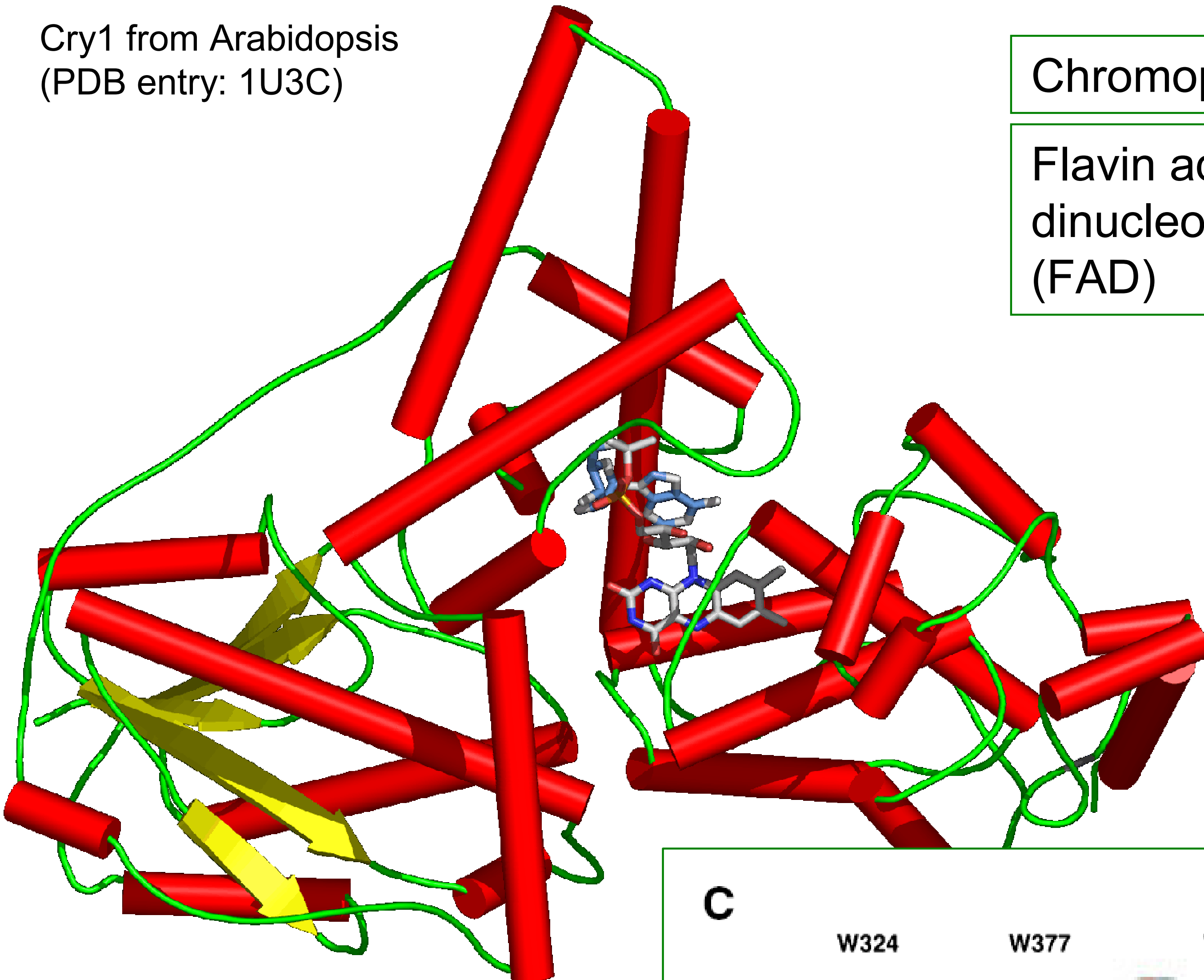


FIGURE 1 Schematic of the radical-pair mechanism. Light-induced electron transfer from a donor molecule D to an acceptor molecule A creates a radical pair, that is, two molecules each with an unpaired electron spin (*up* and *down arrows* next to *D* and *A*). Singlet and triplet states, defined by the relative orientation of the electron spins, interconvert due to the combined effects of internal and external magnetic fields. Singlet and triplet radical pairs decay into singlet and triplet products respectively, with relative yields indicated by the sizes of the circles. The relative yields of singlet and triplet products depend on the orientation of the external magnetic field with respect to that of the radicals. The arrows and circles at the bottom of the diagram symbolize pathways of product formation and reaction yields for two different orientations.

Rodgers & Hore (2009) PNAS 106, 353.

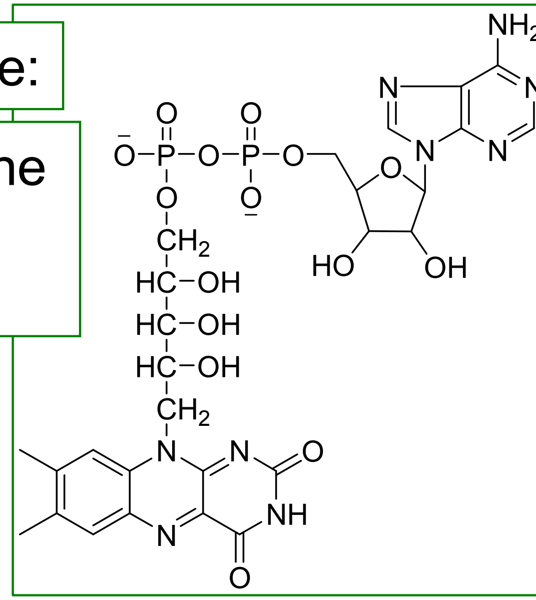
1 Cryptochrome as magnetoreceptor?

Cry1 from Arabidopsis
(PDB entry: 1U3C)

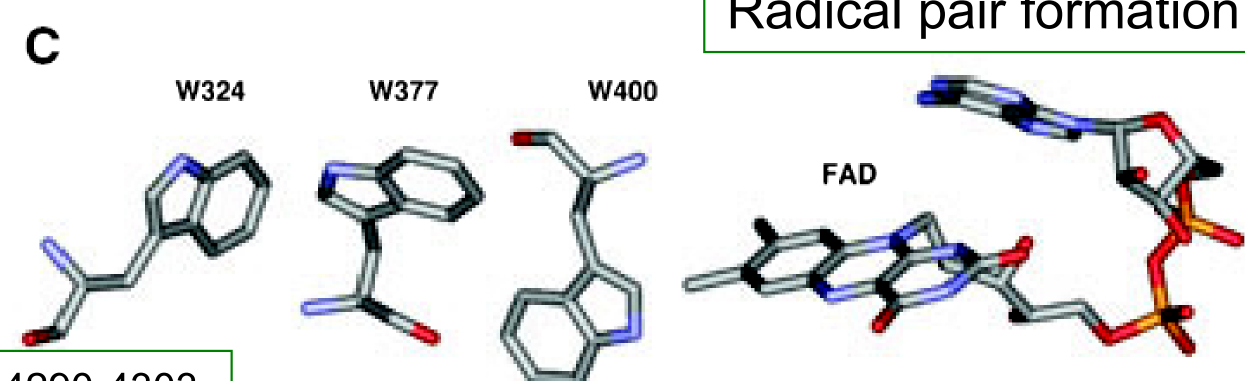


Chromophore:

Flavin adenine dinucleotide (FAD)

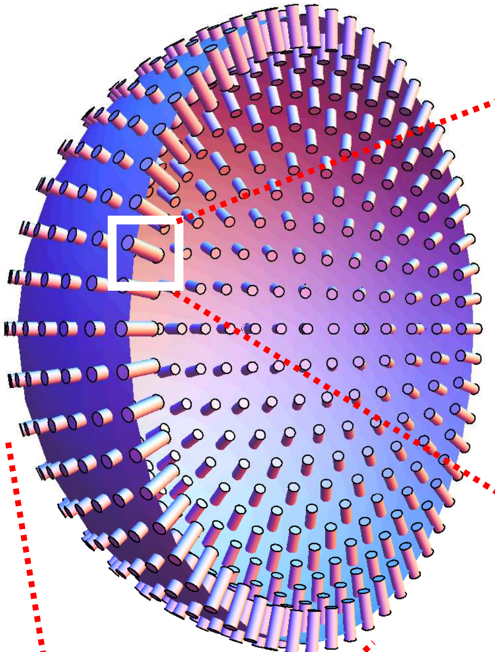


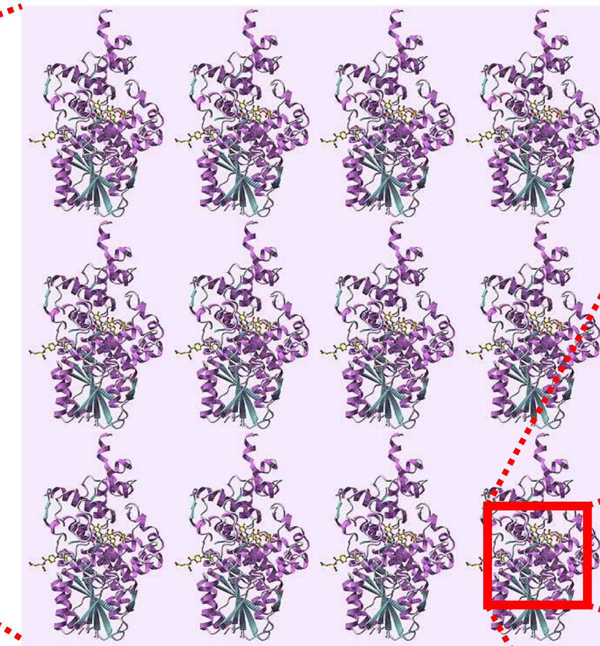
Three tryptophanes:
Radical pair formation



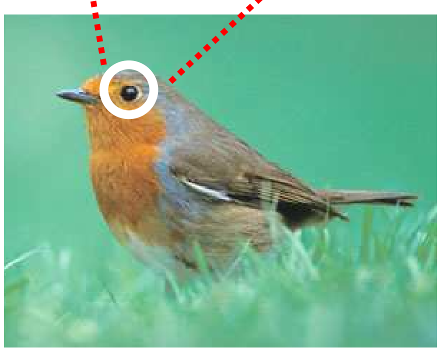
Schleicher & Weber (2009) FEBS J. 276, 4290-4303.

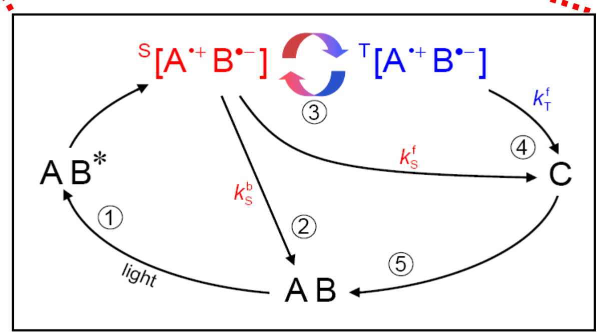
1 Cryptochrome as magnetoreceptor?



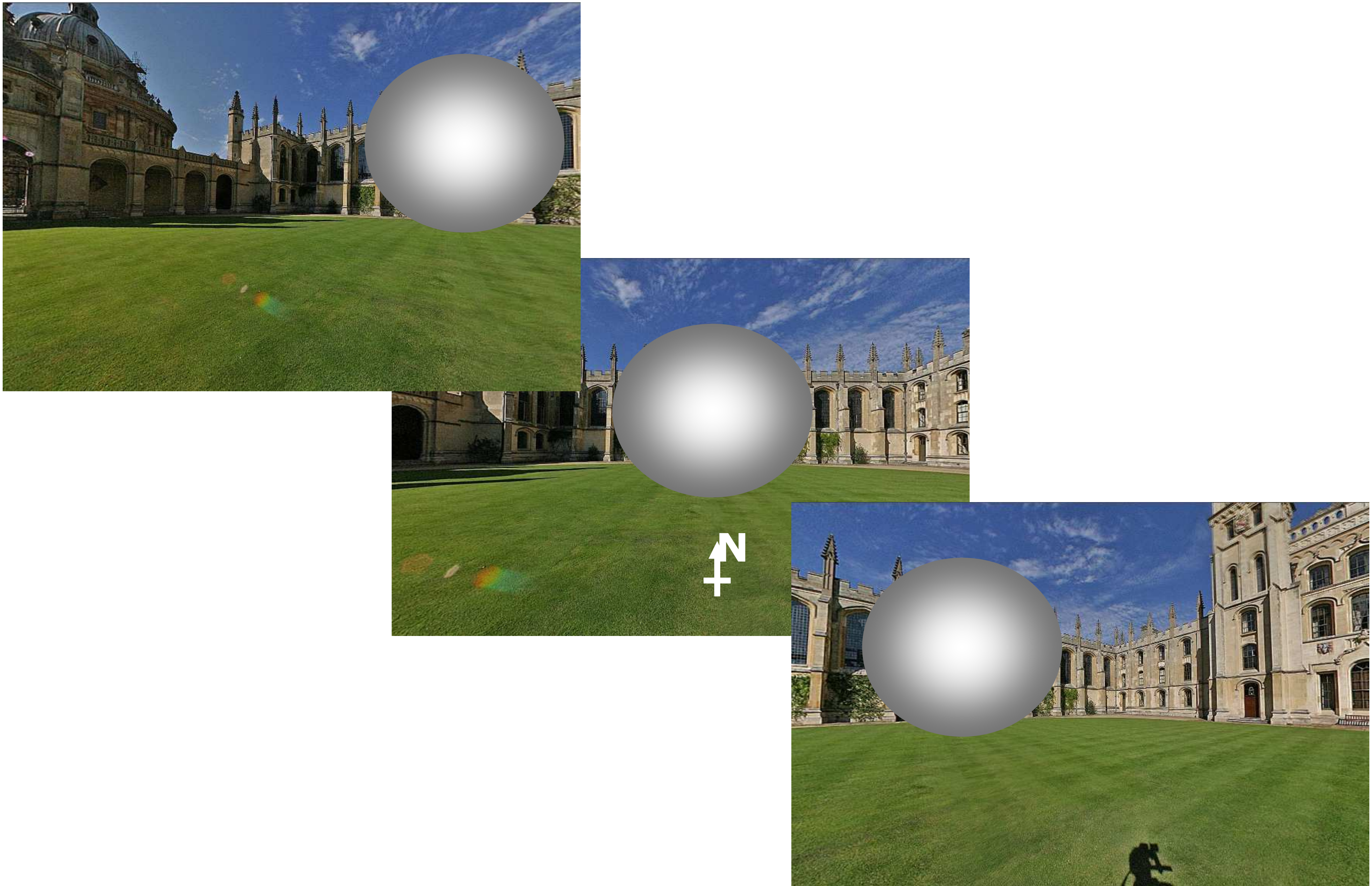


flavin & tryptophan radicals

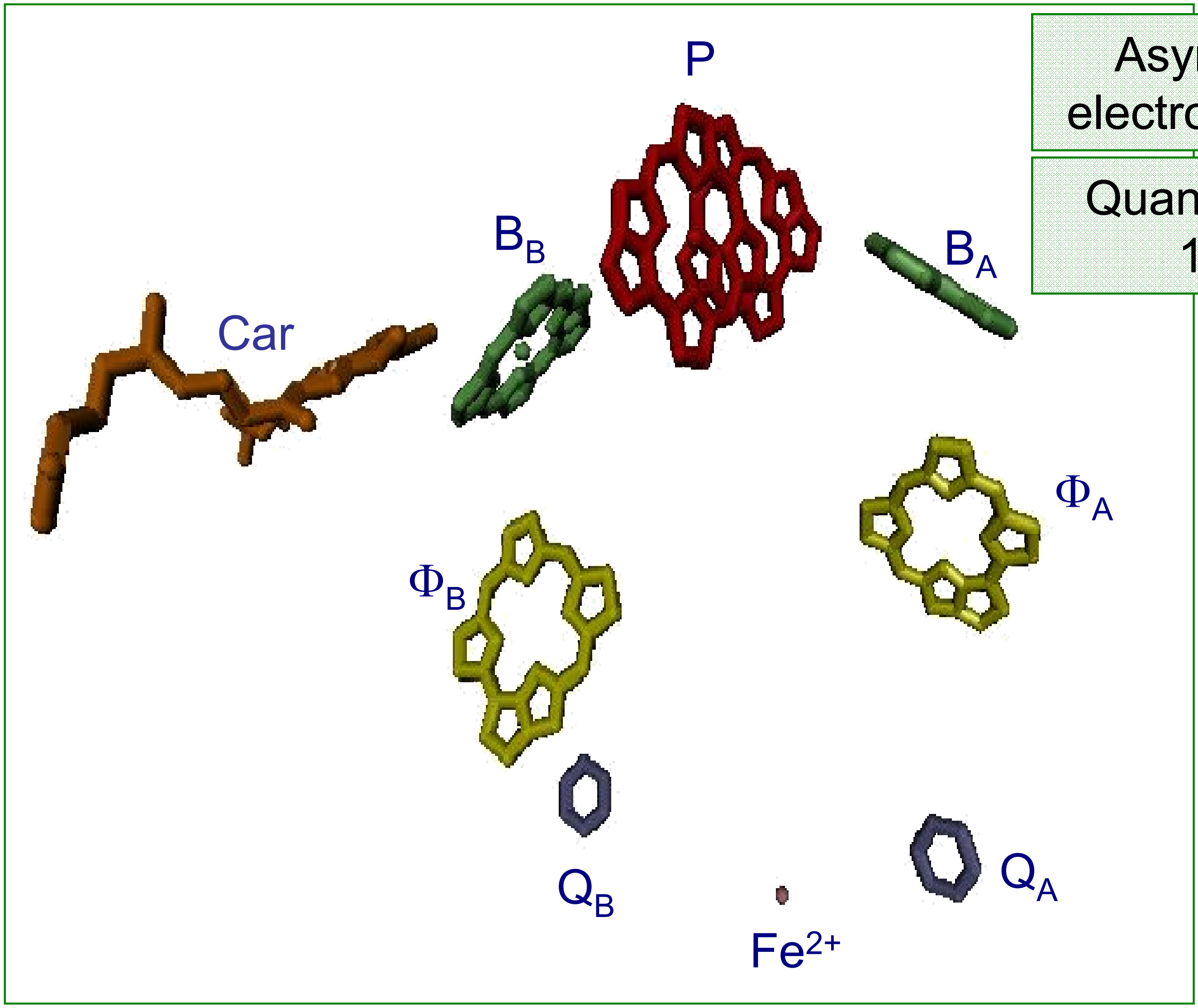




1 Cryptochrome as magnetoreceptor?



2 Spin dynamics in photosynthetic reaction centres (RCs)

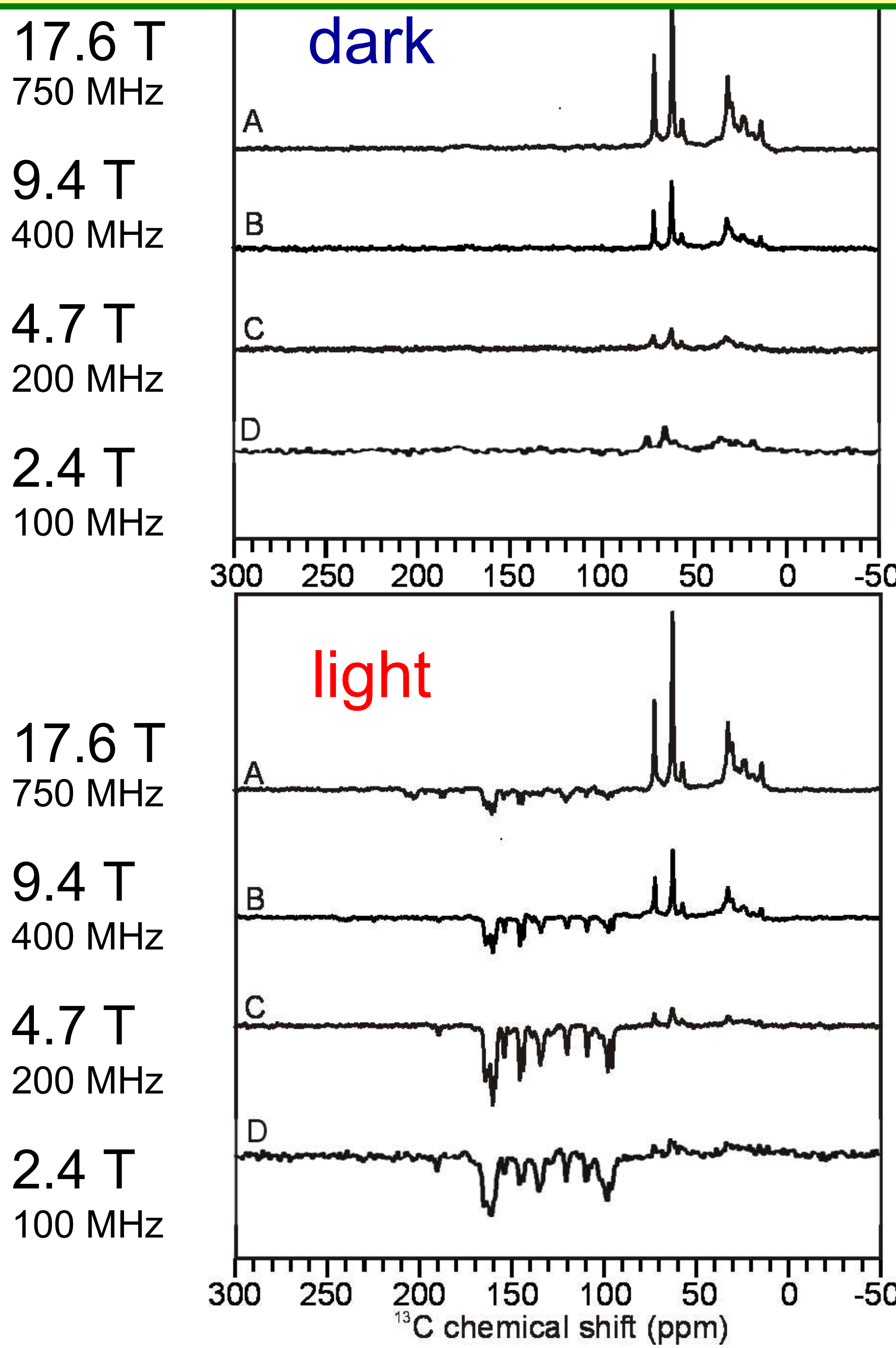


Asymmetric electron transfer

Quantum yield 100%

2 Spin dynamics in photosynthetic reaction centres (RCs)

The solid-state photo-CIDNP effect



Factor ~80

Factor ~800

Factor ~10000

Factor ~20000

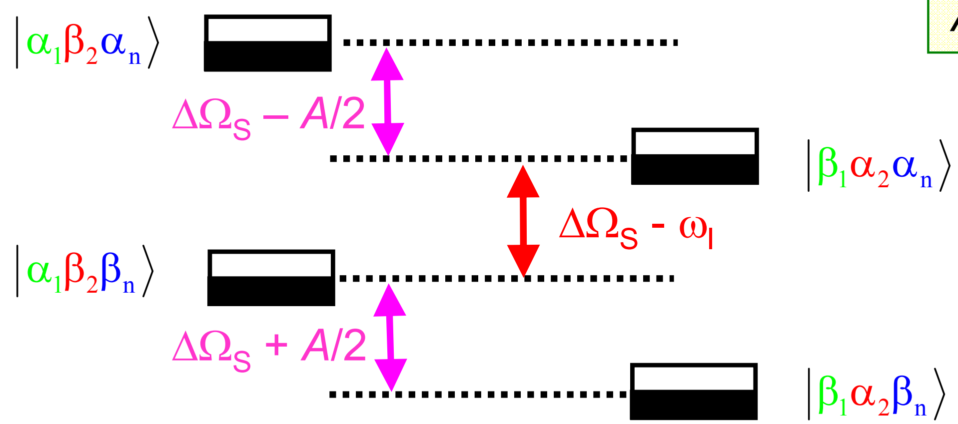
2 Spin dynamics in photosynthetic reaction centres (RCs)

Three-spin mixing (TSM)

Jeschke (1997) J. Chem. Phys. 106, 10072.
Jeschke (1998) JACS 120, 4425.
Daviso et al. (2008) Biophys. Techn. Photosynth. (Aartsma & Matysik, eds) 385.

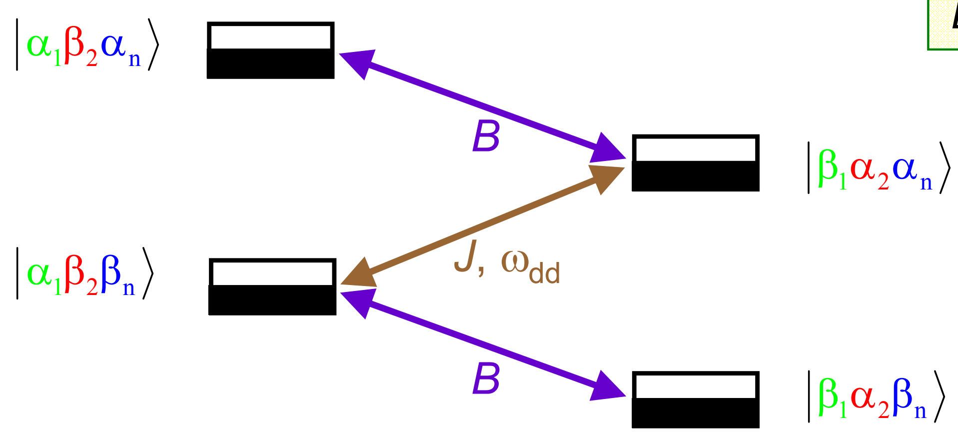
Energy differences

$\Delta\Omega_S$ = Difference in electron Zeeman frequency
ω_I= Nuclear Zeeman frequency
A = Secular part of the hyperfine interaction



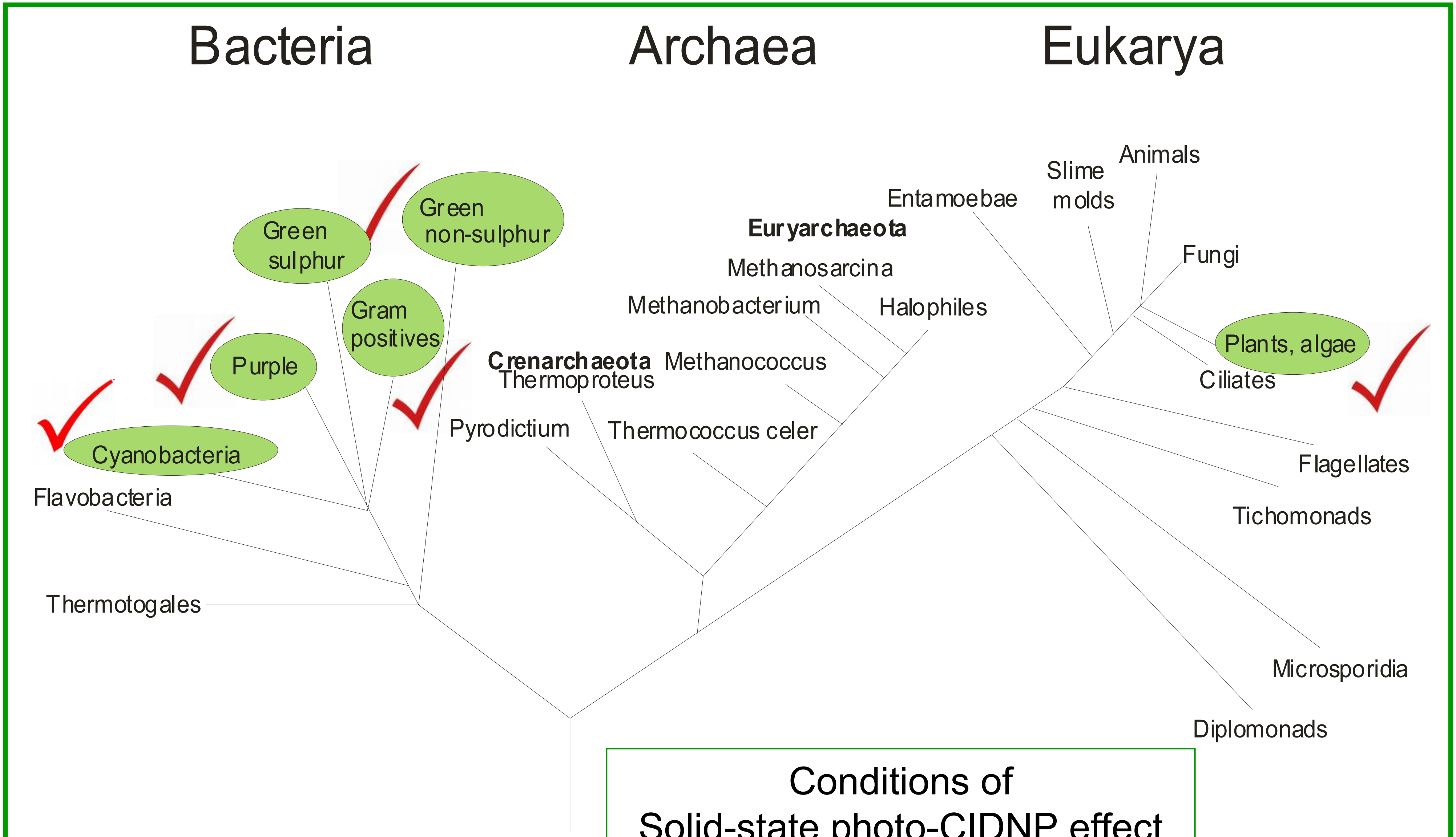
Mixing terms

J = Electron-electron spin coupling
ω_{dd}= Electron-electron dipolar coupling
B = Pseudosecular part of the hyperfine interaction



50

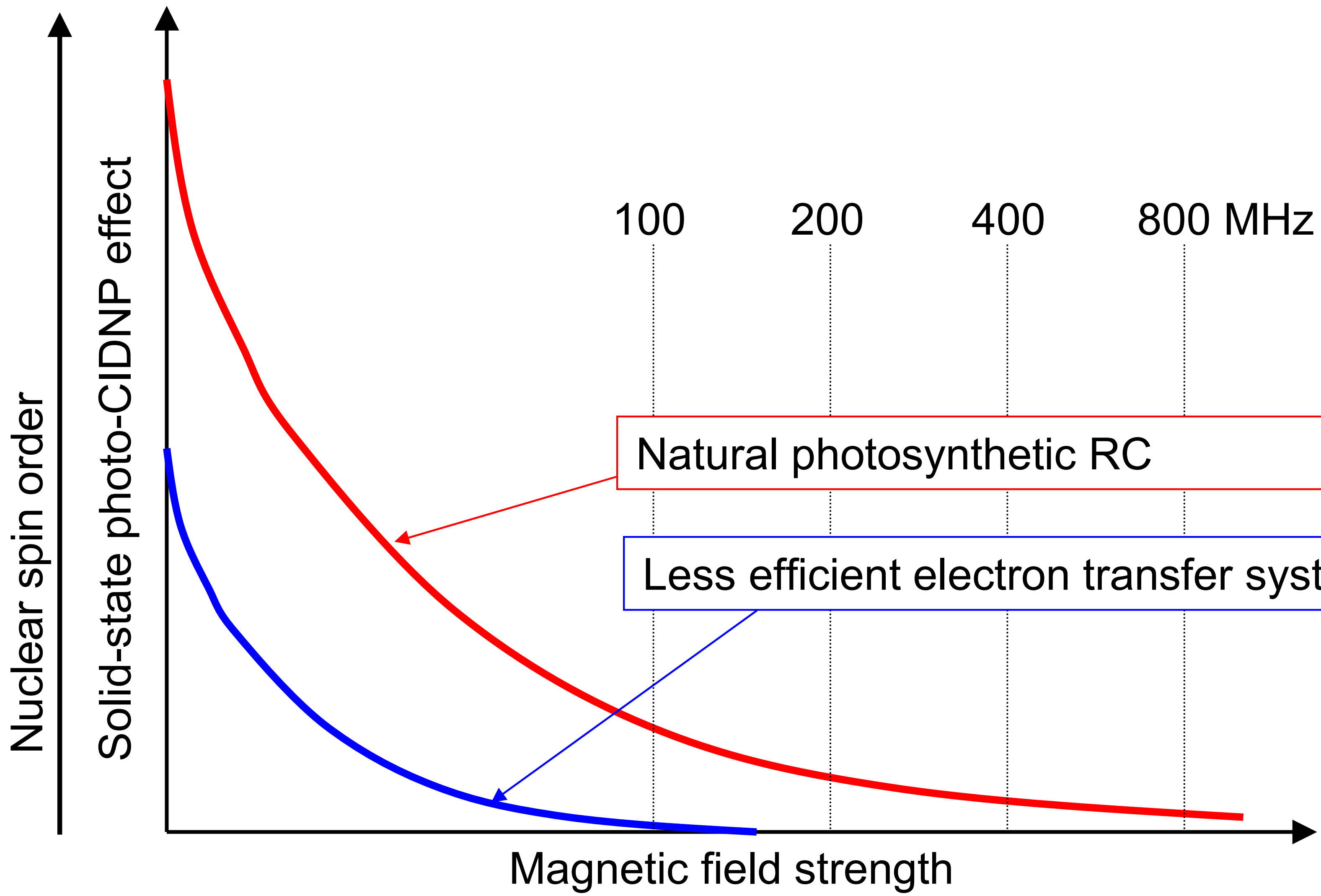
2 Spin dynamics in photosynthetic reaction centres (RCs)



Conditions of
Solid-state photo-CIDNP effect
have been ***conserved***
over ~3•10^{9} years

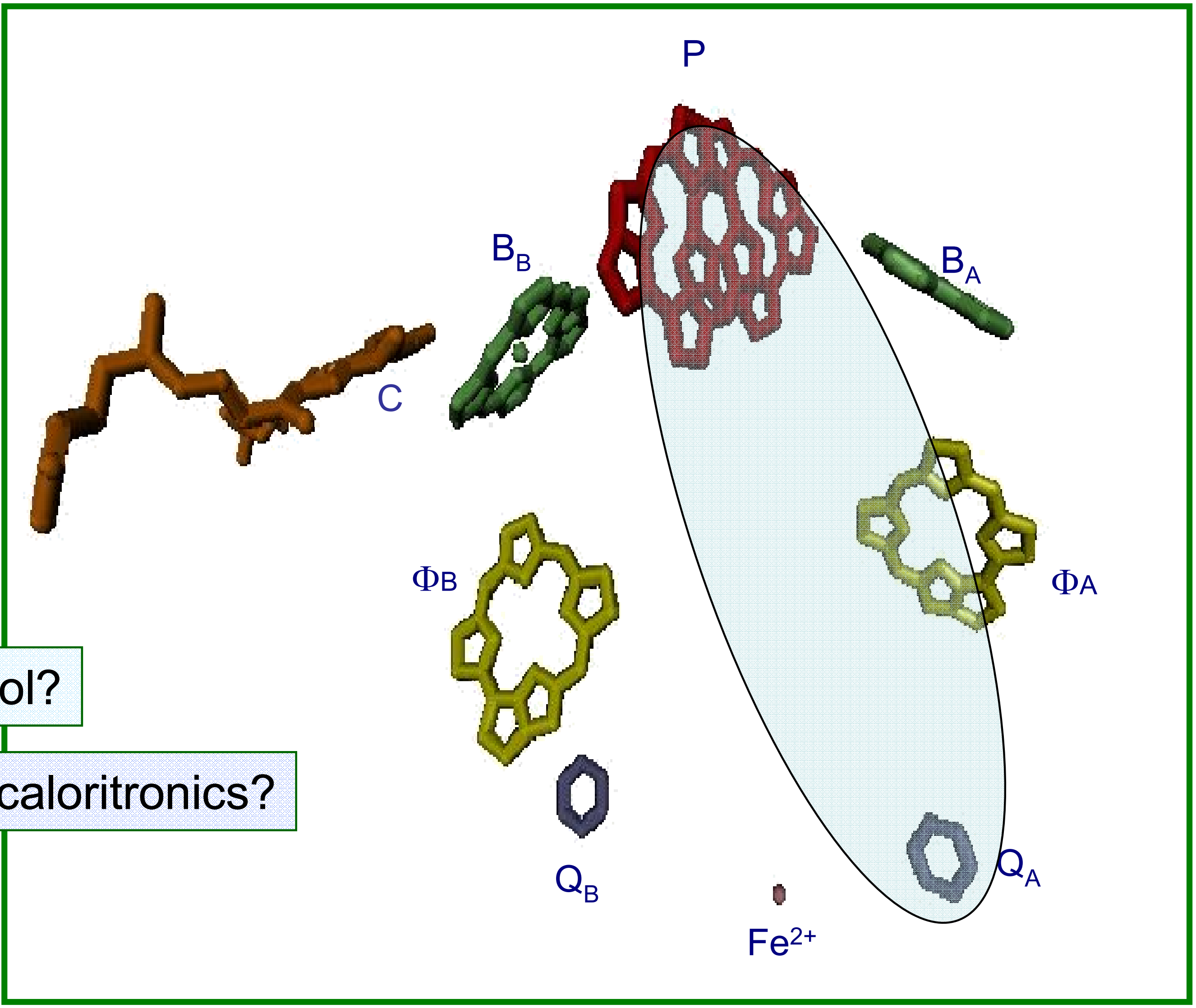
2 Spin dynamics in photosynthetic reaction centres (RCs)

Possible correlation between solid-state photo-CIDNP effect and efficiency of electron transfer



2 Spin dynamics in photosynthetic reaction centres (RCs)

Can the solid-state photo-CIDNP effect
occur under **entirely natural conditions**?



Proton spin pool?

Bio-nano spin caloritronics?

Literature

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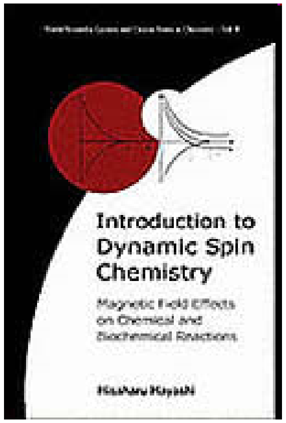
World Scientific Lecture and Course Notes in Chemistry, Vol. 8

INTRODUCTION TO DYNAMIC SPIN CHEMISTRY
Magnetic Field Effects on Chemical and Biochemical Reactions
by Hisaharu Hayashi
(RIKEN, The Institute of Physical and Chemical Research, Japan)



268pp

ISBN: 978-981-238-423-2
March 2004

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1967

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i) Two-dimensional photo-CIDNP MAS NMR

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