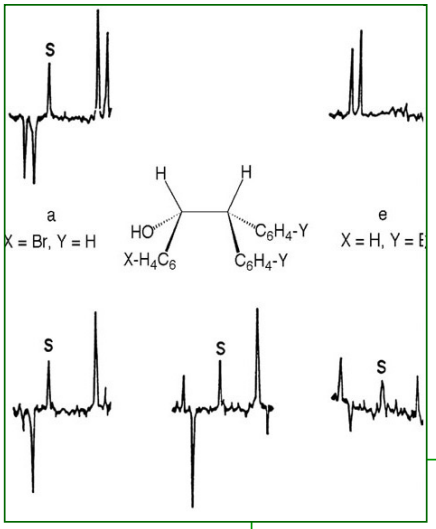
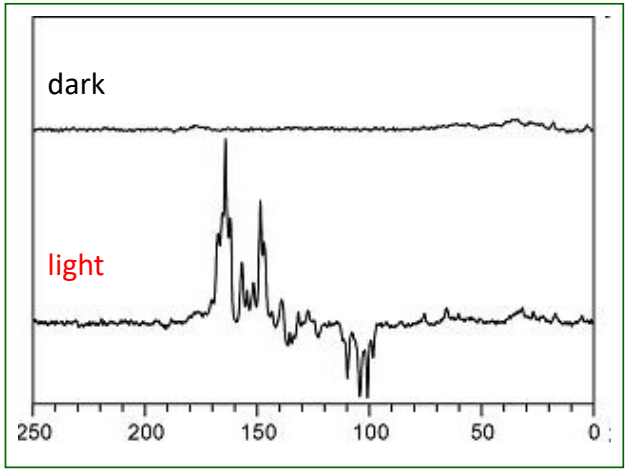


Jörg Matysik, Leipzig University
誉宮, ライプツィヒ大学 (ライ大)

Photo-CIDNP

Photochemically induced dynamic nuclear polarization



神戸市, 2024年9月15日 (日)

Part 1 The radical pair

Part 2 Photo-CIDNP in liquid state

Part 3 Photo-CIDNP in solid state

Part 1

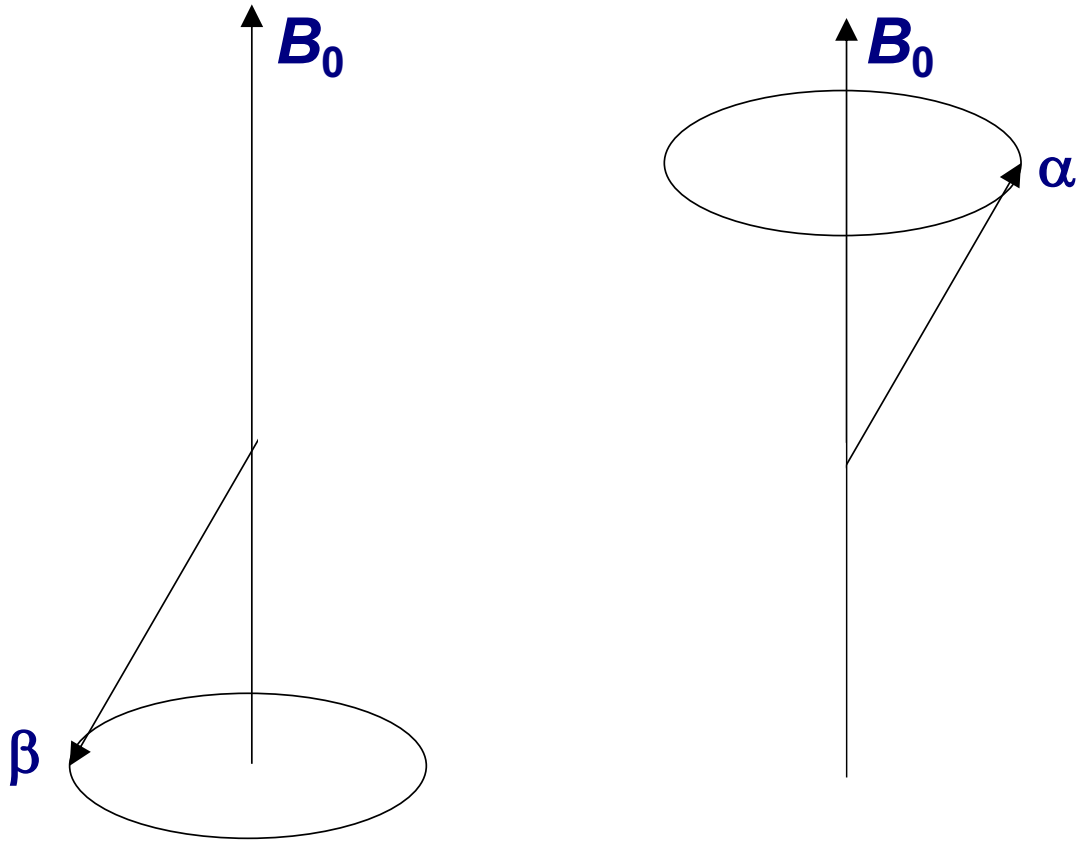
The radical pair

Several figures have been provided by P. Hore, Oxford.

A radical in an external magnetic field

Two states in vector presentation

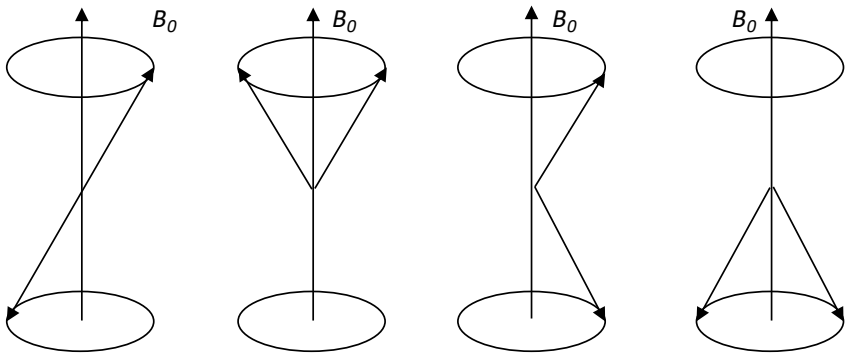
R•



The radical pair

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_-

Spin state S	**0**	**1**	**1**	**1**
Magnetic quantum number m_S	**0**	**+1**	**0**	**-1**
For electrons	$\frac{1}{\sqrt{2}}\langle\alpha\beta\mathrm{I}-\mathrm{I}\beta\alpha\rangle$	$\alpha\alpha$	$\frac{1}{\sqrt{2}}\langle\alpha\beta\mathrm{I}+\mathrm{I}\beta\alpha\rangle$	$\beta\beta$

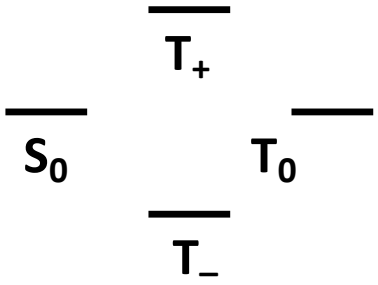
The radical pair

Four spin states

A No field

At zero field, triplet states are labelled T_X, T_Y, and T_Z (corresponding to principal axes direction of zero-field splitting tensor

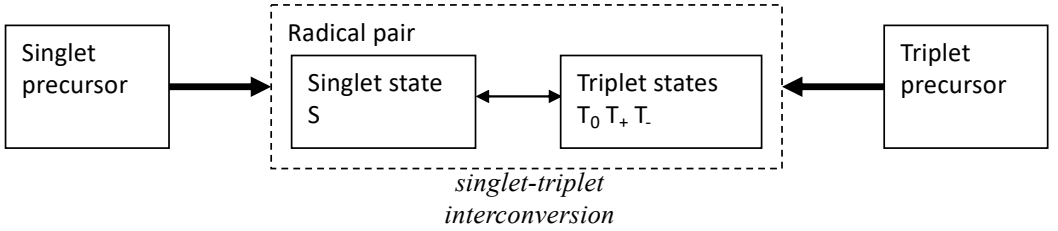
B High field



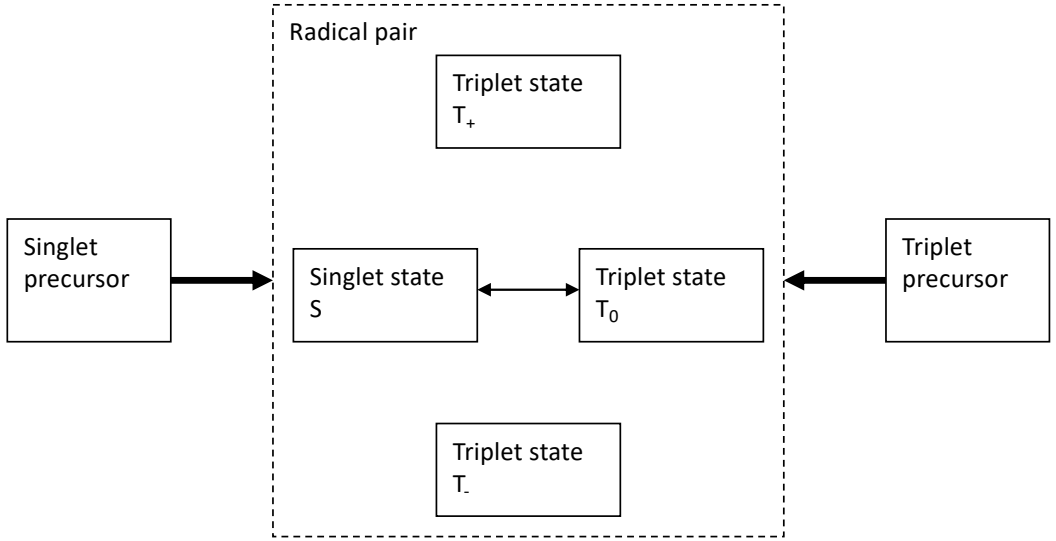
The formation of a radical pair

The conservation of spin

A Low field



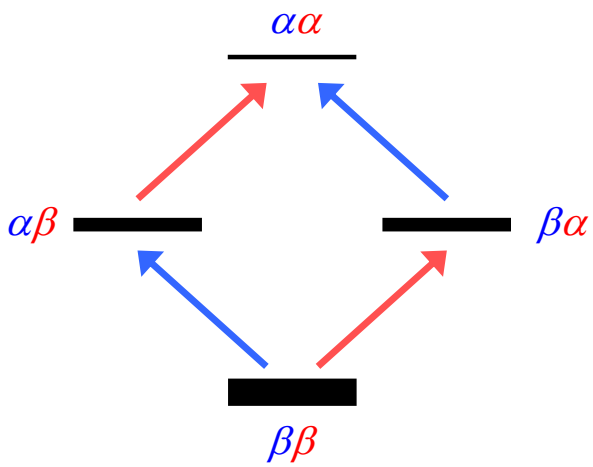
B High field



The spin-correlated (spin-polarized) radical pair

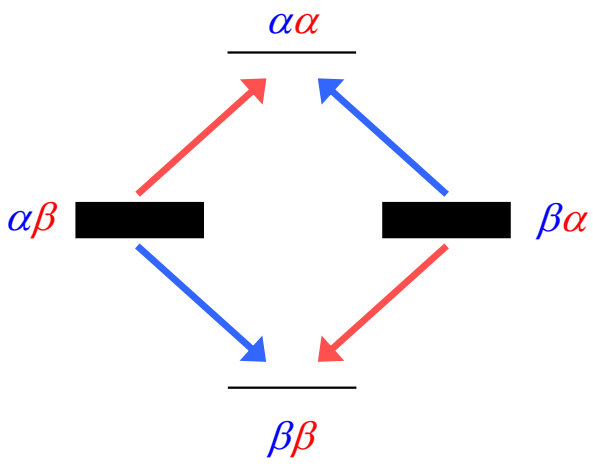
Equilibrium

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

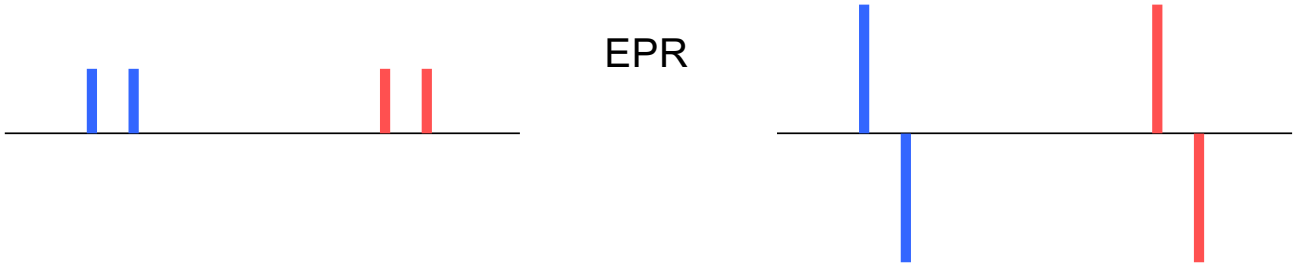


Spin-correlated

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



EPR



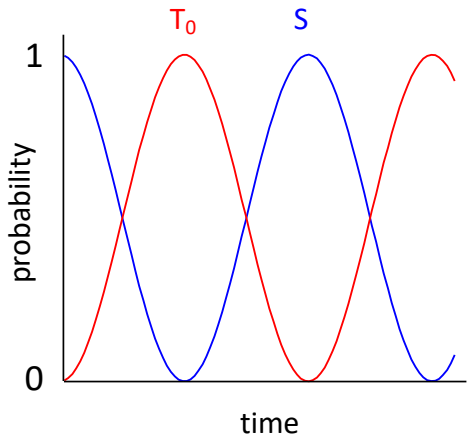
Hore PJ, Hunter DA, McKie CD, Hoff AJ (1987) Chem. Phys. Lett. 137, 495-500.

Closs GL, Forbes MDE, Norris JR (1987) J. Phys. Chem. 91, 3592-3599.

The radical pair

Coherent singlet-triplet interconversion

- S and T states are not stationary states
- Interconverted by weak magnetic interactions (sometimes called: intersystem crossing, ISC)



The radical pair

Interactions

- Electron-nucleus: **hyperfine interaction**
  - 1-100 MHz
- Electron-electron: **exchange & dipolar interactions**
  - Smaller than hyperfine interaction when r_{ee} > ~1.5 nm
- Electron-field: **Electron Zeeman interaction**
  - 28 MHz per mT (for $g \approx 2$)
- Nucleus-field: **Nuclear Zeeman interaction**
  - For ^{1}H only 1/658 of electron Zeeman interaction
- Spin system-surroundings: **Thermal motion**
  - $k_B T/h$: 6×10^6 MHz at 300 K

$$\mathcal{H}_{HF} = \boldsymbol{S}\mathbf{A}\boldsymbol{I}$$

$$\mathcal{H}_{exch} = \boldsymbol{S}_1\mathbf{J}\boldsymbol{S}_2$$

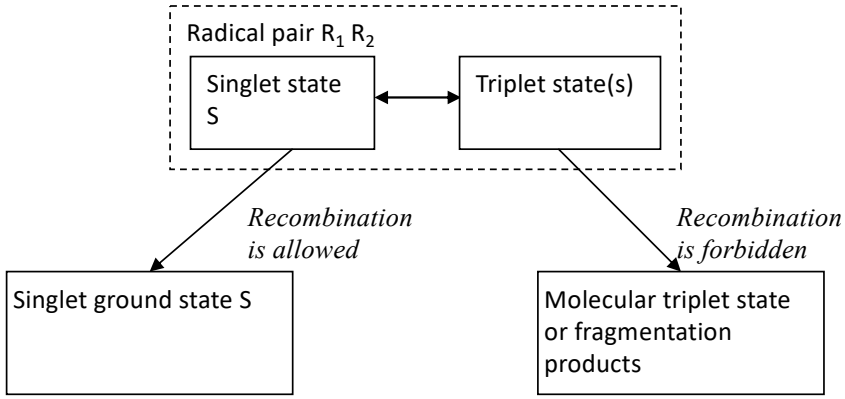
$$\mathcal{H}_{DD} = \boldsymbol{S}_1\mathbf{D}\boldsymbol{S}_2$$

$$\mathcal{H}_{EZ} = \beta_e \boldsymbol{B}_0 \boldsymbol{g} \boldsymbol{S}/\hbar$$

$$\mathcal{H}_{NZ} = -\beta_n \boldsymbol{B}_0 \boldsymbol{g}_n \boldsymbol{I}/\hbar$$

The decay of a radical pair

The conservation of spin

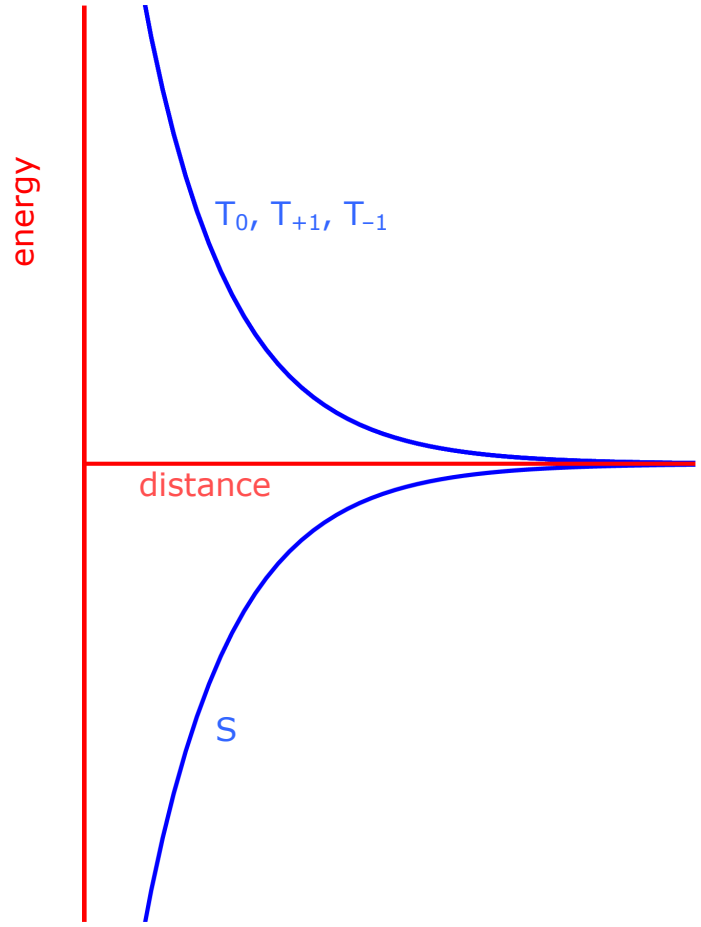


The radical pair

Properties

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

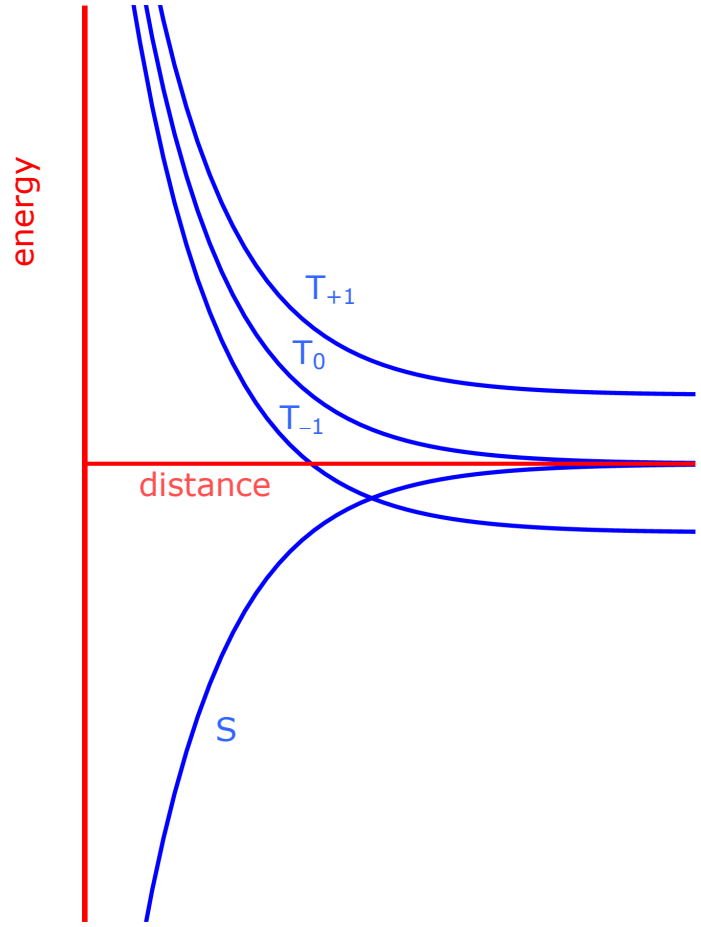
The radical pair



	$\vert S, M_S \rangle$
S	$\vert 0, 0 \rangle$
T_{+1}	$\vert 1, +1 \rangle$
T_0	$\vert 1, 0 \rangle$
T_{-1}	$\vert 1, -1 \rangle$

zero/low field: $S \leftrightarrow T_0, T_{\pm 1}$

The radical pair

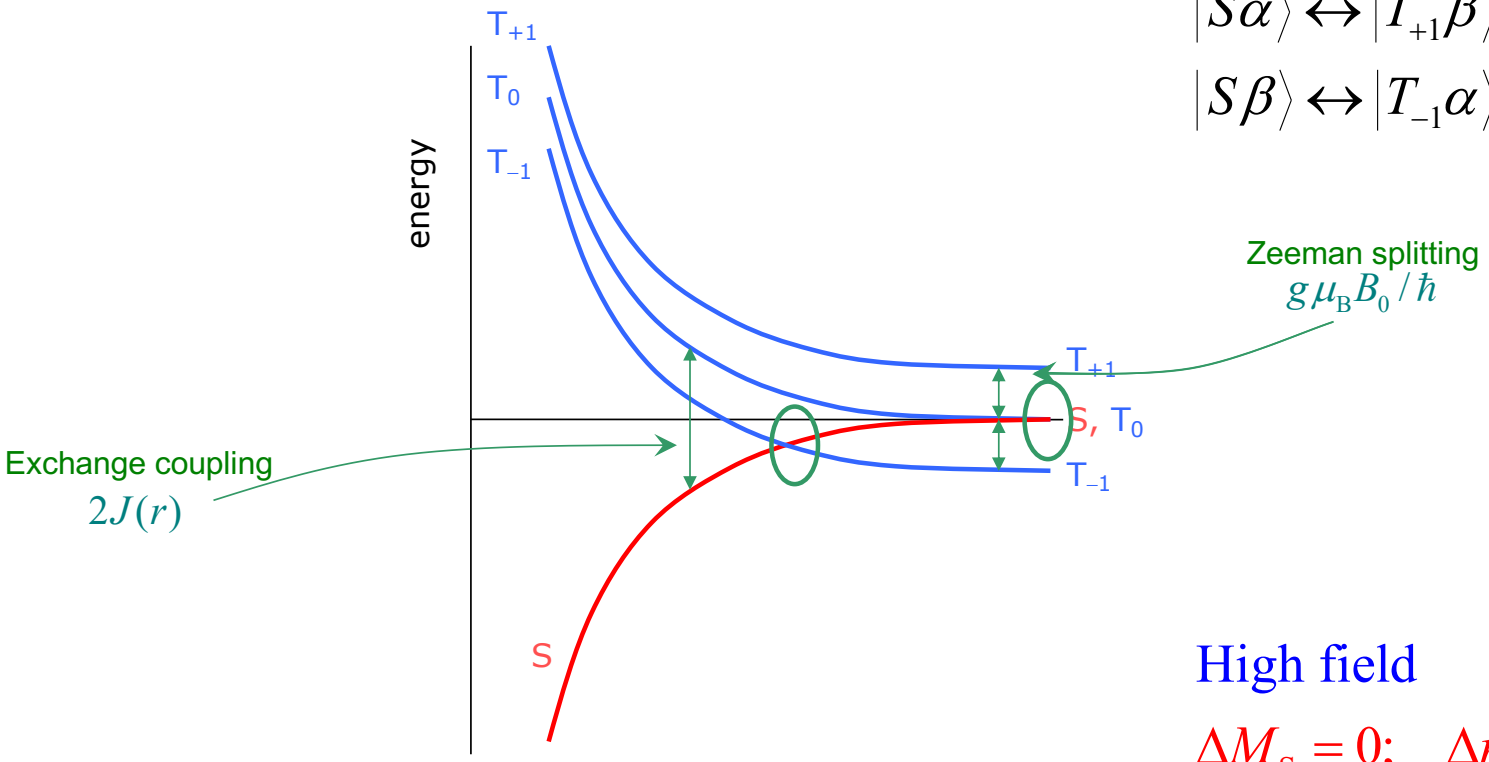


	$\vert S, M_S \rangle$
S	$\vert 0, 0 \rangle$
T_{+1}	$\vert 1, +1 \rangle$
T_0	$\vert 1, 0 \rangle$
T_{-1}	$\vert 1, -1 \rangle$

zero/low field: $S \leftrightarrow T_0, T_{\pm 1}$

high field: $S \leftrightarrow T_0$

The radical pair



Low field

$\Delta M_S = \pm 1; \quad \Delta m_I = \mp 1$

$|S\alpha\rangle \leftrightarrow |T_{+1}\beta\rangle$

$|S\beta\rangle \leftrightarrow |T_{-1}\alpha\rangle$

High field

$\Delta M_S = 0; \quad \Delta m_I = 0$

$|S\alpha\rangle \leftrightarrow |T_0\alpha\rangle$

$|S\beta\rangle \leftrightarrow |T_0\beta\rangle$

Part 2

Photo-CIDNP in liquid state

Several figures have been provided by P. Hore, Oxford.

A review from Konstantin Ivanov (1977-2021)

ChemPubSoc Europe

DOI: 10.1002/cphc.201800566

CHEMPHYSCHEM Reviews

Special Issue

Time-Resolved Chemically Induced Dynamic Nuclear Polarization of Biologically Important Molecules

Olga B. Morozova[a, b] and Konstantin L. Ivanov*[a, b]

ChemPhysChem **2019**, *20*, 197 – 215

The (photo-) **CIDNP** effect

Kernresonanz-Emissionslinien während rascher Radikalreaktionen

I. Aufnahmeverfahren und Beispiele

J. Bargon, H. Fischer und U. Johnsen

Deutsches Kunststoff-Institut Darmstadt

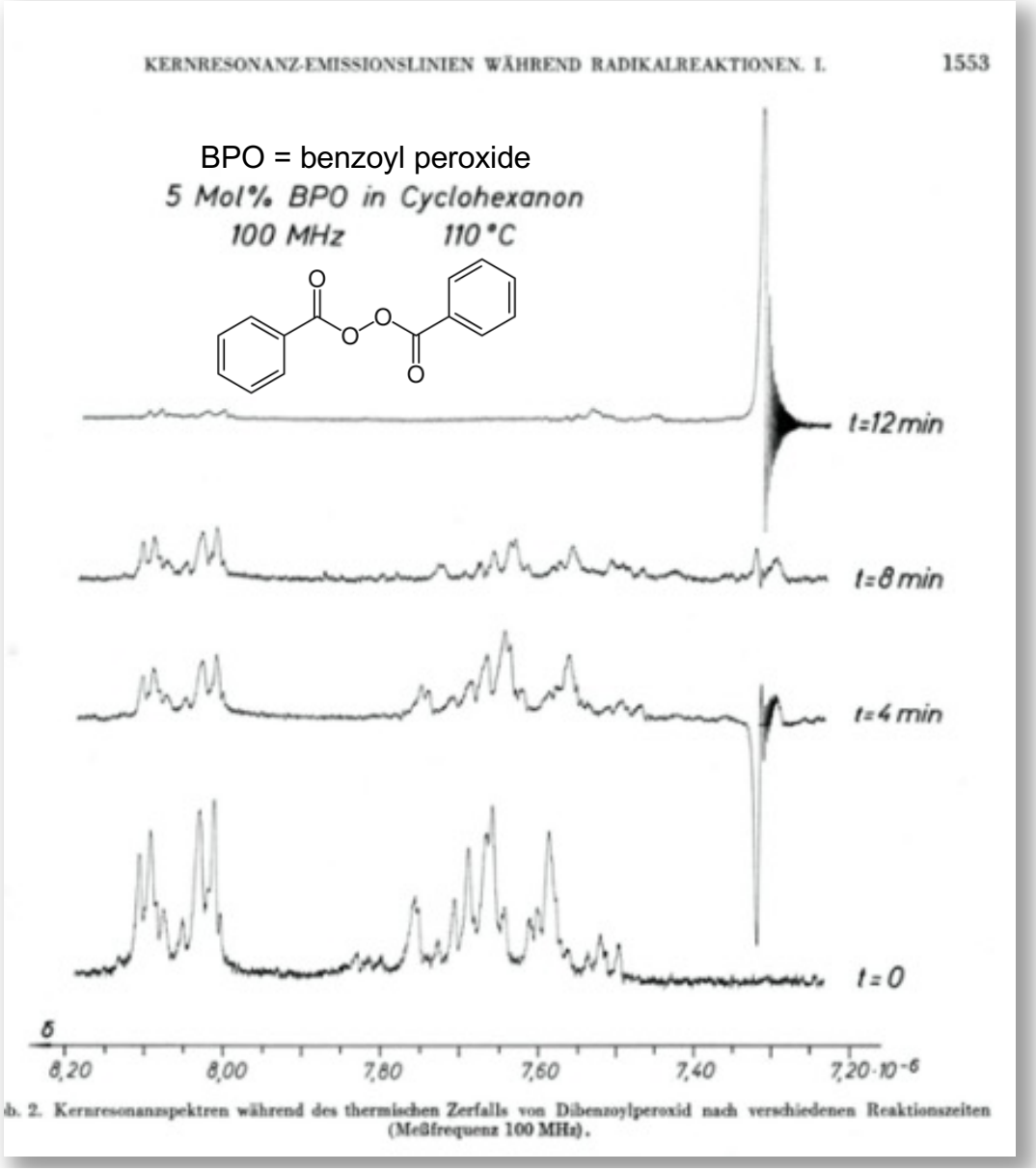
(Z. Naturforschg. **22 a**, 1551—1555 [1967]; eingegangen am 16. Juni 1967)

he detection of unstable intermediates during rapid chemical reactions an experimental e has been developed which allows tracing of reactions with reaction times of minutes or by nuclear magnetic resonance spectroscopy. By this technique series of NMR spectra en during thermal decomposition of peroxides and azo-compounds, and the following un- effect was observed: During some reactions the proton resonance lines of reaction products appear intermediately in emission instead of absorption. The emission lines in the decomposition reactions of dibenzoylperoxide and di-p-chlorbenzoylperoxide are treated in detail, and are shown to be due to benzene and chlorobenzene molecules formed in the reactions. Obviously these molecules are formed initially with a negative spin polarization of their proton spin systems which is assumed to be a consequence of a chemically induced dynamic nuclear polarization.

Joachim Bargon, *1939

Im Verlauf vieler chemischer Reaktionen treten kurzzeitig instabile Zwischenprodukte auf, die meist nicht quantitativ gefaßt werden können. Zum Nachweis dieser Zwischenprodukte bieten sich im Prinzip empfindliche spektroskopische Methoden an. Ihr

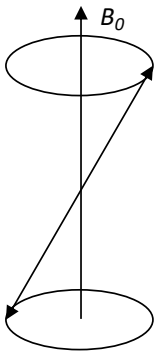
delt. In der unmittelbar anschließenden Veröffentlichung II [1] wird eine mögliche Deutung des Effektes angegeben. Die bei den Reaktionen beobachteten Zwischenprodukte sollen in späteren Veröffentlichungen beschrieben werden.



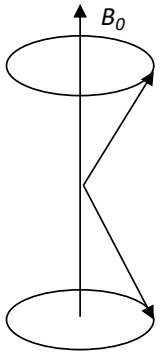

Joachim Bargon, *1939

Radical pair dynamics

Reaction dynamics at high fields



Singlet S



Triplet T_0

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

1. **Δg** mechanism:

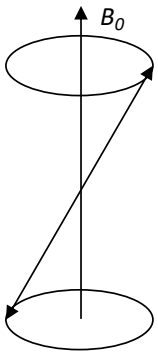
   difference in electron Larmor precession

2. **hf** mechanism:

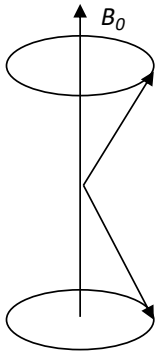
   hyperfine interaction unpaired e^-/nucleus

Radical pair dynamics

Reaction dynamics at high fields



Singlet S



Triplet T_0

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

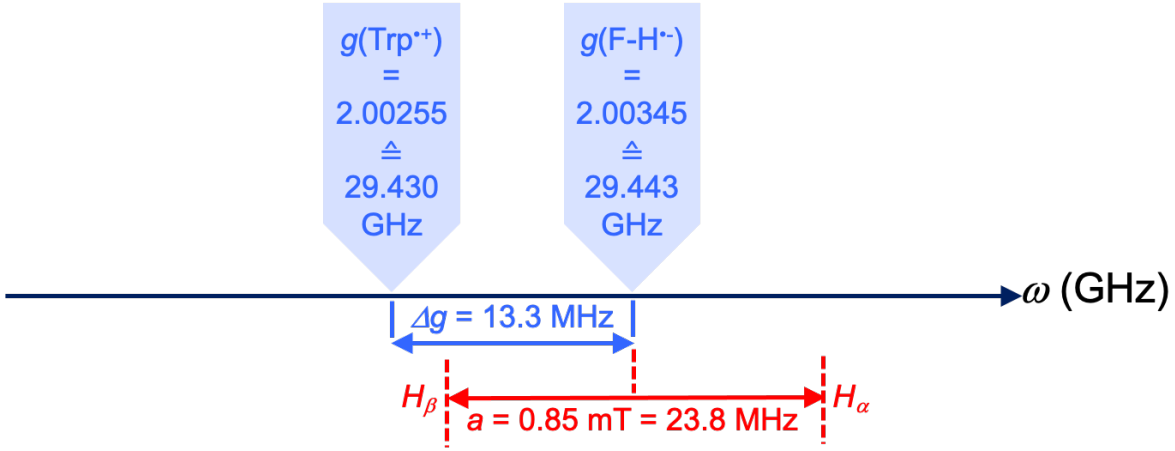
1. Δg mechanism:

   difference in electron Larmor precession

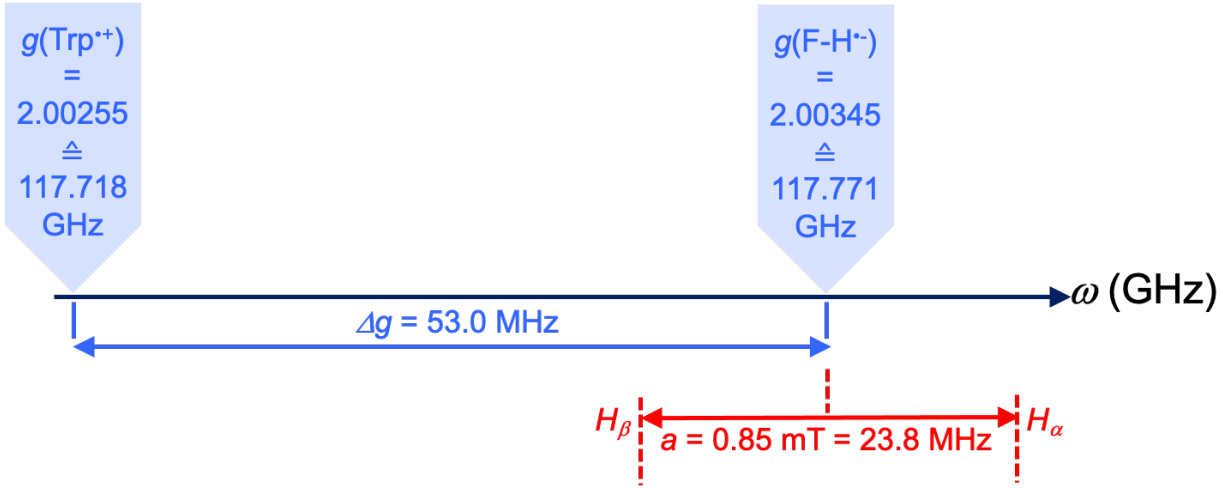
2. **hf** mechanism:

   hyperfine interaction unpaired e^-/nucleus

1.1 Tesla



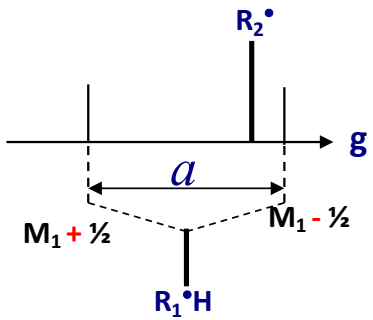
4.2 Tesla



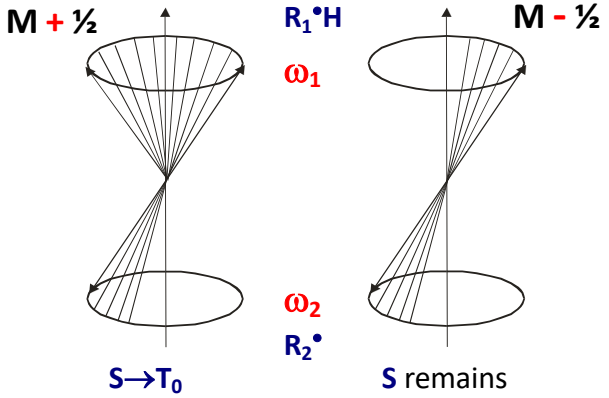
Radical pair dynamics

Reaction dynamics at high fields

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



hyperfine coupling constant a

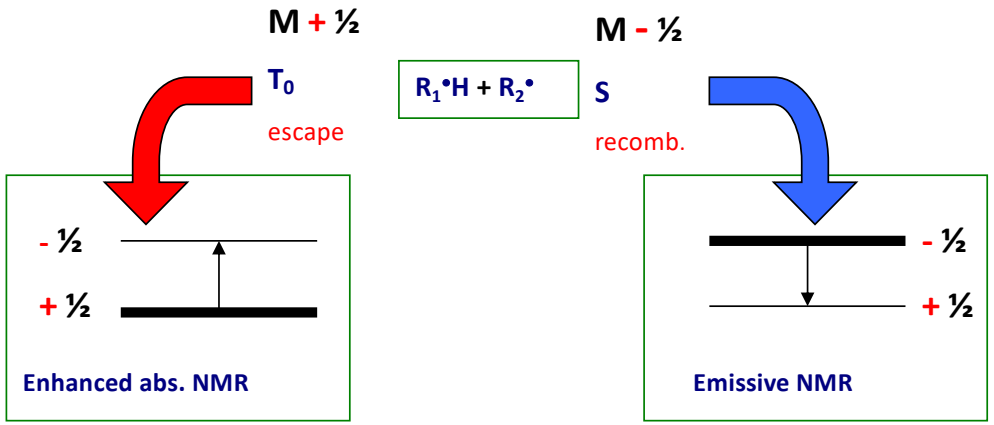


$$\Delta\omega = (g_1 - g_2)\,\frac{\beta B_0}{h}\,\pm ½\, a_H$$

Nuclear spins control reaction path

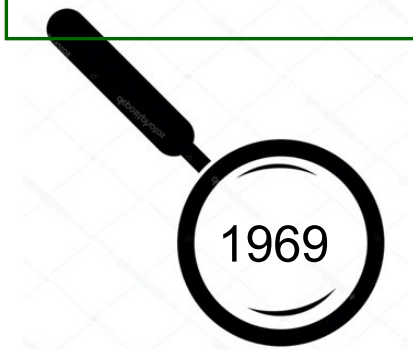
Radical pair dynamics in liquids

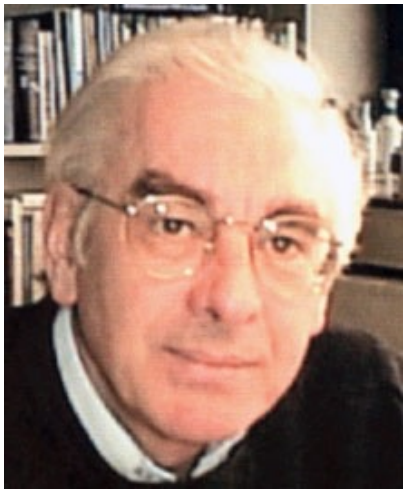
The classical **Radical-Pair Mechanism** (RPM)



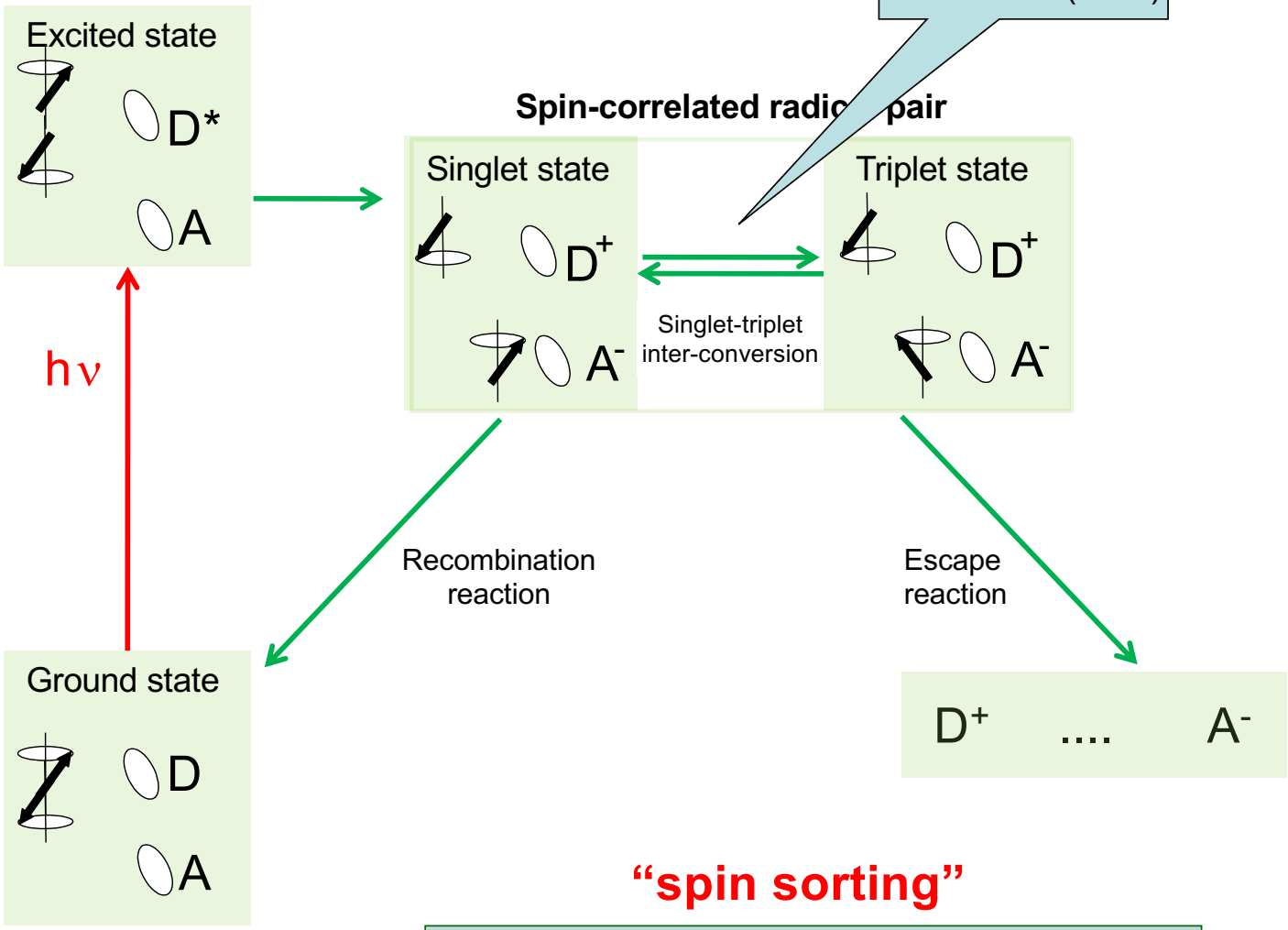
- Reaction products **out of Boltzmann** equilibrium
- **Enhanced polarization** observable by NMR, if
  1. different photo-products, or
  2. selective relaxation

The Radical-Pair Mechanism (RPM)





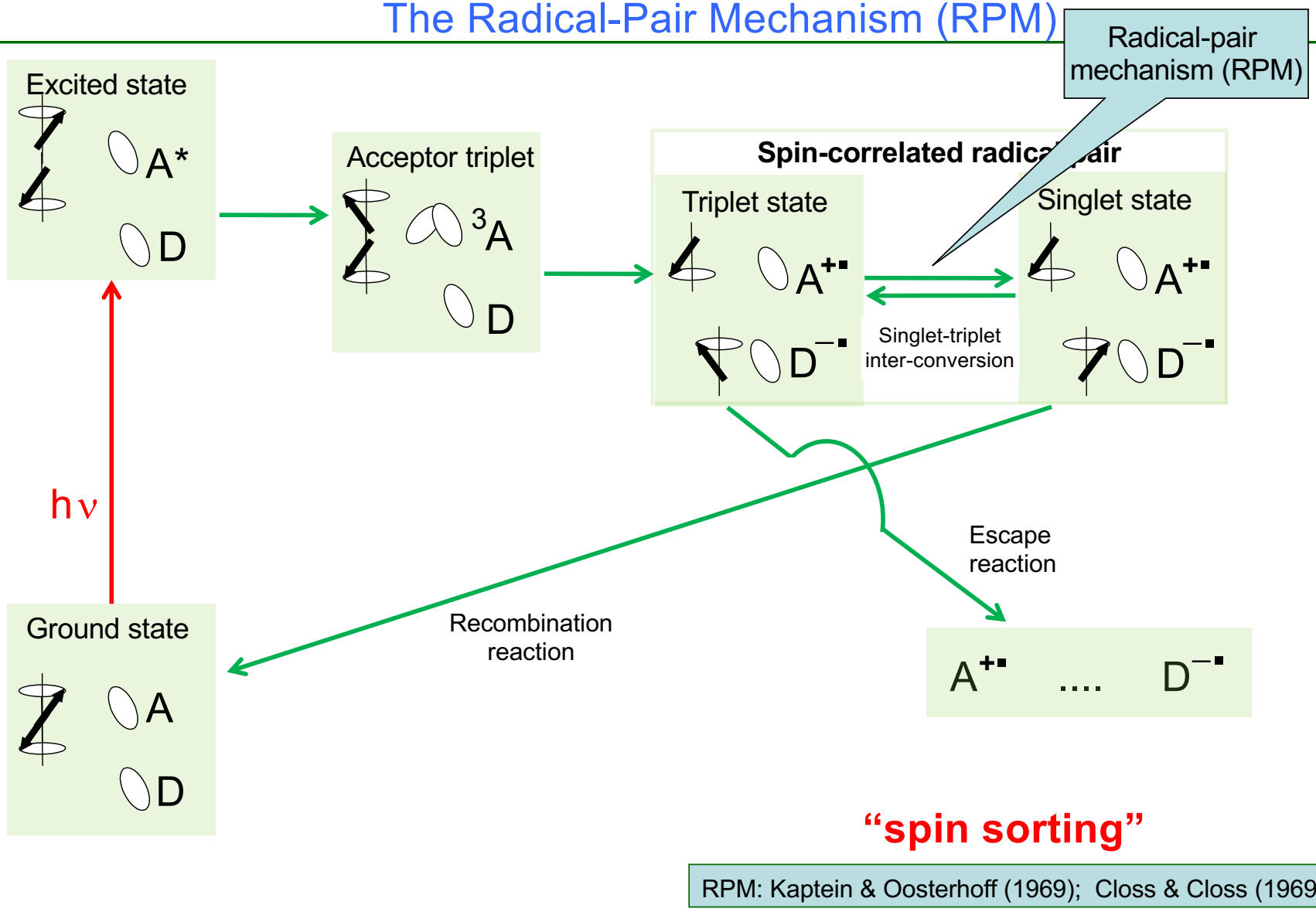
Rob Kaptein (*1941)
University of Leiden,
Title of PhD thesis:
"Chemically induced dynamic nuclear polarization" (1971)



"spin sorting"

RPM: Kaptein & Oosterhoff (1969); Closs & Closs (1969)

The Radical-Pair Mechanism (RPM)

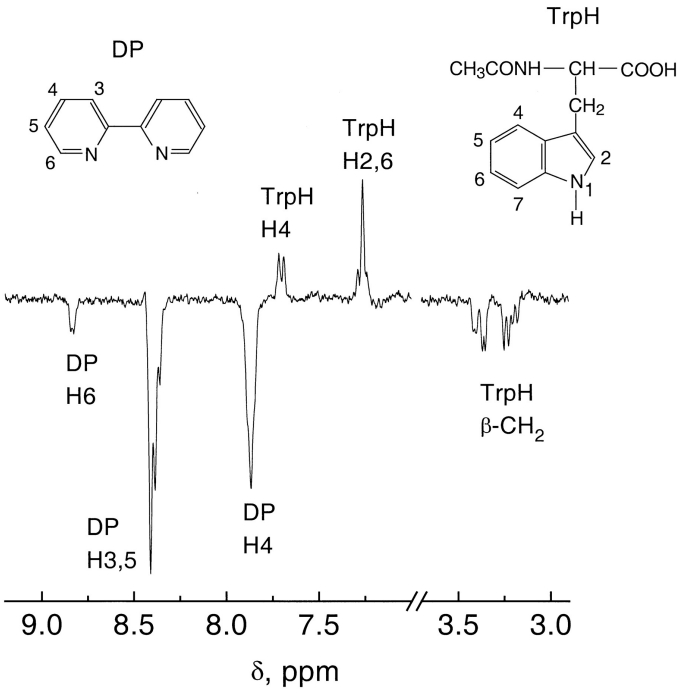


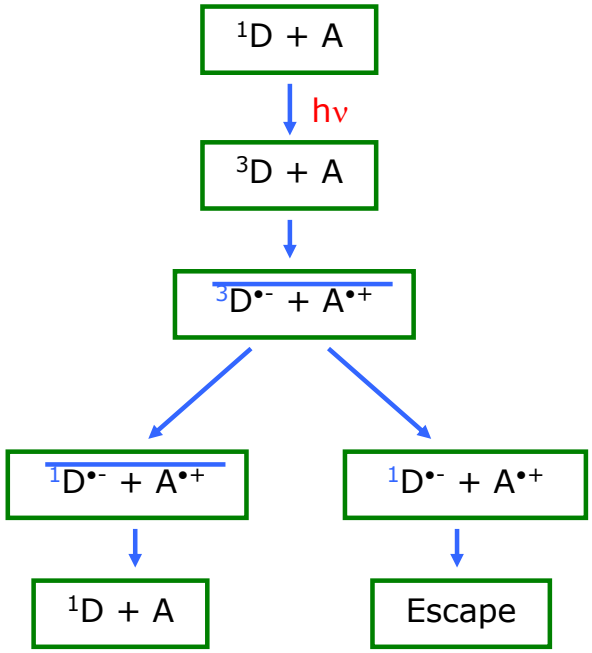
“spin sorting”

RPM: Kaptein & Oosterhoff (1969); Closs & Closs (1969)

Radical pair dynamics in liquids

Chemically induced dynamic nuclear polarization (CIDNP)



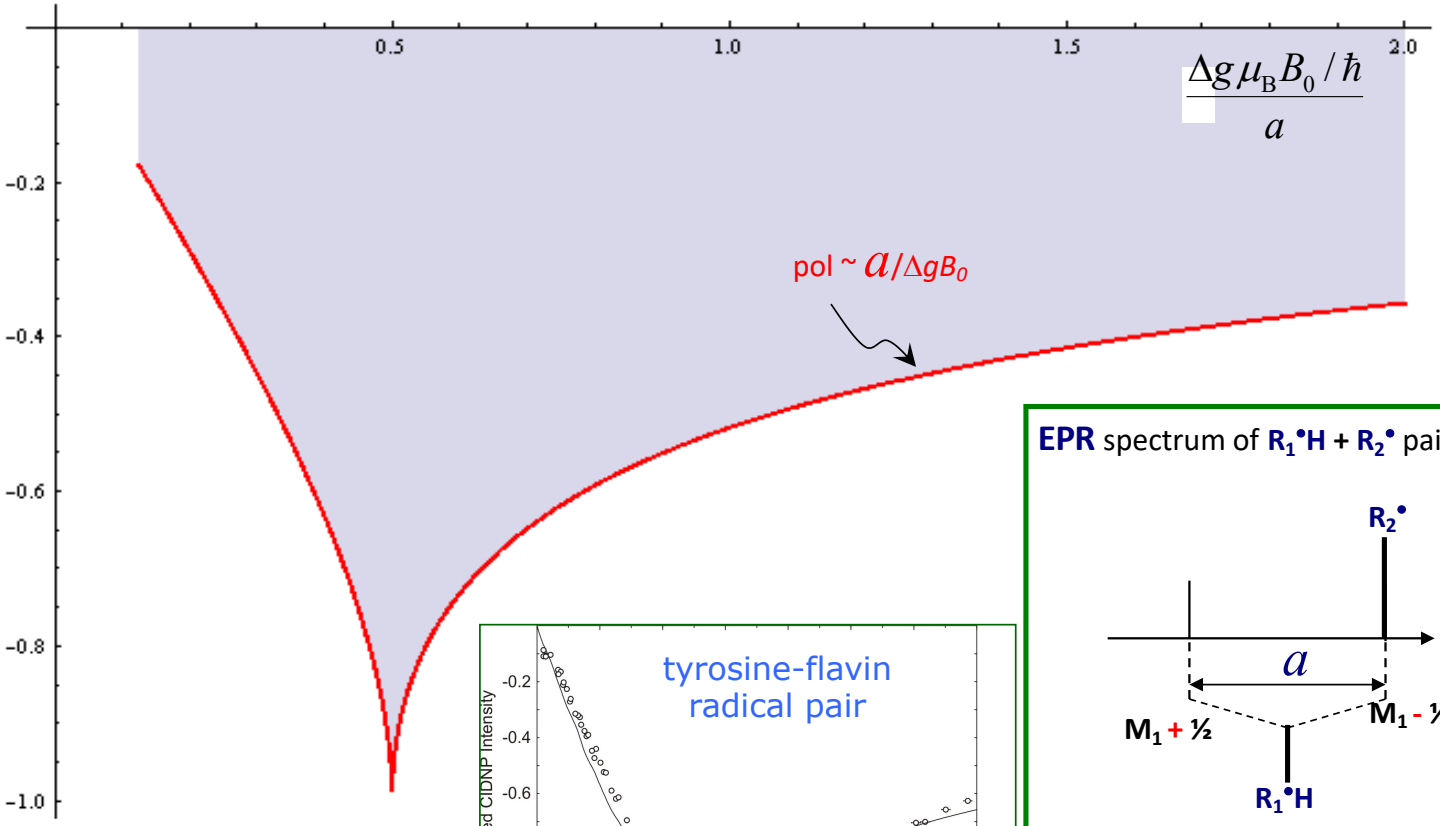


CIDNP spectrum, obtained during the irradiation of 4.4 10-4 M DP and 1.6 10-3 M TrpH solution.

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

Radical pair dynamics in liquids

Field dependence of liquid-state CIDNP



Lyon *et al.*

Molec. Phys. **100** (2002) 1261

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

hyperfine coupling constant a

Kaptein's sign rules

$\Gamma_{\mathrm{n}}(i) = \mu \cdot \varepsilon \cdot \Delta g \cdot A_i$	$\begin{cases} + \mathrm{A} \\ - \mathrm{E} \end{cases}$	net effect
$\Gamma_{\mathrm{m}}(i,j) = \mu \cdot \varepsilon \cdot A_i \cdot A_i \cdot J_{ij} \cdot \sigma_{ij}$	$\begin{cases} + \mathrm{E/A} \\ - \mathrm{A/E} \end{cases}$	multiplet effect

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

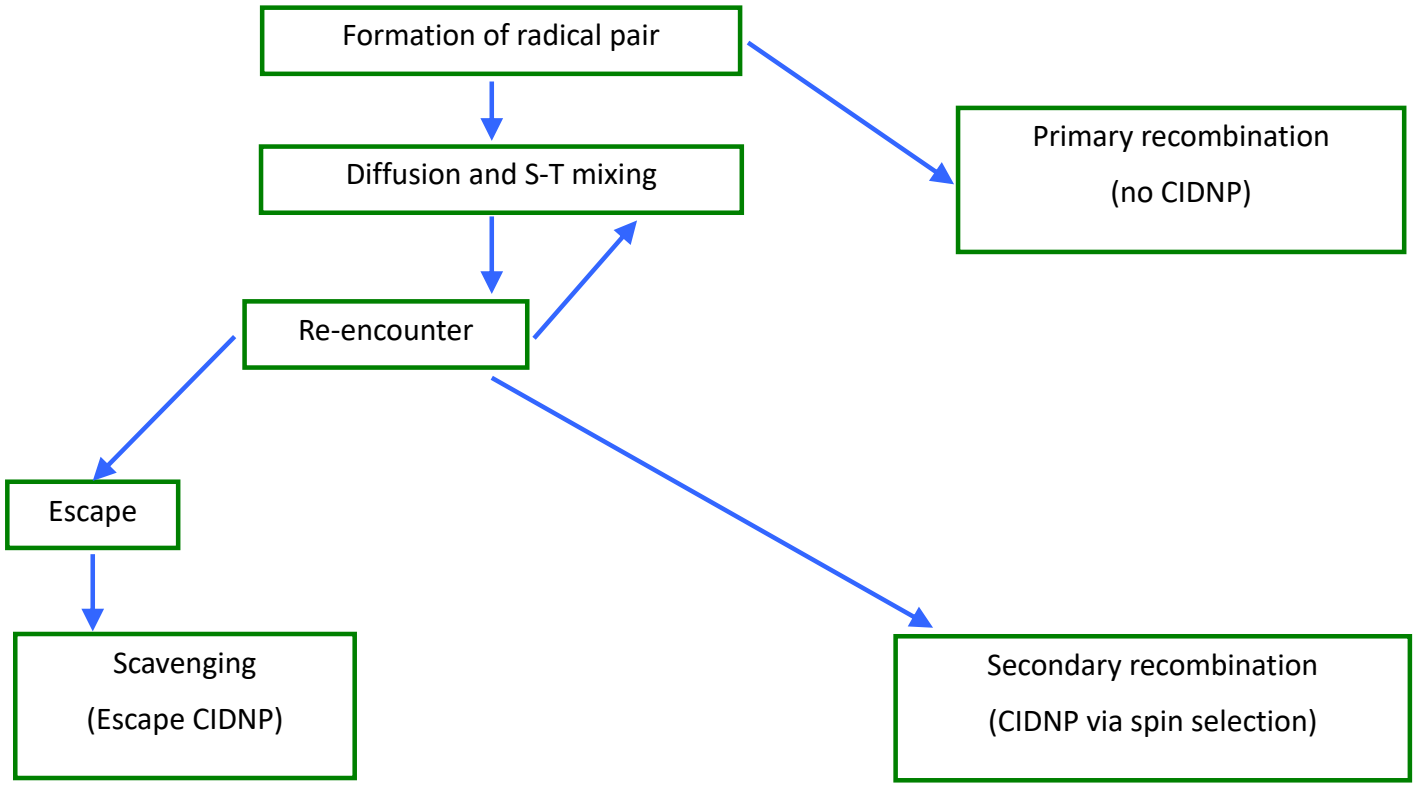
$$\varepsilon \begin{cases} + \text{ recombination products} \\ - \text{ escape products} \end{cases}$$

$$\sigma_{ij} \begin{cases} + \, i \text{ and } j \text{ in same radical} \\ - \, i \text{ and } j \text{ in different radicals} \end{cases}$$

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

Radical pair dynamics in liquids

CIDNP: The diffusion model



Radical pair dynamics

Master equation: Liquid state

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

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

Superoperators

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

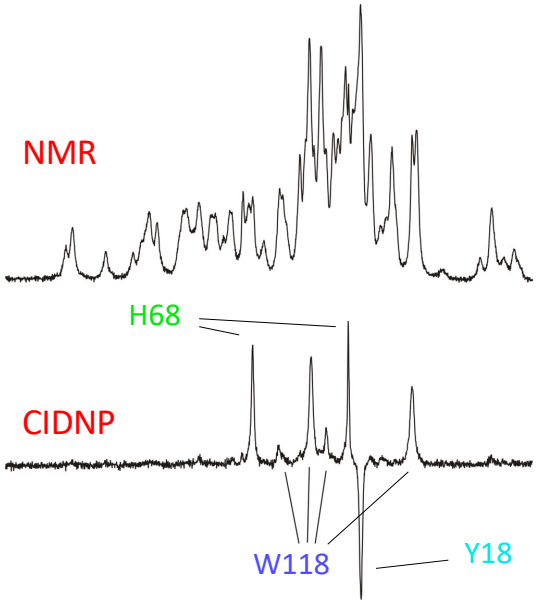
$\hat{\hat{K}}$ chemical kinetics: formation, reaction, electron hopping, …

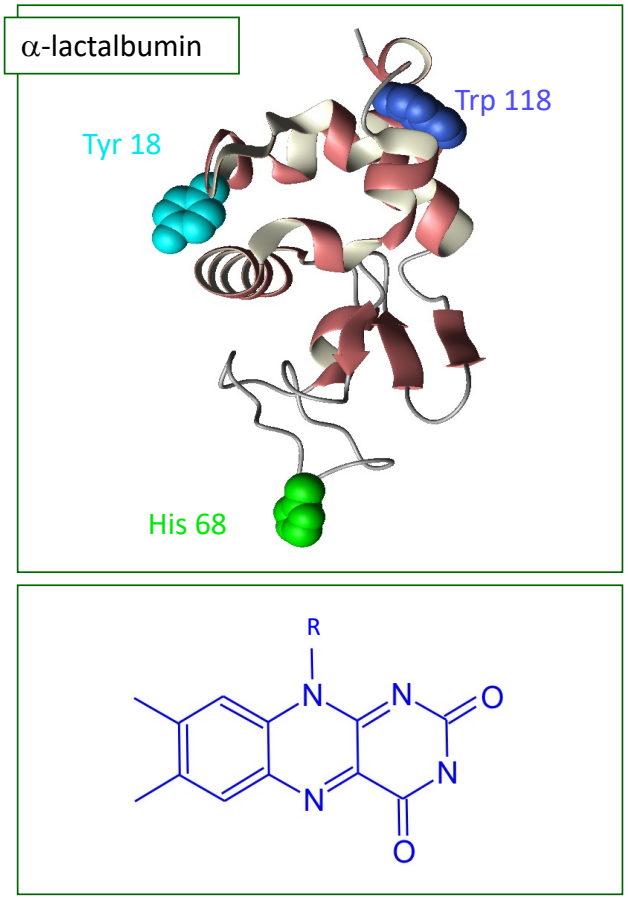
$\hat{\hat{R}}$ spin relaxation: usually *ad hoc* but also e.g. Redfield theory

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

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

^{1}H photo-CIDNP NMR on proteins





Kaptein, Dijkstra, Nicolay, *Nature* (1978)

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

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

Part 3

Photo-CIDNP in solid state

A recent review

Applied Magnetic Resonance (2022) 53:521–537
https://doi.org/10.1007/s00723-021-01322-5

Applied
Magnetic Resonance

REVIEW

Check for updates

Photo-CIDNP in Solid State

Jörg Matysik[1] · Yonghong Ding[1] · Yunmi Kim[1] · Patrick Kurle[1] · Alexandra Yurkovskaya[2] · Konstantin Ivanov[2] · A. Alia[3,4]

Received: 25 November 2020 / Revised: 8 February 2021 / Accepted: 11 February 2021 /
Published online: 6 April 2021

Most recent conclusive article

molecules

MDPI

Article

Electronic Structures of Radical-Pair-Forming Cofactors in a Heliobacterial Reaction Center

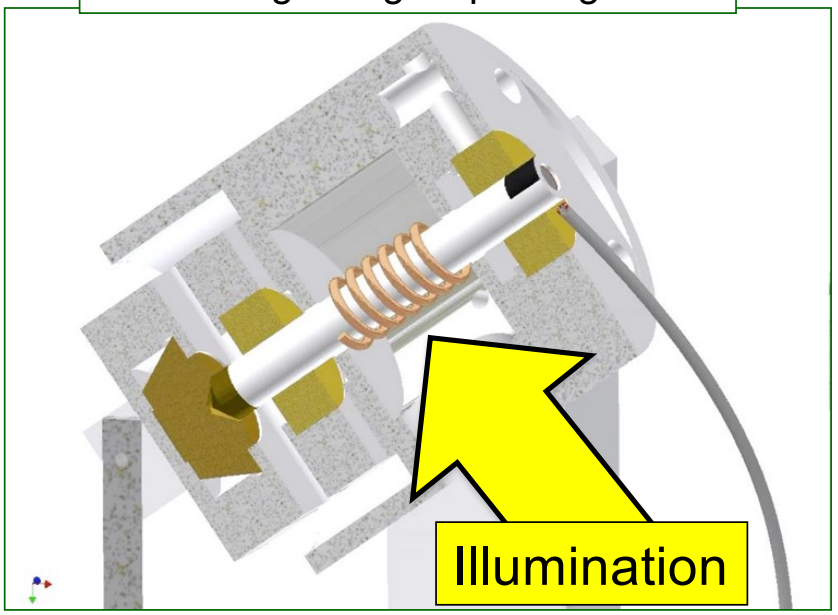
Yunmi Kim [1], A. Alia [2,3], Patrick Kurle-Tucholski [1], Christian Wiebeler [1,4] and Jörg Matysik [1,*]

Molecules **2024**, *29*, 1021. https://doi.org/10.3390/molecules29051021

The solid-state photo-CIDNP **effect**

Photo-CIDNP MAS NMR **method**

Magic-angle spinning



The solid-state photo-CIDNP effect: 1994 discovered

J. Am. Chem. Soc. **1994,** *116,* 8362–8363

Photochemically Induced Dynamic Nuclear Polarization in the Solid-State ^{15}N Spectra of Reaction Centers from Photosynthetic Bacteria *Rhodobacter sphaeroides* R-26

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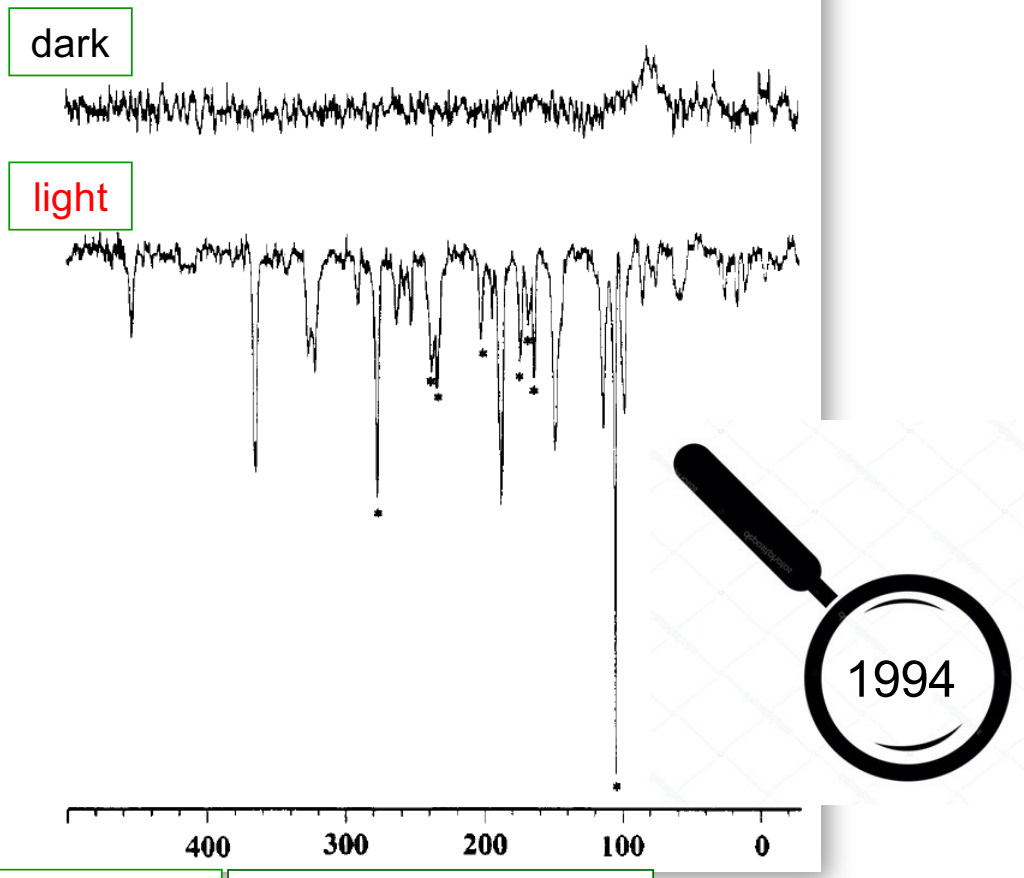
Department of Chemistry, Columbia University
New York, New York 10027

Received February 18, 1994

We present here a novel application of solid-state nuclear magnetic resonance (SSNMR) to bacterial photosynthesis: we have observed photochemically induced dynamic nuclear polarization (photo-CIDNP) in the ^{15}N-SSNMR-magic-angle spinning (MAS) spectra of reaction centers from photosynthetic bacteria. In nonspecifically ^{15}N-labeled reaction centers, when forward electron transfer was blocked either by removal (Q-dep) or prereduction (Q-red) of the quinone acceptor, strongly emissive ^{15}N signals were observed (Figure 1). As elaborated below, we attribute these signals to the tetrapyrrole nitrogens of the ground state of the special pair P. CIDNP is a well-known effect in



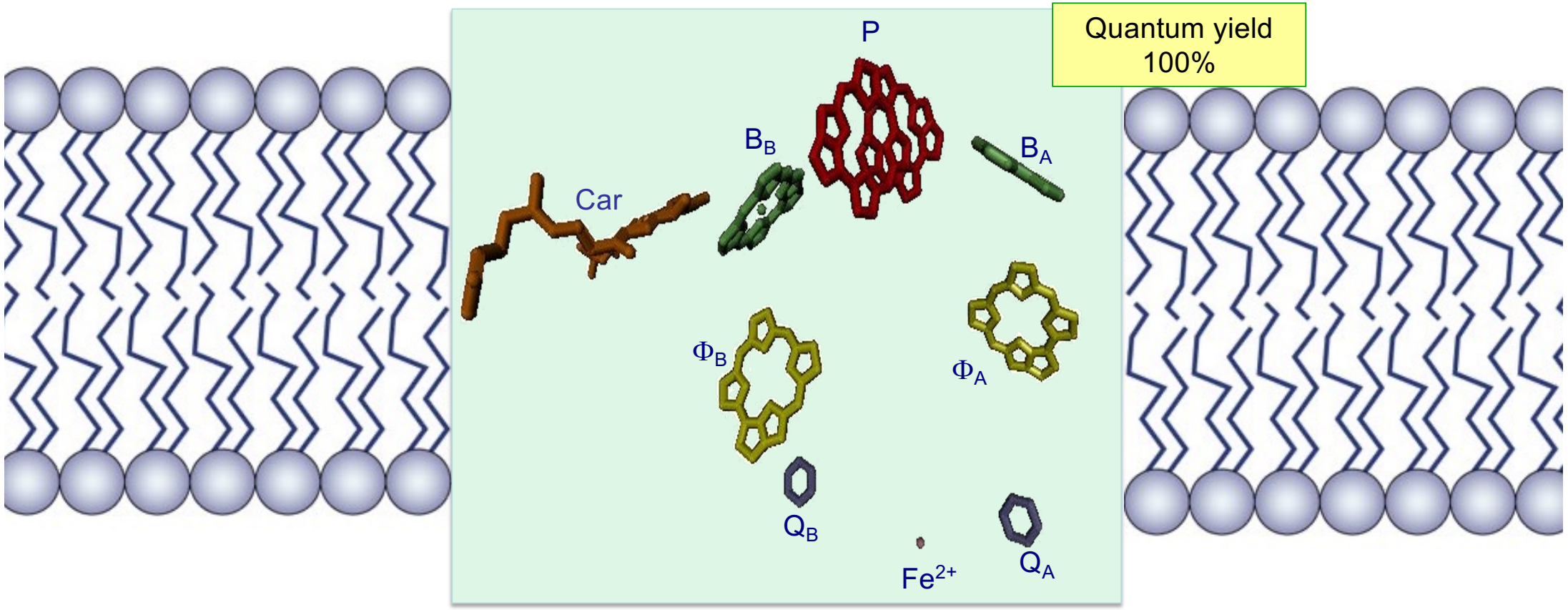
9.4 T, 3.6 kHz MAS | ^{15}N chemical shift

The purple bacterial Reaction Center (RC) protein

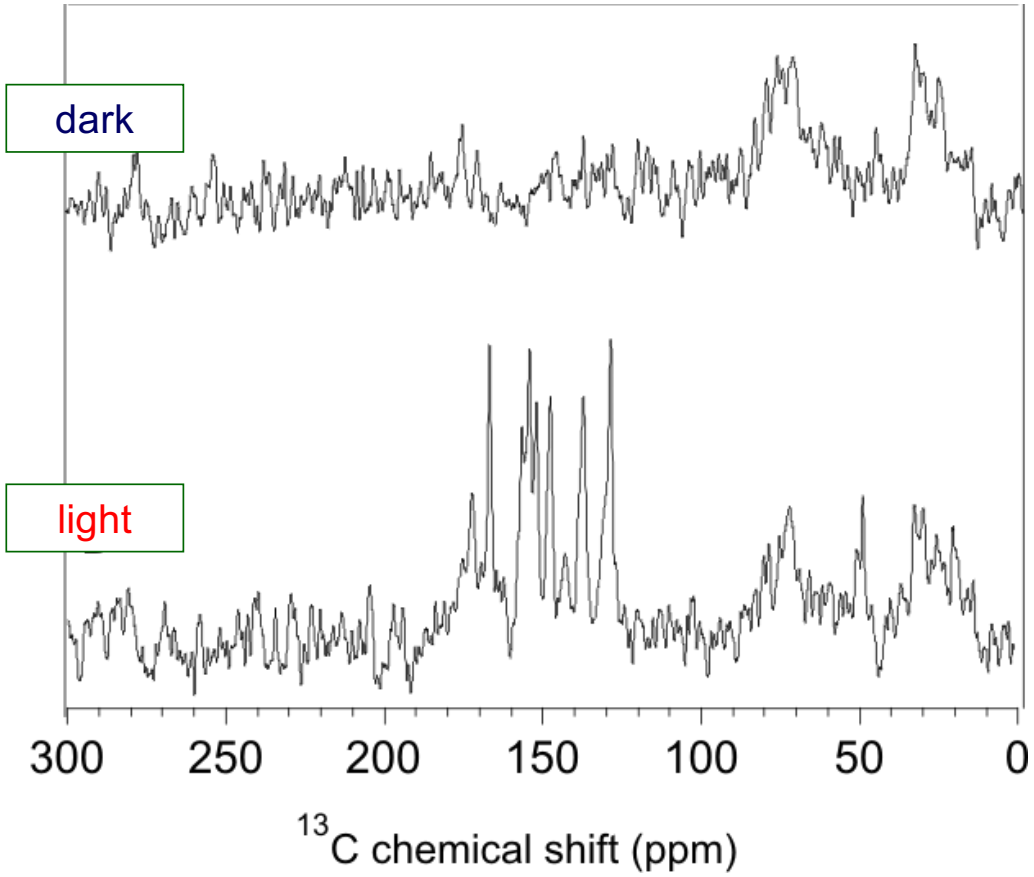
Rhodobacter sphaeroides WT
PDB entry 1M3X

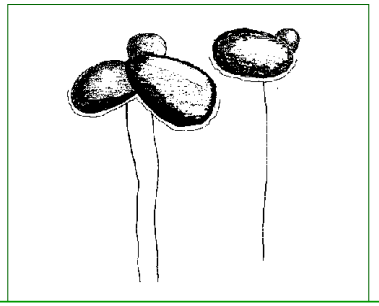
Asymmetric electron transfer

Quantum yield 100%

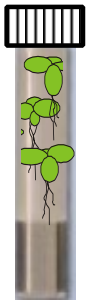


The solid-state photo-CIDNP effect in entire plants





Spirodela (duckweed)



Sapphire
4mm
70μL

Entire plants, 4-ALA ^{13}C-labelled, reduced 100 mM sodium dithionite.
Continuous illumination with white light, 4.7 Tesla, 235 K, 8 kHz MAS.
G.J. Janssen et al., Scientific Reports 8, 17853 (2018).

Photo-CIDNP MAS ^{13}C NMR on RCs with different cycle delay

Radiation damping?

R26

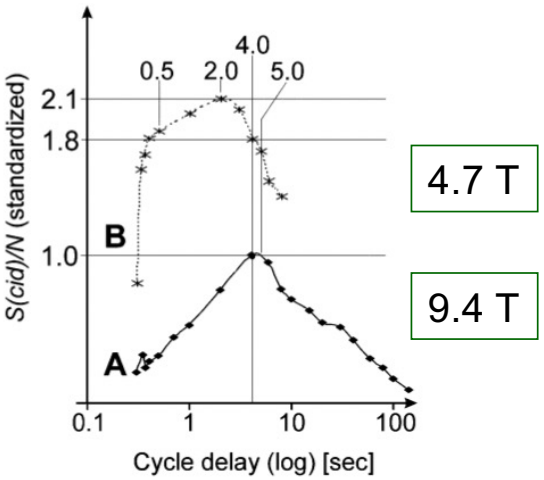


Figure 4. Dependence of the photo-CIDNP signal intensity on the cycle delay time at 9.4 (A) and 4.7 T (B), obtained for the signal at 160.1 ppm as observed in the spectrum of RC of *Rb. sphaeroides* R26 (spectrum 3B). The photo-CIDNP signal intensity is expressed relative to the noise level (*S*(cid)/*N*). Each data point represents the standardized *S*(cid)/*N* of a photo-CIDNP MAS NMR spectrum obtained in 4 h. For the standardization, the *S*(cid)/*N* of the photo-CIDNP MAS NMR spectrum measured a 9.4 T and a cycle delay of 4 s was set to unity. Under identical conditions, the photo-CIDNP MAS NMR spectrum obtained at 4.7 T reveals a 1.8 times better *S*(cid)/*N* ratio than at 9.4 T.

4.7 T

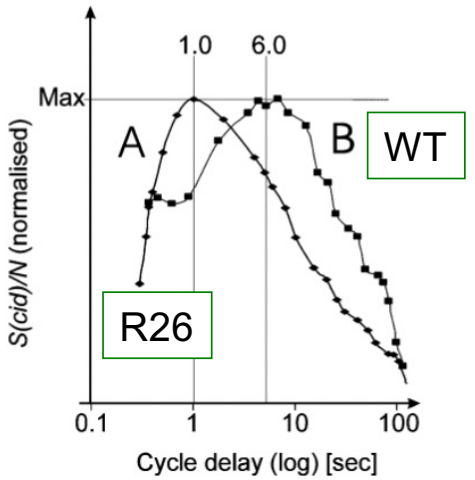


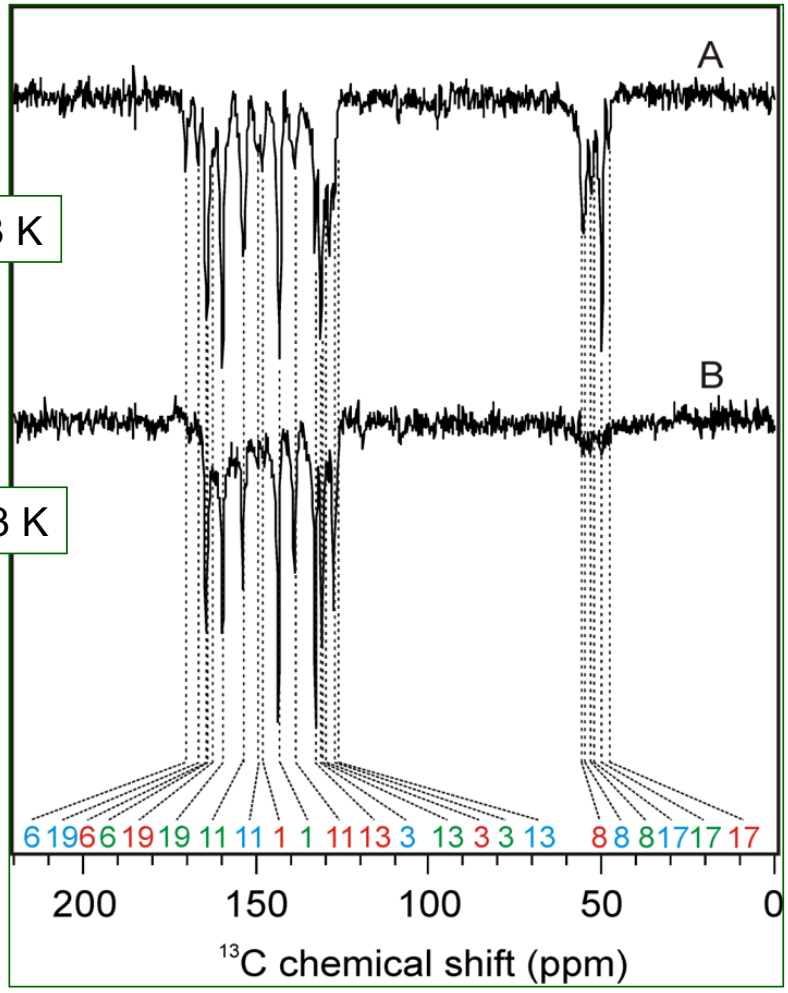
Figure 5. Dependence of the photo-CIDNP signal intensity on the cycle delay time obtained at 4.7 T for the signal 160.1 ppm in the spectrum of RC of (A) *Rb. sphaeroides* R26 (spectrum 3D) and (B) WT (spectrum 3F). The photo-CIDNP signal intensity is expressed relative to the noise level (*S*(cid)/*N*). Each data point represents the *S*(cid)/*N* of a photo-CIDNP MAS NMR spectrum obtained in 4 h. For normalization, the strongest (*S*(cid)/*N*) values were set to unity.

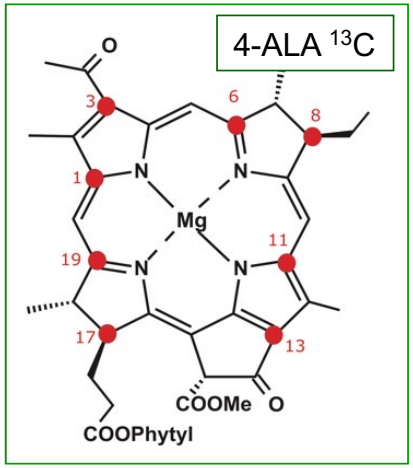
A. Diller et al. (2007) J. Phys. Chem. B 111, 10606-10614.

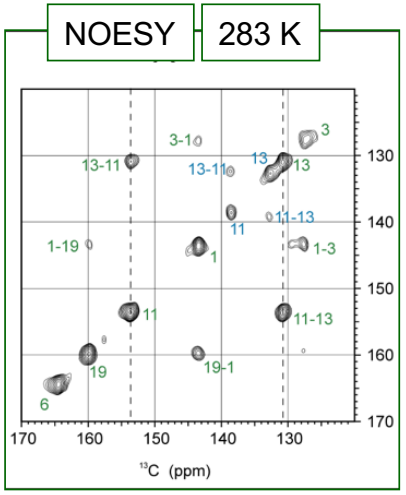
Photo-CIDNP MAS ^{13}C NMR on RCs in liquid membranes

233 K

283 K

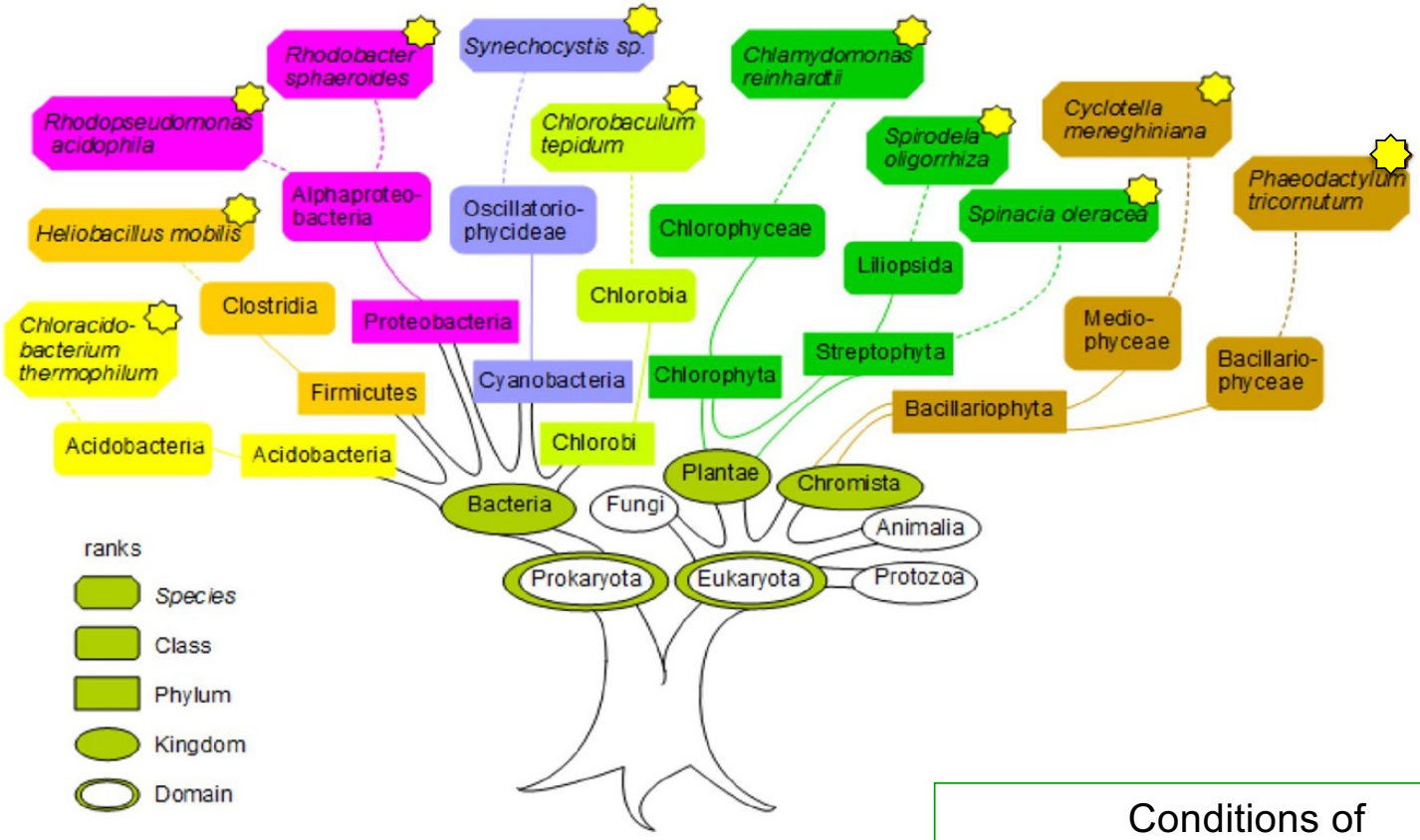






E. Daviso et al. (2011) JACS 133, 16754-16757.

Tree of life



Jörg Matysik, Anna Diller, Esha Roy, A. Alia,
"The solid-state photo-CIDNP effect", Photosynth. Res. 102, 427-435 (2009).

Conditions of
Solid-state photo-CIDNP effect
have been ***conserved***
over ~$3 \cdot 10^9$ years

Chloracidobacterium (Cab.) thermophilum

Zill et al. (2018) Photosynth. Res. 137, 295-305.
Collaboration with D. Bryant and J. Golbeck (Penn State Univ.) & I. Schapiro (Hebr. Univ. Jerusalem)

- **Bacteriochlorophyll *a* (BChl *a*)**
- **Zn-bacteriochlorophyll *a'* (Zn-BChl *a'*)**
  → **primary electron donor**
- **Chlorophyll *a* (Chl *a*)**
  → **primary electron acceptor**
  (in all homodimeric type-I RCs)

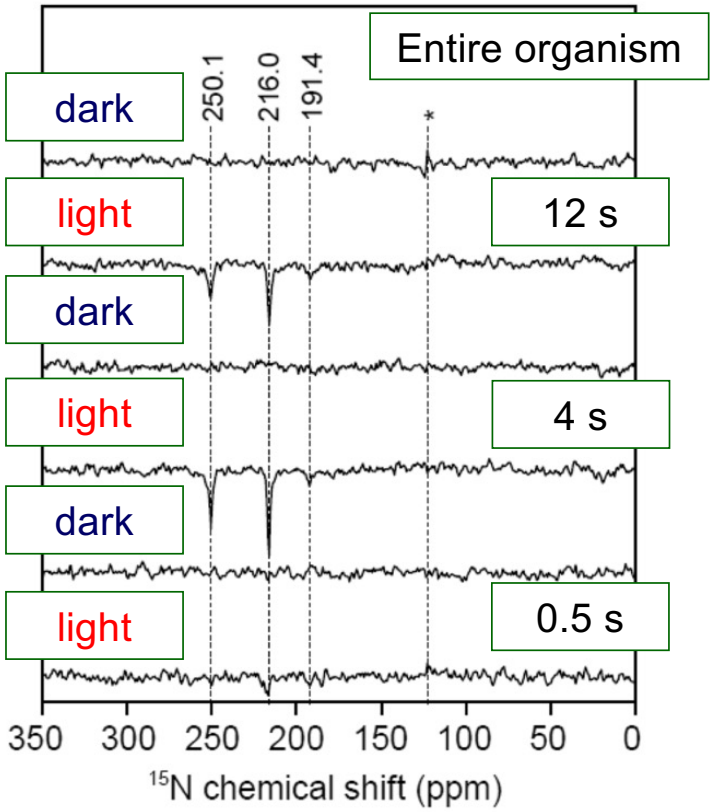
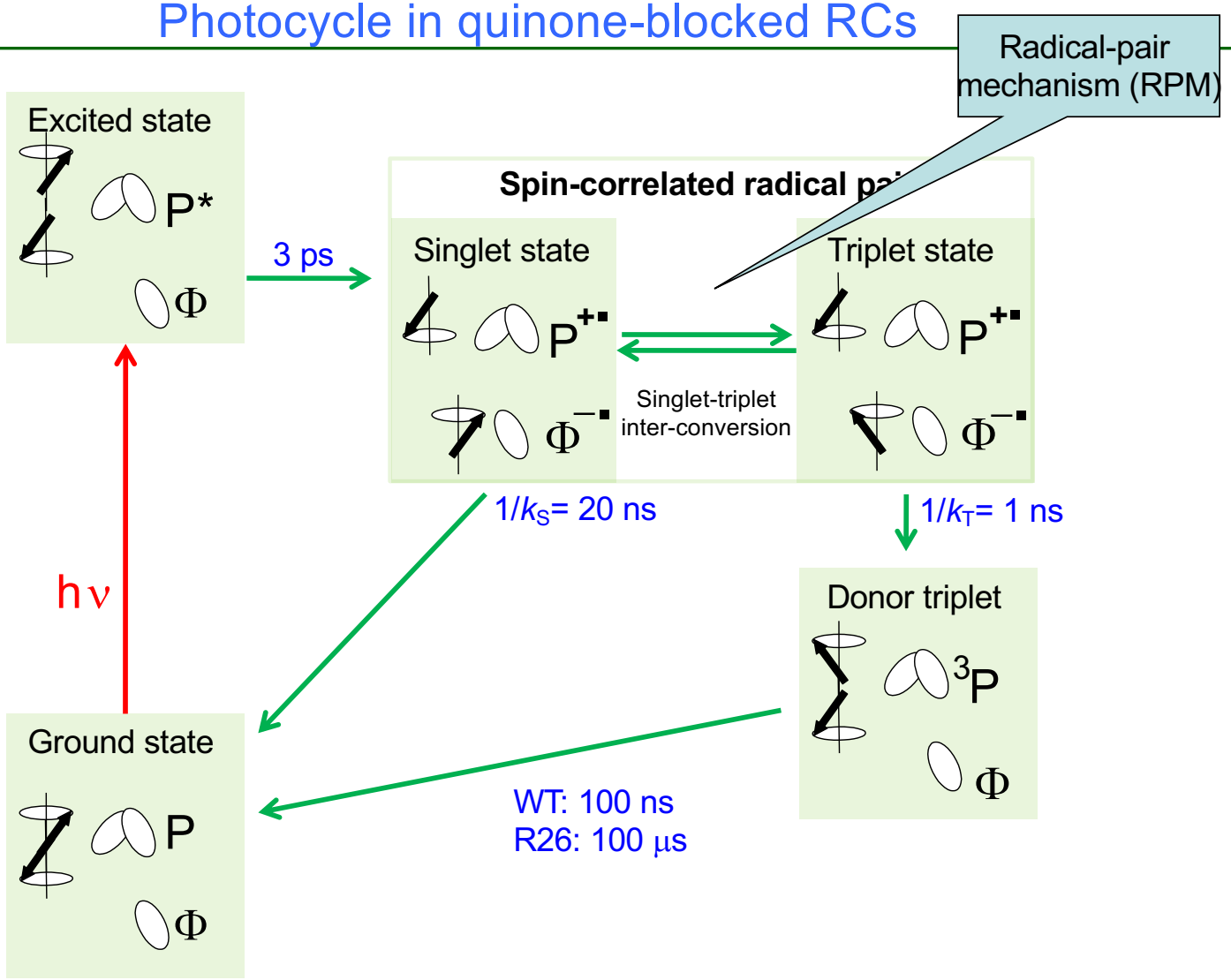


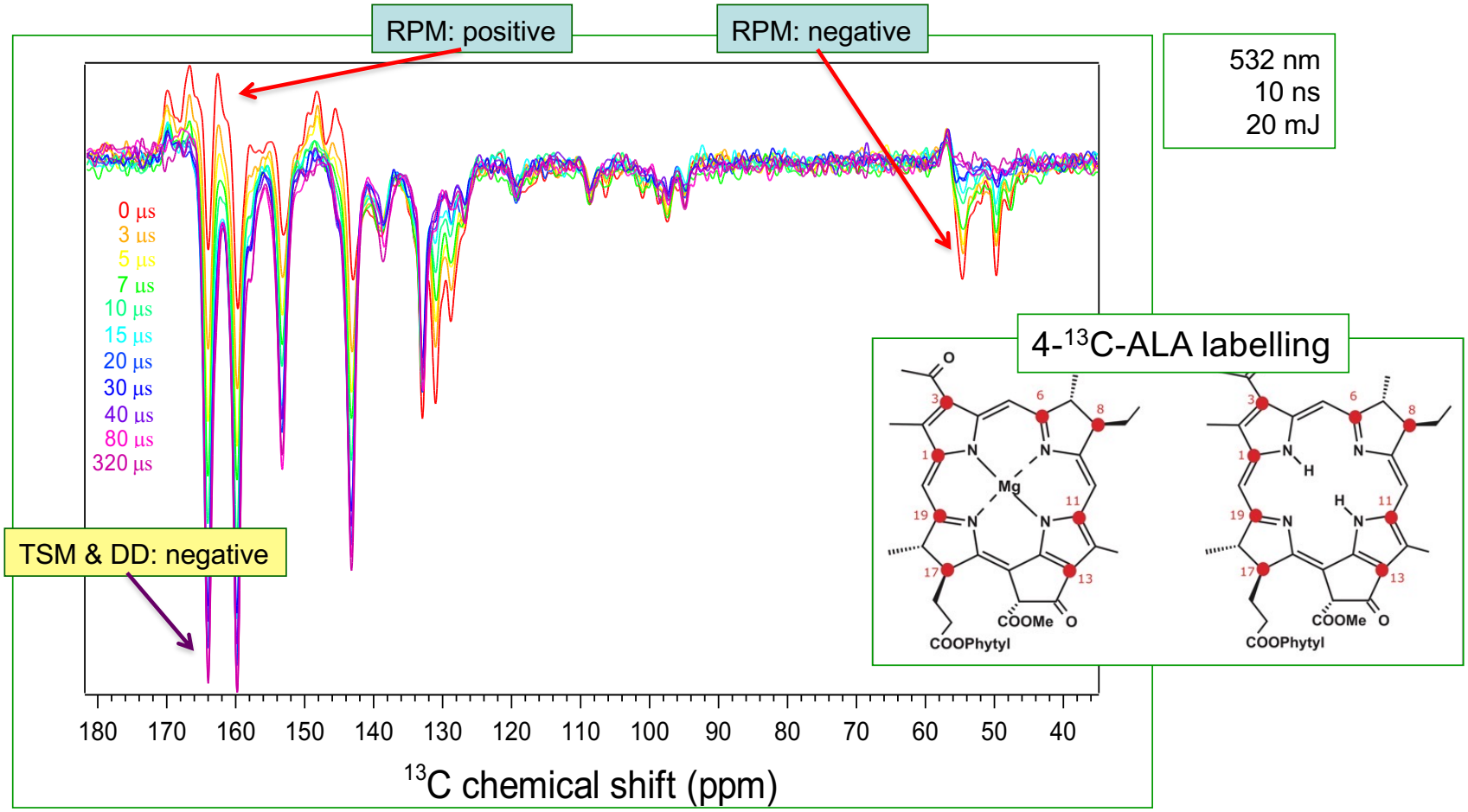
Fig. 4 ^{15}N-photo-CIDNP effect observed on *Cab. thermophilum*: **a** dark, cycle delay = 12 s, 16,300 scans; **b** light, cycle delay = 12 s, 16,300 scans; **c** dark, cycle delay = 4 s, 45,000 scans; **d** light, cycle delay = 4 s, 45,000 scans; **e** dark, cycle delay = 0.5 s, 345,000 scans; **f** light, cycle delay = 0.5 s, 345,000 scans, *spectrometer signal

Photocycle in quinone-blocked RCs



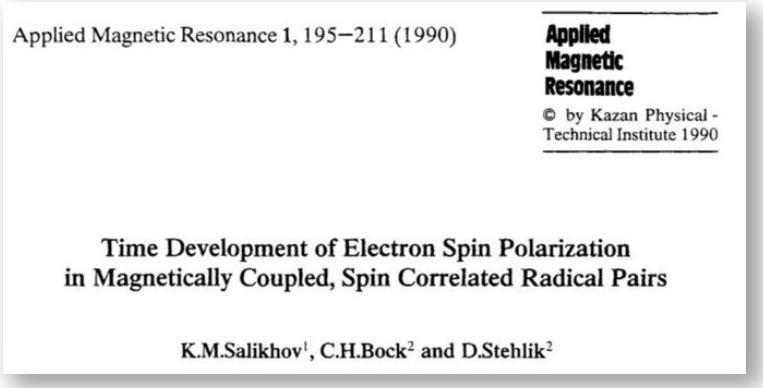
RPM: Kaptein & Oosterhoff (1969); Closs & Closs (1969)

Nanosecond ^{13}C photo-CIDNP MAS NMR



E. Daviso et al. (2008) JMR 190, 170-178; E. Daviso et al. (2009) JPCC 113, 10269-10278.

Quantum-beat experiments (Kothe et al.)



Applied Magnetic Resonance 1, 195–211 (1990)

Applied Magnetic Resonance

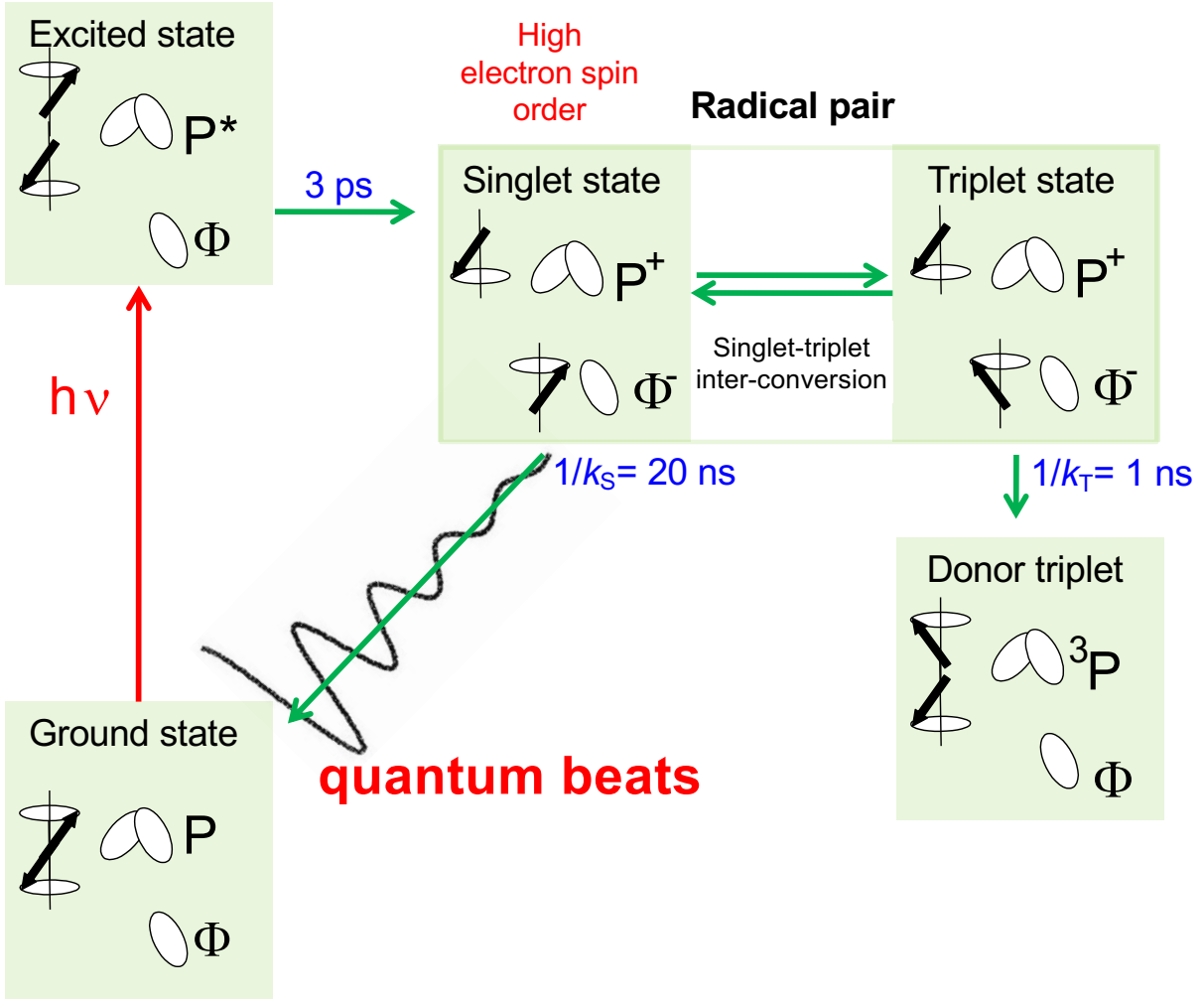
© by Kazan Physical - Technical Institute 1990

Time Development of Electron Spin Polarization in Magnetically Coupled, Spin Correlated Radical Pairs

K.M.Salikhov[1], C.H.Bock[2] and D.Stehlik[2]

G. Kothe et al. (1991) Chem. Phys. Lett. 186, 474.

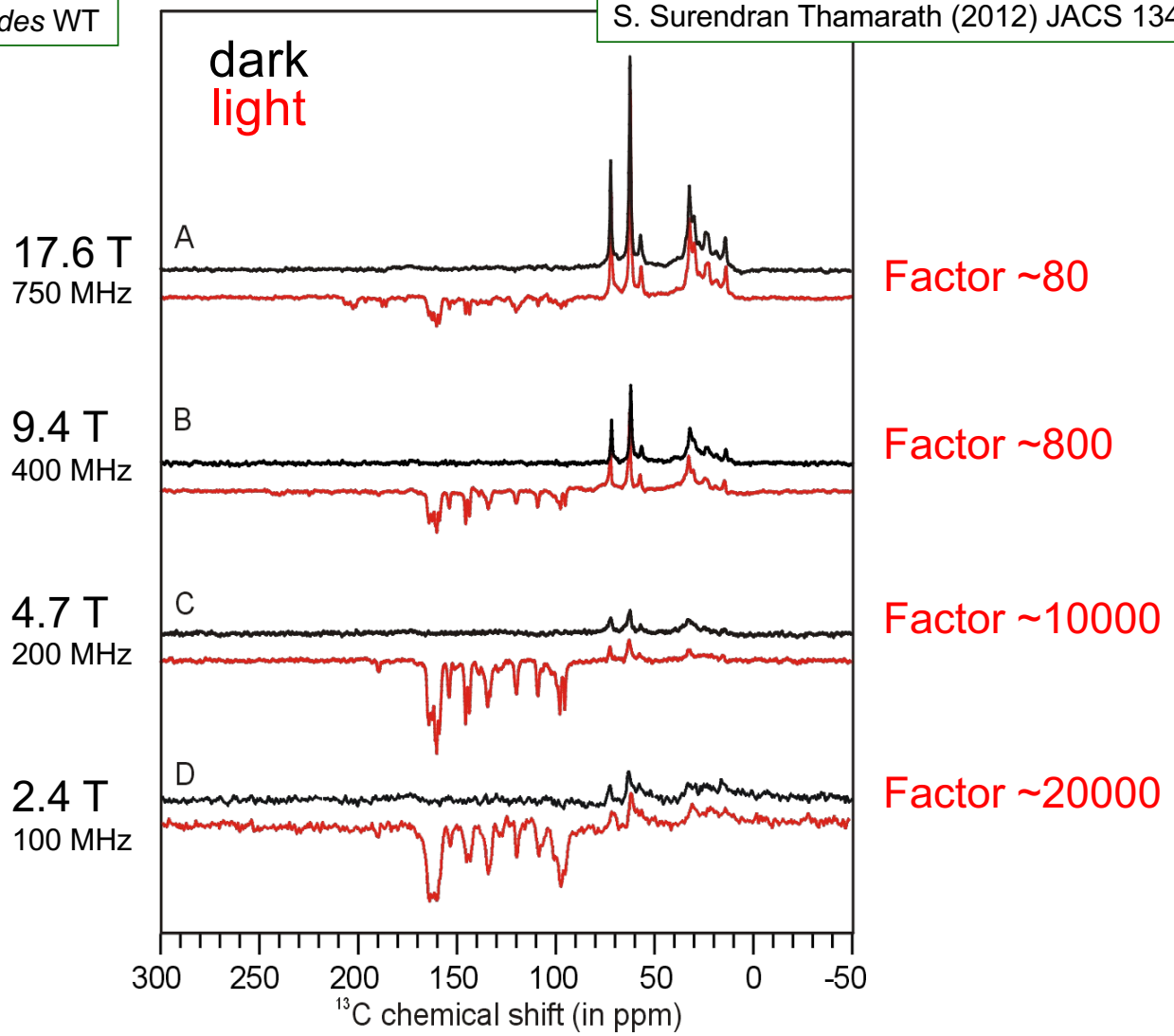
For review: G. Kothe et al., in Biophysical Techniques in Photosynthesis II, ed. T.J. Aartsma, J. Matysik (Springer, Dordrecht, 2008), p.305.



The solid-state photo-CIDNP effect: Field-dependence

R. sphaeroides WT

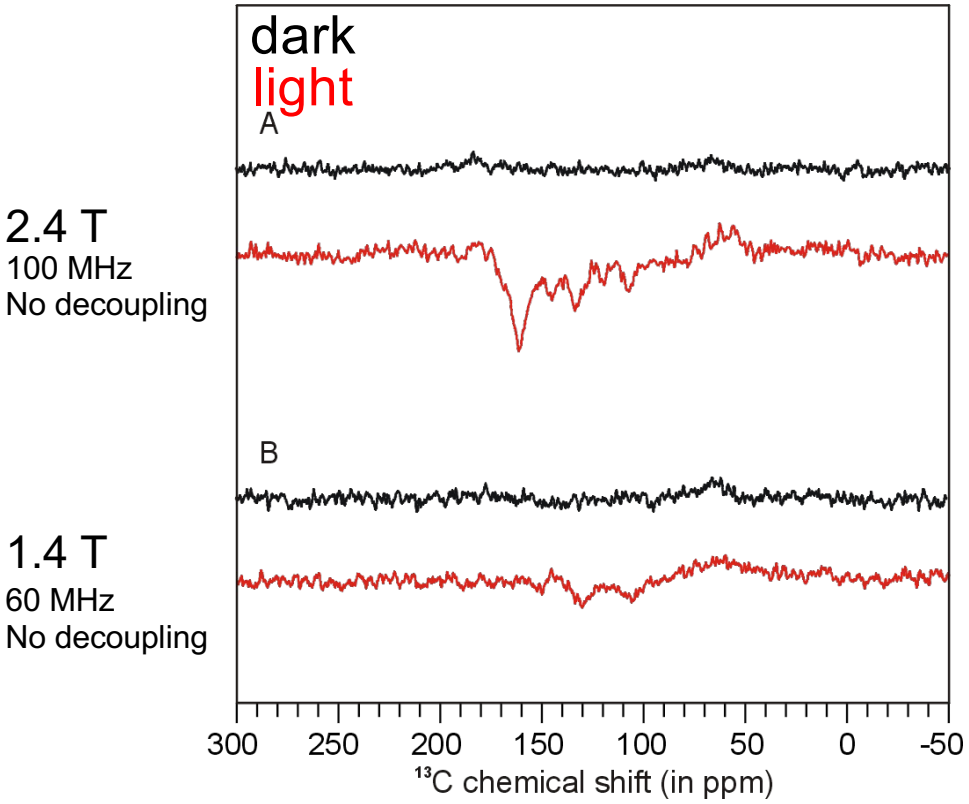
S. Surendran Thamarath (2012) JACS 134, 5921.



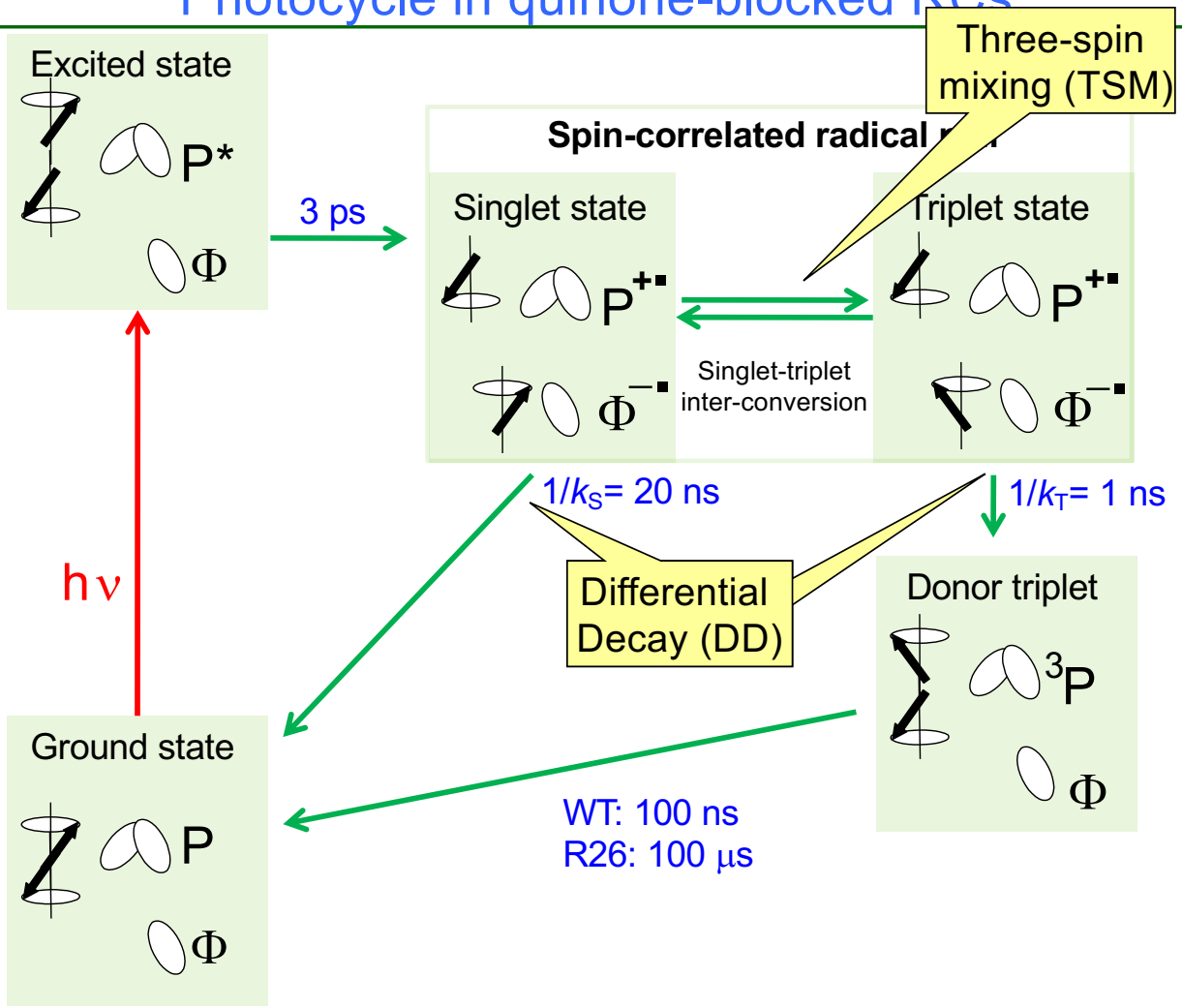
The solid-state photo-CIDNP effect: Field-dependence

R. sphaeroides WT

S. Surendran Thamarath (2012) JACS 134, 5921.



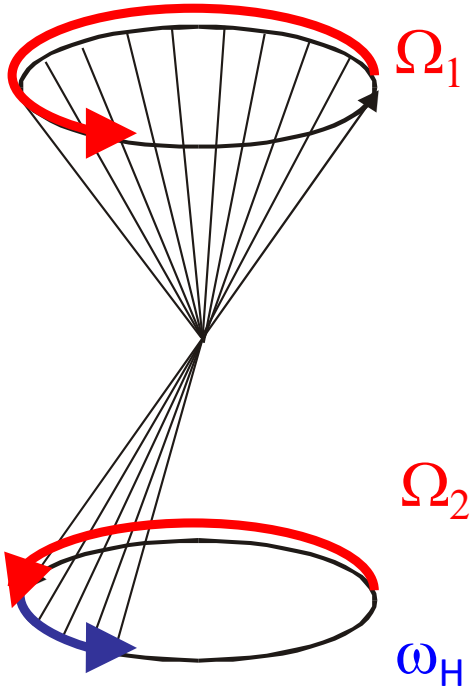
Photocycle in quinone-blocked RCs



TSM: Jeschke (1998); DD: Polenova & McDermott (1999)

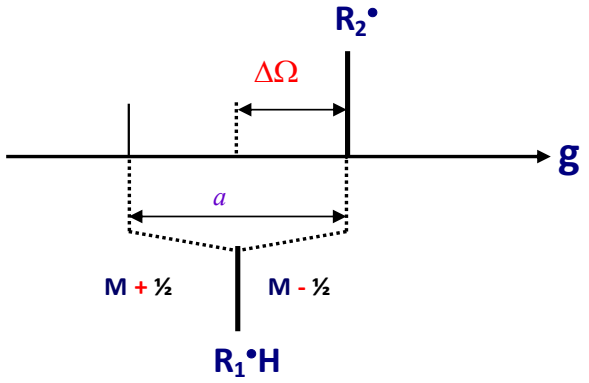
Electron-electron-nuclear **three-spin mixing** in spin-correlated radical pairs

1st condition: **Resonance**



Ω = electron Zeeman frequency
ω = nuclear Zeeman frequency

2nd condition: **Hyperfine matching**
EPR spectrum of **$R_1^{\bullet}H$ + $R_2^{\bullet}$** pair:



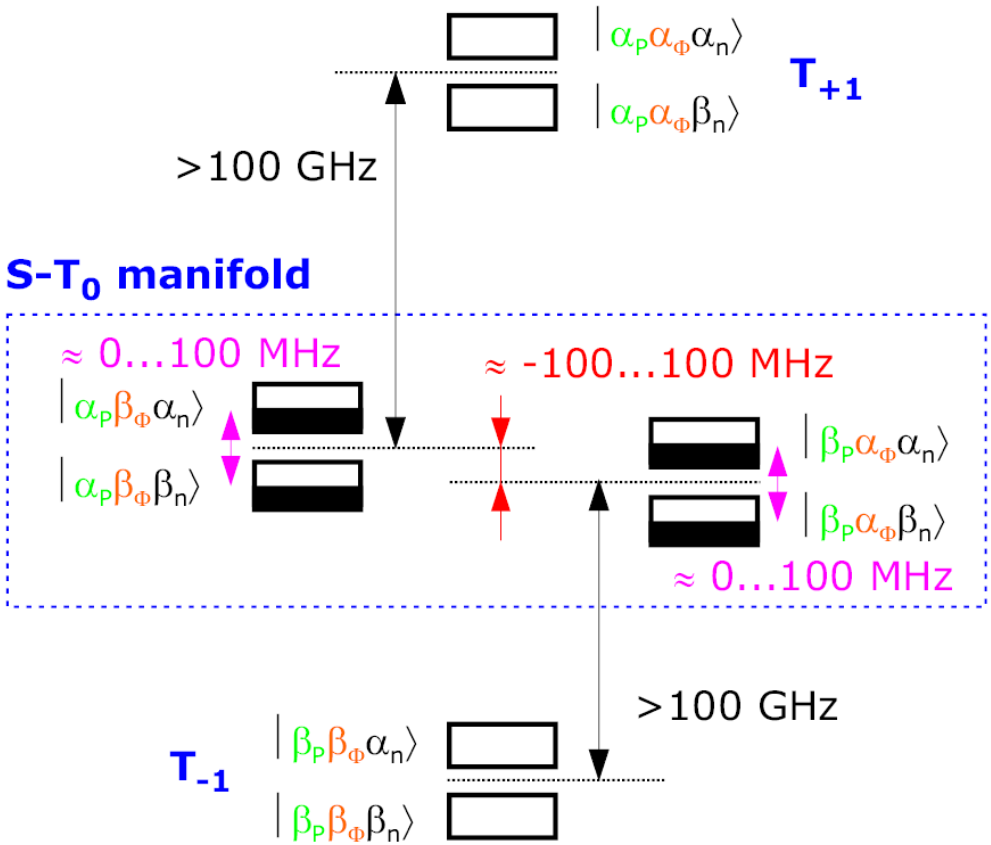
a = hf coupling constant

Double matching condition:

$$2\,|\Delta\Omega| = 2\,|\omega_H| = |a|$$

Jeschke (1997) J. Chem. Phys. 106, 10072
Jeschke (1998) JACS 120, 4425

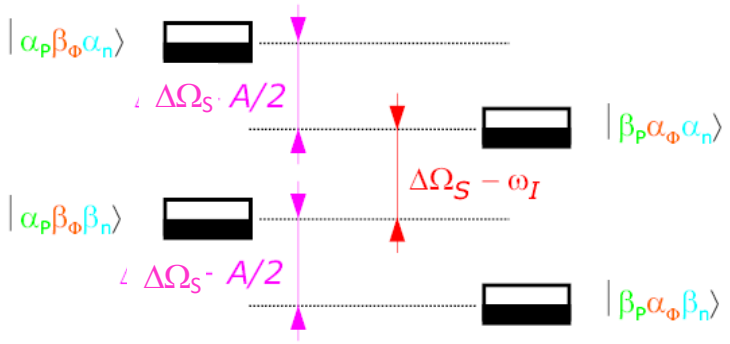
Evolution of the spin-correlated radical pair



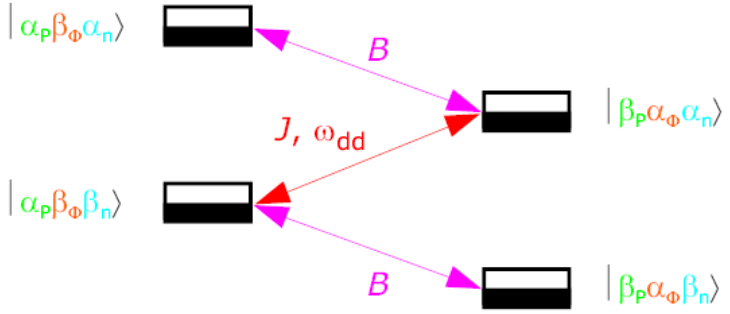
Electron-electron-nuclear three-spin mixing (TSM)

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



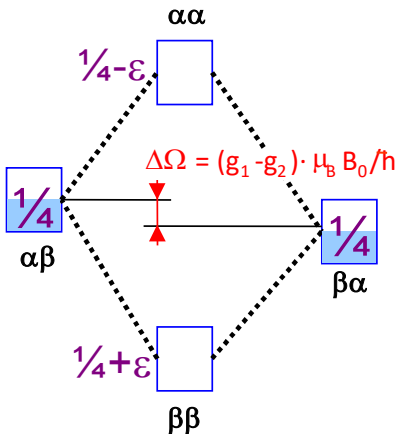
Mixing terms



Electron-electron-nuclear three-spin mixing (TSM)

Jeschke (1997) JCP 106, 10072 & (1998) JACS 120, 4425

1. Initial singlet radical pair is highly ordered



Boltzmann distribution:

¼-ε, ¼, ¼, ¼+ε , with ε ~0.001.

Due to spin conservation, only αβ and βα are populated. Superposition. Two-spin order ($S_{1Z}S_{2Z}$) and zero-q coherence ($S_{1X}S_{2X} + S_{1Y}S_{2Y}$). No eigen state.

P↑ Φ↓

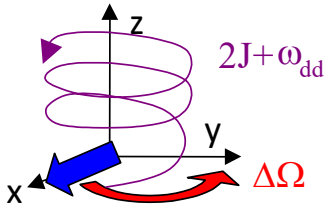
2. Spin coupling polarises the two radicals

	|αβ>	|βα>
<αβ|	ΔΩ/2	J + ω_{dd}/2
<βα|	J + ω_{dd}/2	ΔΩ/2

J = isotropic part of exchange interaction

ω_{dd} = electron dip-dip interaction

Similar size of ΔΩ, J and ω_{dd}.
Effect of $2J+\omega_{dd}$ like a pulse.



P↑ Φ↓

3. Anisotropic hf-coupling polarises nuclei

	|αβIα>	|βαIβ>	|βαIα>	|αβIβ>
<αβIα|	+A/4	+B/4		
<βαIβ|	+B/4	-A/4		
<βαIα|			-A/4	-B/4
<αβIβ|			-B/4	+A/4

Only hf coupling can transfer electron polarisation to nuclei

Isotropic hf has no **B** term
→ effect only in ssNMR

Double matching condition
2 |ΔΩ| = 2 |ω_I| = |A|

$P_{N\alpha}$↑ $\Phi_{N\beta}$↓

Differential decay (DD)

Photoinduced Nuclear Polarization

Polenova & McDermott (1999) J. Phys. Chem. B, 103, 535-548.

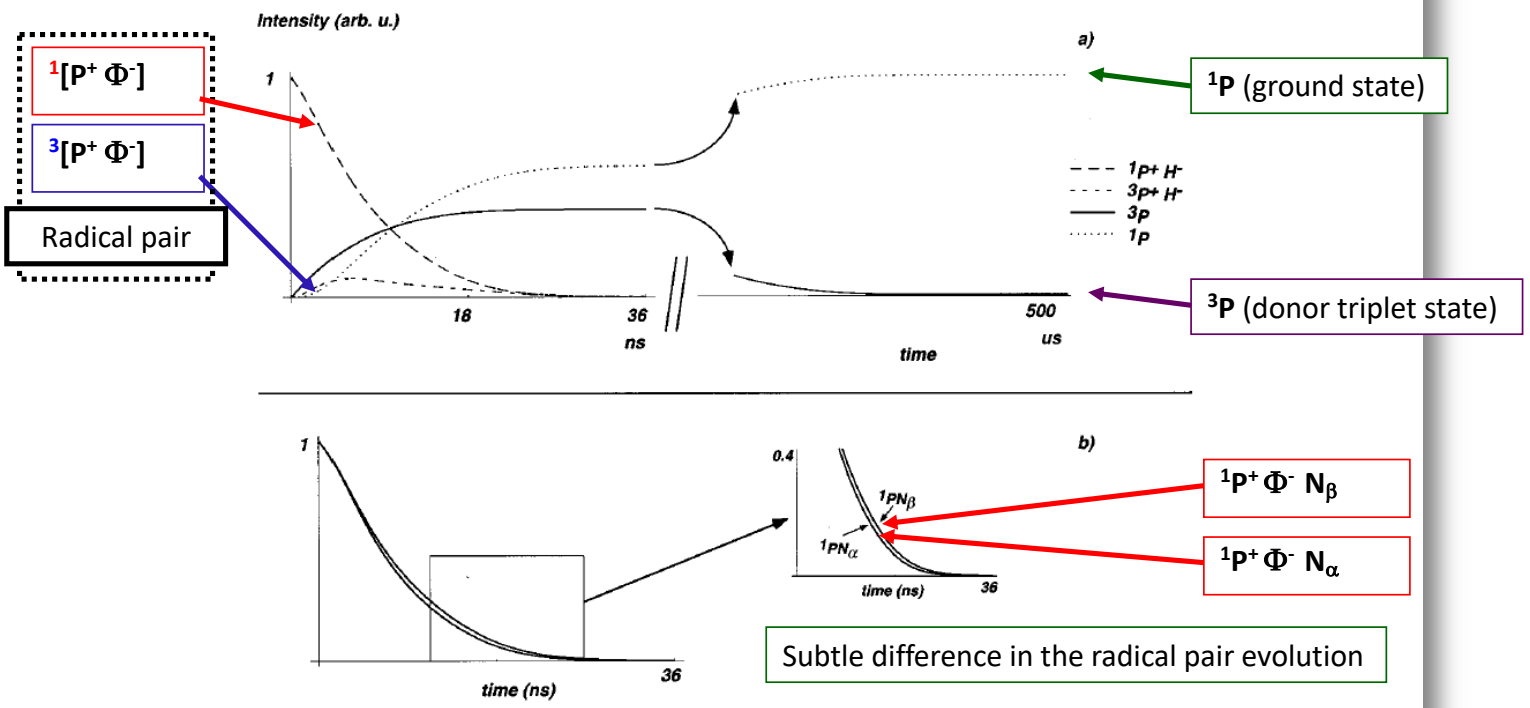


Figure 2. The concentrations of the four chemical species: radical pair singlet $^1(P^{\bullet+}\ H^{\bullet-})$, radical pair triplet $^3(P^{\bullet+}\ H^{\bullet-})$, molecular triplet ^3P, and ground state P, are plotted as a function of time, as computed for the propagation of the radical pair states $^1(P^{\bullet+}H^{\bullet-})$ and $^3(P^{\bullet+}H^{\bullet-})$ with the Hamiltonian described in the text (Chart 1) with assumed coupling strengths of: $\Delta g = -2.06 \times 10^8$ Hz, $A = -3.42 \times 10^7$ Hz, $C = 1.22 \times 10^7 - i4.16 \times 10^7$ Hz, $D = 1.22 \times 10^7 + i4.16 \times 10^7$ Hz. The Euler angles describing this particular orientation are: $\alpha = 2.88$ rad, $\beta = 2.22$ rad, and $\gamma = 5.55$ rad. These orientations result in largest single turnover nuclear polarization. The decay kinetics of the photochemically formed singlet are clearly non exponential due to pronounced effects of the coherent mixing, as pointed out by Goldstein and Boxer.[27] The trajectories of the molecular triplet and the ground state were calculated as described in the text (eqs 13 and 14). On a much longer time scale the molecular triplet would decay to form the ground state as illustrated in Figure 1; a broken scale is indicated with the final populations shown. These longer (microsecond) time scales are not described in this model; they can be treated in a separate case due to the separation of the time scales. For the singlet radical pair species two curves are shown to illustrate the subtle difference in precession for a nucleus assumed to be in an α vs a β state.

Level-crossings (LCs) & Level anti-crossings (LAC)

Denis V. Sosnovsky et al., J. Chem. Phys. 144, 144202 (2016).

TSM

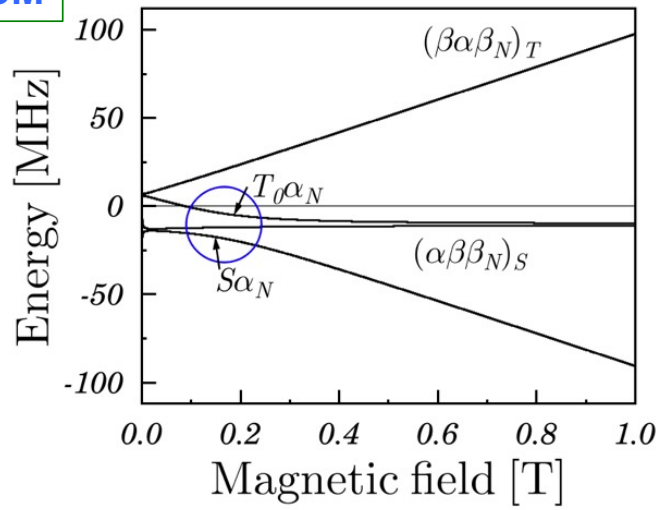


FIG. 8. Field dependence of energy levels in the TSM case; the relevant LAC is indicated. Parameters used in calculation: $g_1 = 2$ and $g_2 = 2.0067$; the nucleus is a proton; $A = 1$ mT; $d = 0.5$ mT; $b = 0, k_S = k_T = 0.1$ ns^{-1}, $k_{sc} = 0.002$ ns^{-1}. The notation $(\alpha\beta\beta_N)_S$ means that the corresponding state has S-character higher than 1/2; $(\alpha\beta\beta_N)_T$ has higher T_0-character; the pseudo-secular HFC is omitted in the calculation to visualize the LAC more clearly.

DR & DD

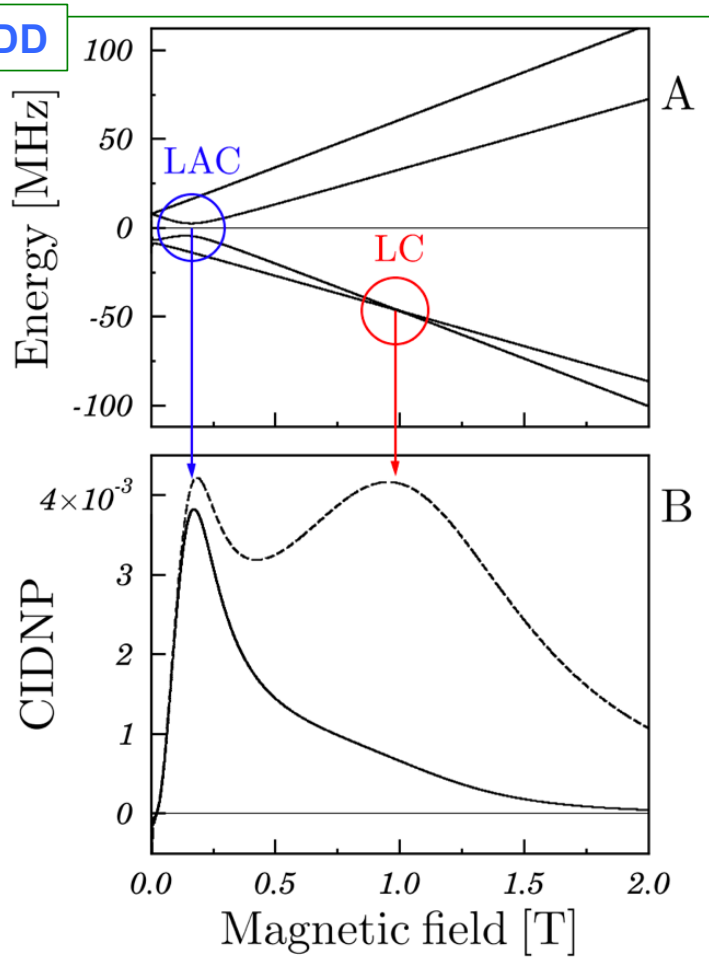


FIG. 5. Field dependence of energy levels (a) and field dependence of CIDNP (b). Parameters used in calculation: $g_1 = 2$ and $g_2 = 2.001$; the nucleus is a proton; $A = 1$ mT; $d = 0$; $k_S = 2k_T = 0.08$ ns^{-1}, $b = 0.5$ mT, $k_{sc} = 0.002$ ns^{-1} (dashed line), $k_{sc} = 0$ (solid line); the calculated CIDNP is polarization per RP. In (a) the LAC is highlighted by a blue circle and LC is highlighted by a red circle.

The solid-state photo-CIDNP effect: Field-dependence

R. sphaeroides WT

• Enhancement curve is very broad

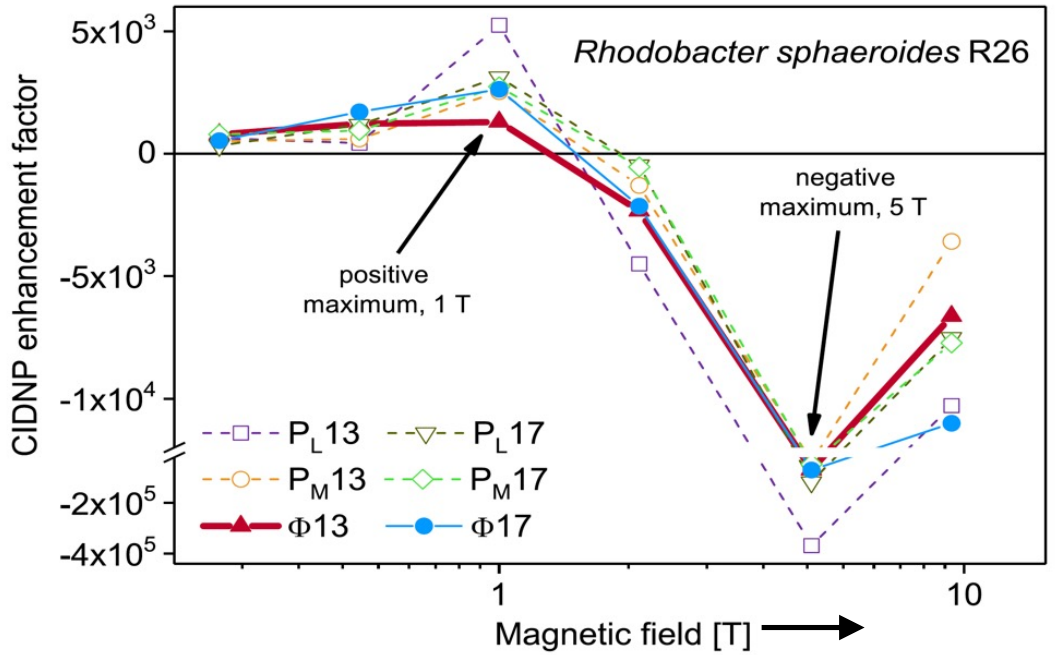


FIG. 1. Experimental CIDNP field dependence obtained for the photosynthetic reaction center of the purple bacterium *Rhodobacter sphaeroides* R26. The field dependence of the **C13Φ** nucleus is highlighted. See text for further explanation.

Daniel Gräsing et al., Scientific Reports 7, 12111 (2017).

Denis V. Sosnovsky et al., J. Chem. Phys. 150, 094105 (2019).

Level-cossings & anti-crossings

product.

Previously, TSM was considered in situations where $|\Delta\omega_e| \leq |\omega_N|$. In this work, we also consider the opposite case $|\Delta\omega_e| > |\omega_N|$ and find a different behavior of the LACs and CIDNP field dependence. Since such a case has not been analyzed before, we discuss it here in detail assuming that d

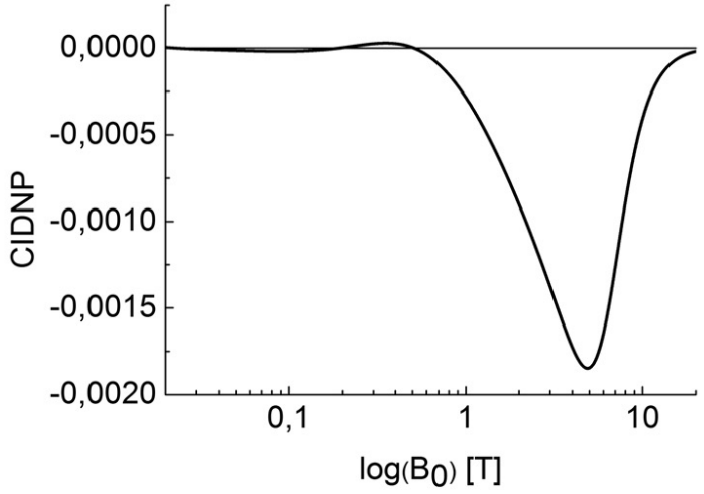
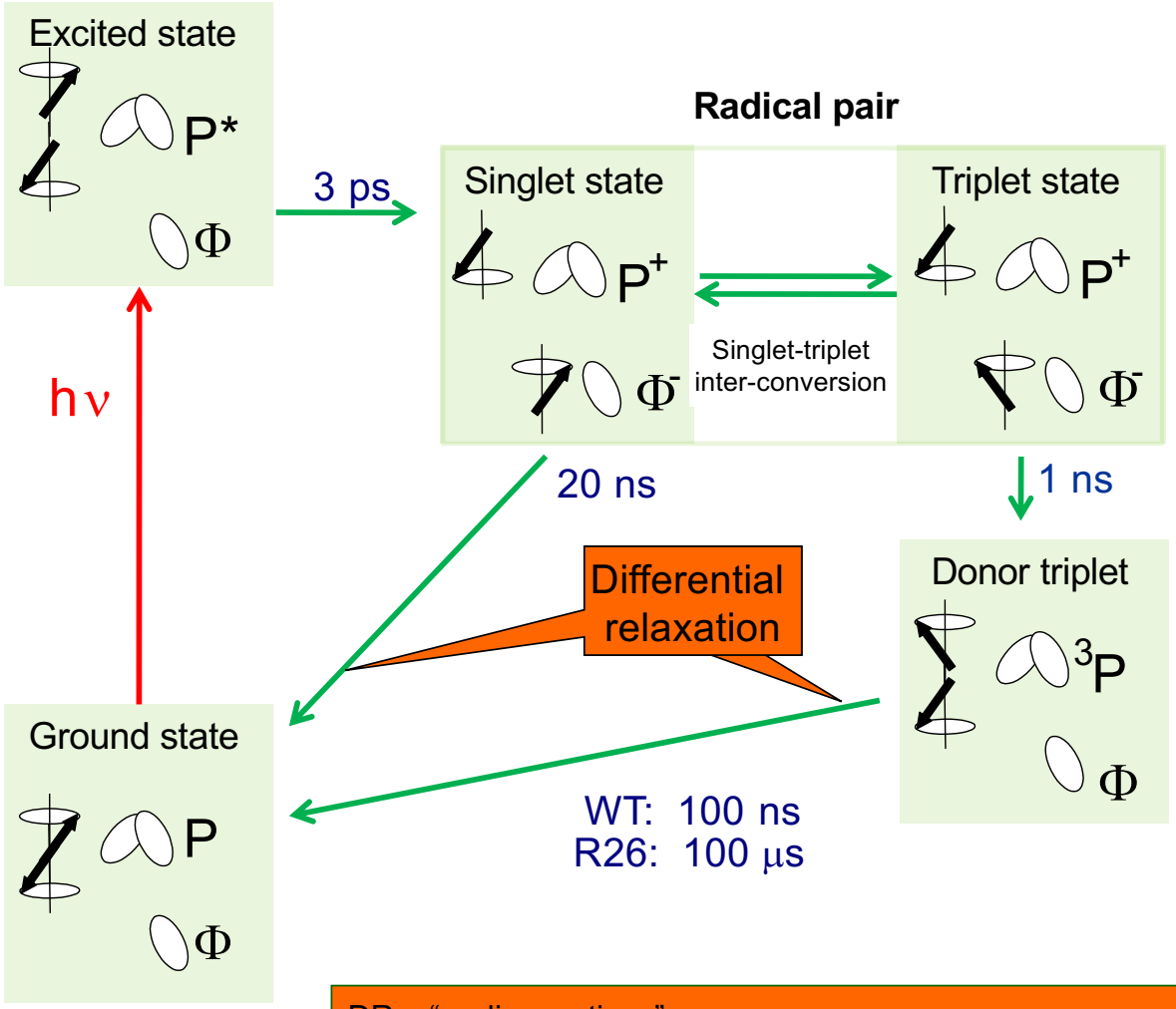


FIG. 8. CIDNP field dependence of a photosynthetic reaction center protein of *Rhodobacter sphaeroides* averaged over all possible orientations. Simulation parameters: nucleus is the ^{13}C nucleus **C13Φ**; k_S = 0.015 ns^{-1}, k_T = 0.4 ns^{-1}, ξ = 0.98.

Denis V. Sosnovsky et al., J. Chem. Phys. 150, 094105 (2019).

Photocycle in quinone-blocked RCs R26

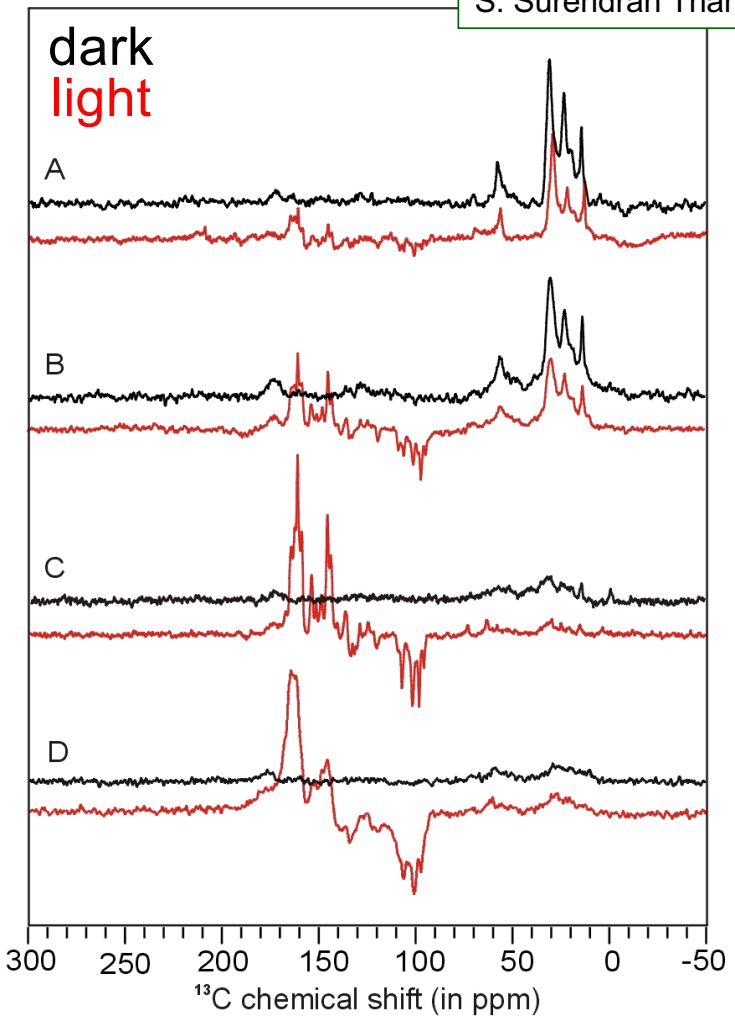


DR = “cyclic reactions”:
Closs 1975 , Goldstein & Boxer 1987, McDermott et al. 1998.

The solid-state photo-CIDNP effect

R. sphaeroides R26

S. Surendran Thamarath (2012) JACS 134, 5921.



DR: positive

TSM & DD: negative

17.6 T
750 MHz

Factor ~80

9.4 T
400 MHz

Factor ~800

4.7 T
200 MHz

Factor ~10000

2.4 T
100 MHz

Factor ~20000

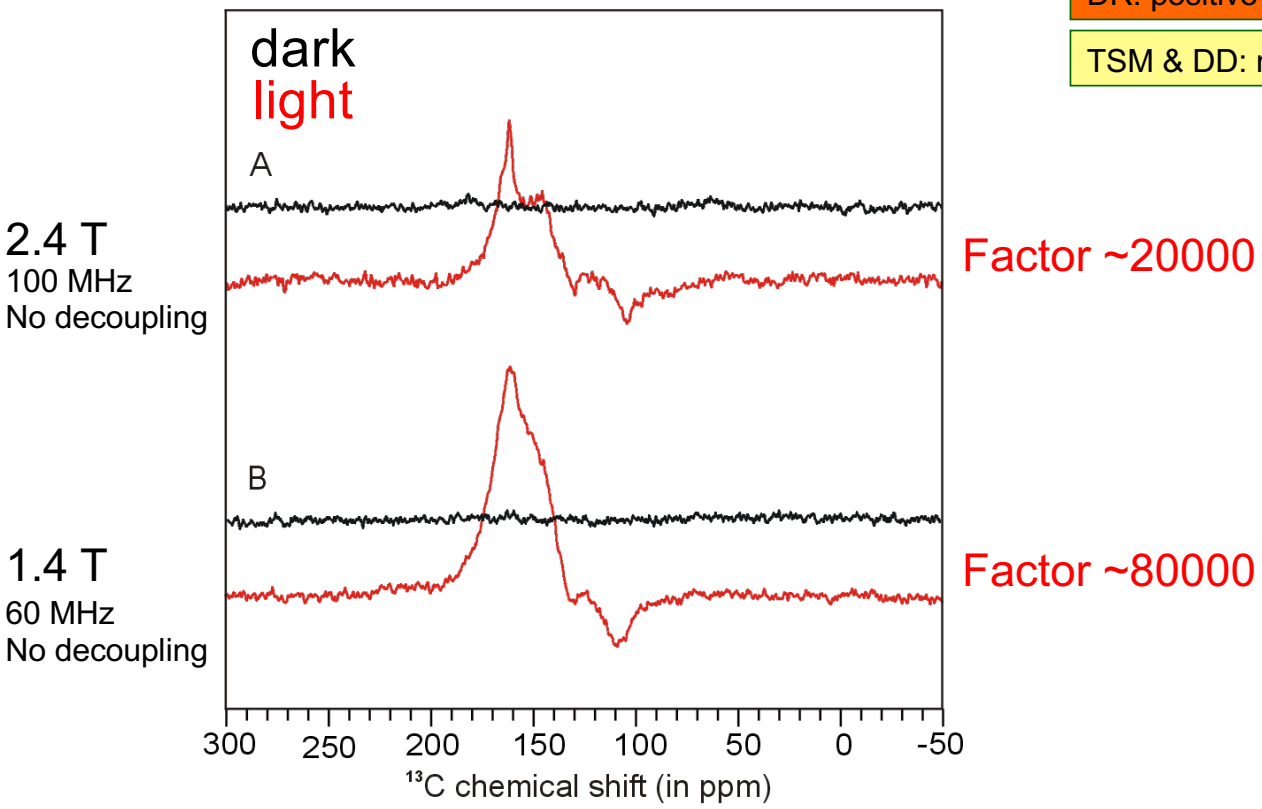
The solid-state photo-CIDNP effect

R. sphaeroides R26

S. Surendran Thamarath (2012) JACS 134, 5921.

DR: positive

TSM & DD: negative



Factor ~20000

Factor ~80000

Photo-CIDNP MAS NMR as analytical method

^{13}C-^{13}C photo-CIDNP DARR & INADEQUATE → **chemical-shift** assignment → electronic ground-state structure.

Time-resolved ^{13}C-photo-CIDNP **intensites** → related to RPM → isotropic hyperfine interactions.
Steady-state ^{13}C-photo-CIDNP **intensies** → related to TSM → electron-spin density in p_z orbitals.
Steady-state low-field ^{13}C-photo-CIDNP **intensies** → related to DR → electron-spin density in ^3P state.

^{13}C photo-CIDNP DIPSHIFT → local **dynamics** (Marcus theory *vs* polaron theory)

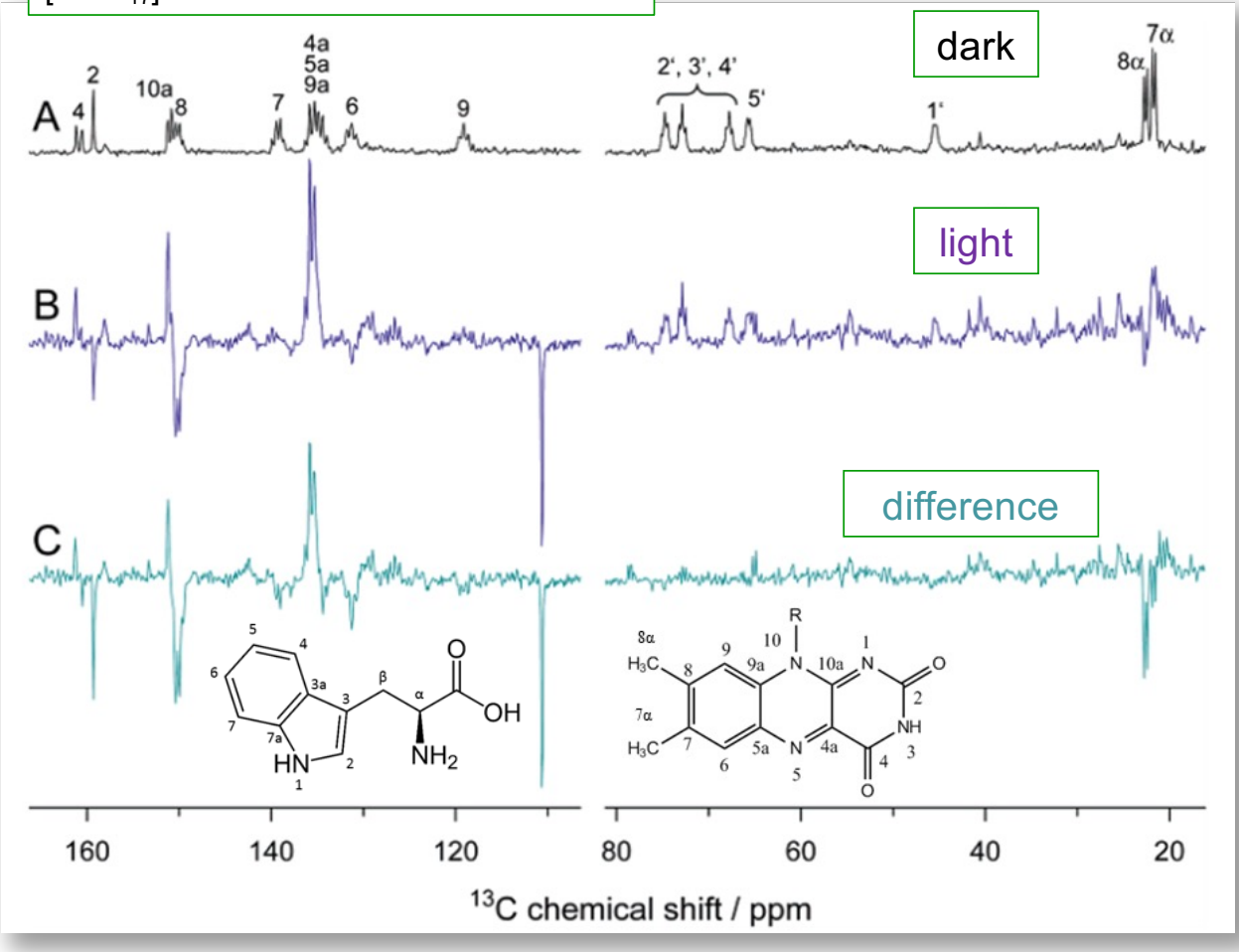
„Spin-torch“ experiments → chemical shifts of **surrounding groups** → tuning effects

Photo-CIDNP MRI using selective CIDNP agents → **images** as fluorescence microscopy → diagnostics

Bela Bode et al. (2013) “The solid-state photo-CIDNP effect and its analytical application”, In: Hyperpolarization methods in NMR spectroscopy (Lars Kuhn, ed.) Springer, pp. 105-121 (Review).

Flavin protein: Photo-CIDNP effect observed in phototropin

500 MHz ^{1}H freq. (11.7 Tesla),
Liquid-state NMR,
[u-$^{13}C_{17}$]-FMN reconstituted LOV2 C540A

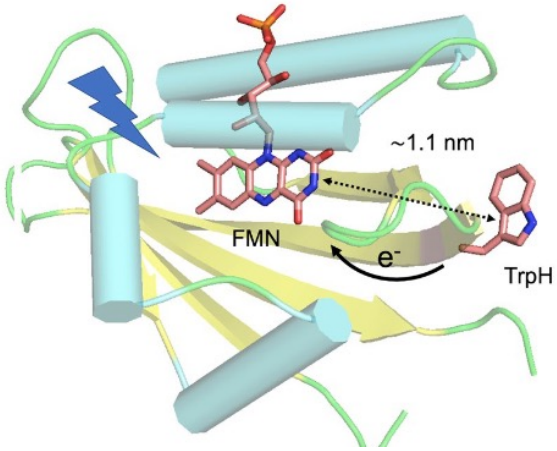


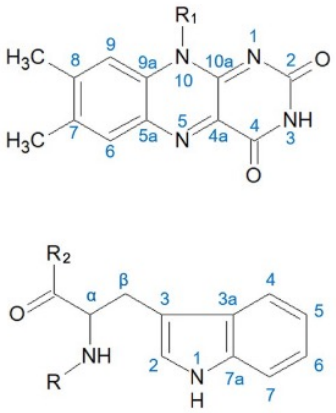
J|A|C|S
ARTICLES
Published on Web 11/18/2005

Photochemically Induced Dynamic Nuclear Polarization in a C450A Mutant of the LOV2 Domain of the *Avena sativa* Blue-Light Receptor Phototropin

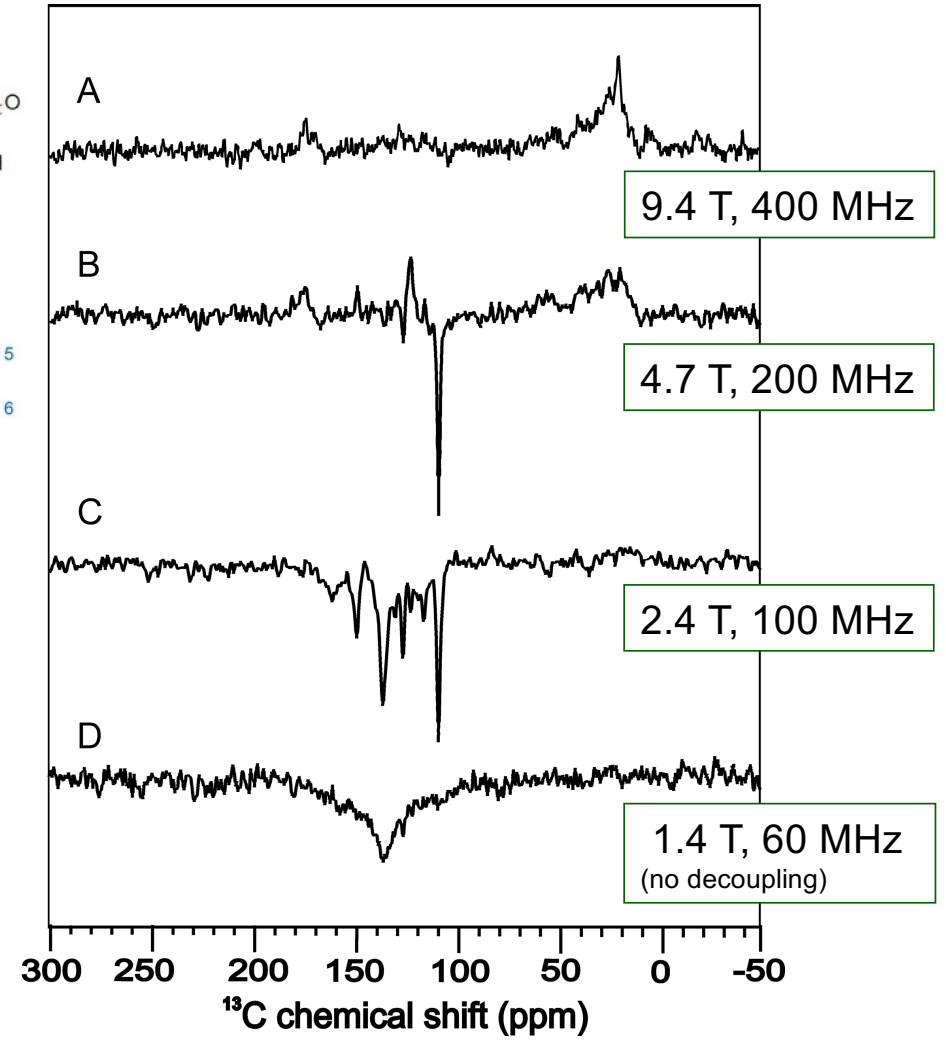
Gerald Richter,*,†,§ Stefan Weber,*,‡ Werner Römisch,† Adelbert Bacher,† Markus Fischer,† and Wolfgang Eisenreich*,†

Flavin protein: experimental field-dependence





Phototropin LOV1-C57S



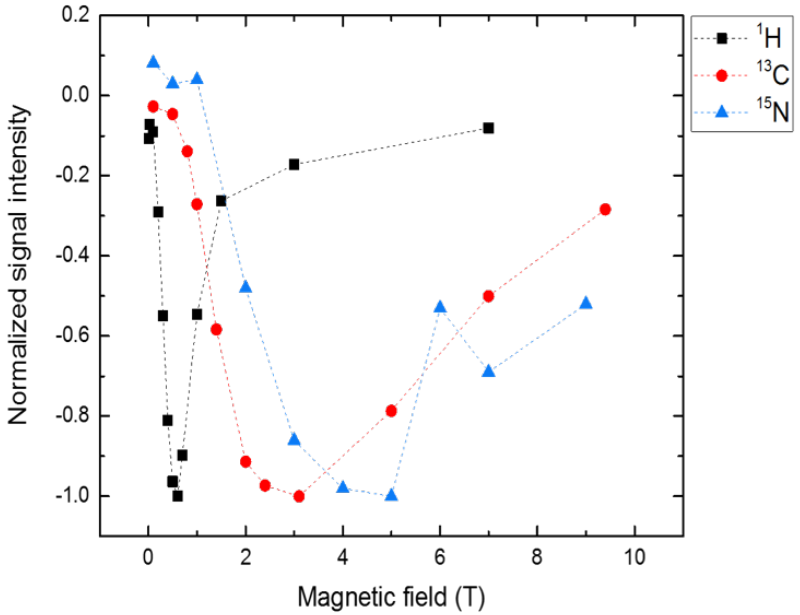
Collaboration T. Kottke

S. Surendran Thamarath et al. (2010) JACS 132, 15542–15543.

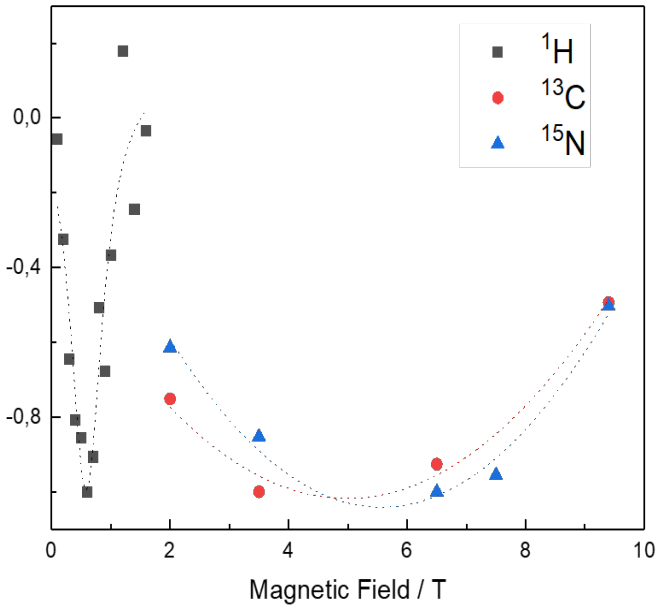
Xiaojie Wang (王孝杰), Smitha Surendran Thamarath, A. Alia, Bela E. Bode, Jörg Matysik (誉宫) Acta Phys. Chem. Sin. 32, 399-404 (2016).

Flavin proteins: Magnetic-field dependence

Phototropin-LOV1-C57S



Aureochrome-LOV-C287S



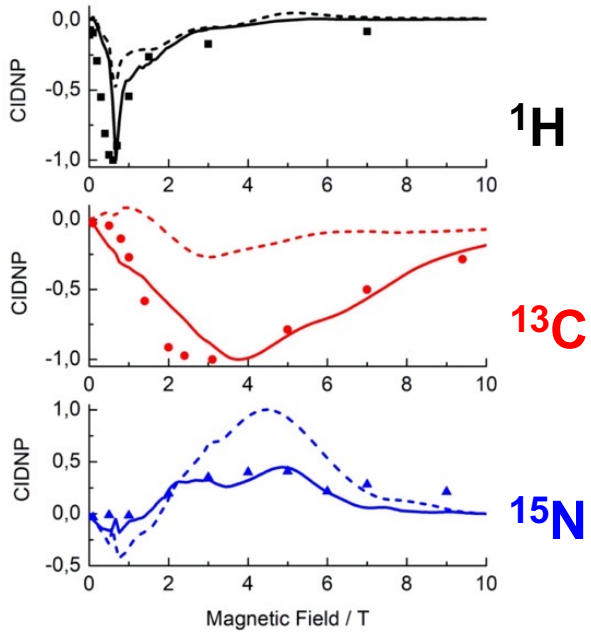
Liquid-state ^{1}H, ^{13}C and ^{15}N NMR

Collaboration with Alexandra Yurkovskaya and Konstantin Ivanov (Novosibirsk) and Tilman Kottke (Bielefeld)

Yonghong Ding et al., Scientific Reports (2019) 9, 18436.

Flavin proteins: Magnetic-field dependence

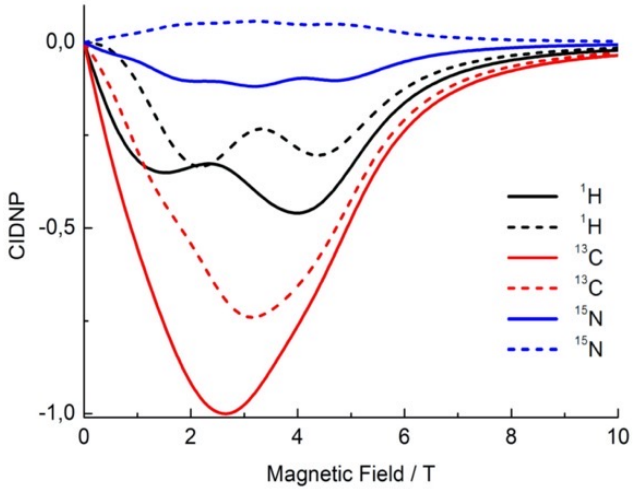
Anisotropic interactions



$$\omega_{Nuclear} \approx d = 2J_{ex} - D$$

Sosnovsky D. et al. (2016)

Isotropic interactions



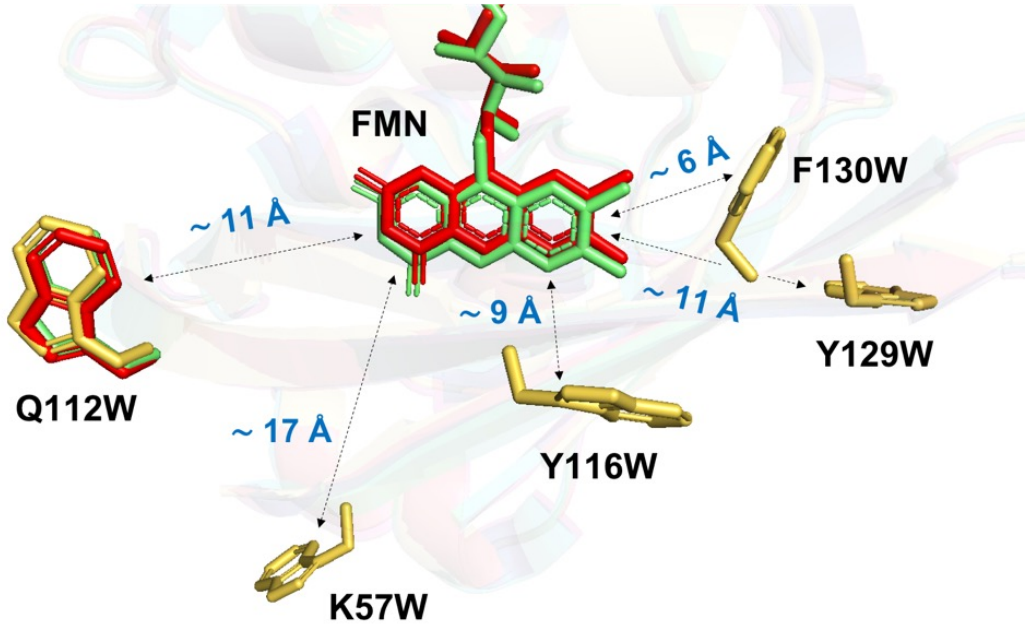
$a_{H_1} = 0.7$ mT
$a_{H_2} = 0.5$ mT
$a_{C_1} = 1.25$ mT
$a_{C_2} = 1$ mT
$a_{N_1} = 0.2$ mT
$a_{N_2} = -0.1$ mT

Liquid-state ^{1}H, ^{13}C and ^{15}N NMR

Collaboration with Alexandra Yurkovskaya and Konstantin Ivanov (Novosibirsk) and Tilman Kottke (Bielefeld)

Yonghong Ding et al., Scientific Reports (2019) 9, 18436.

Flavin proteins: Magnetic-field dependence

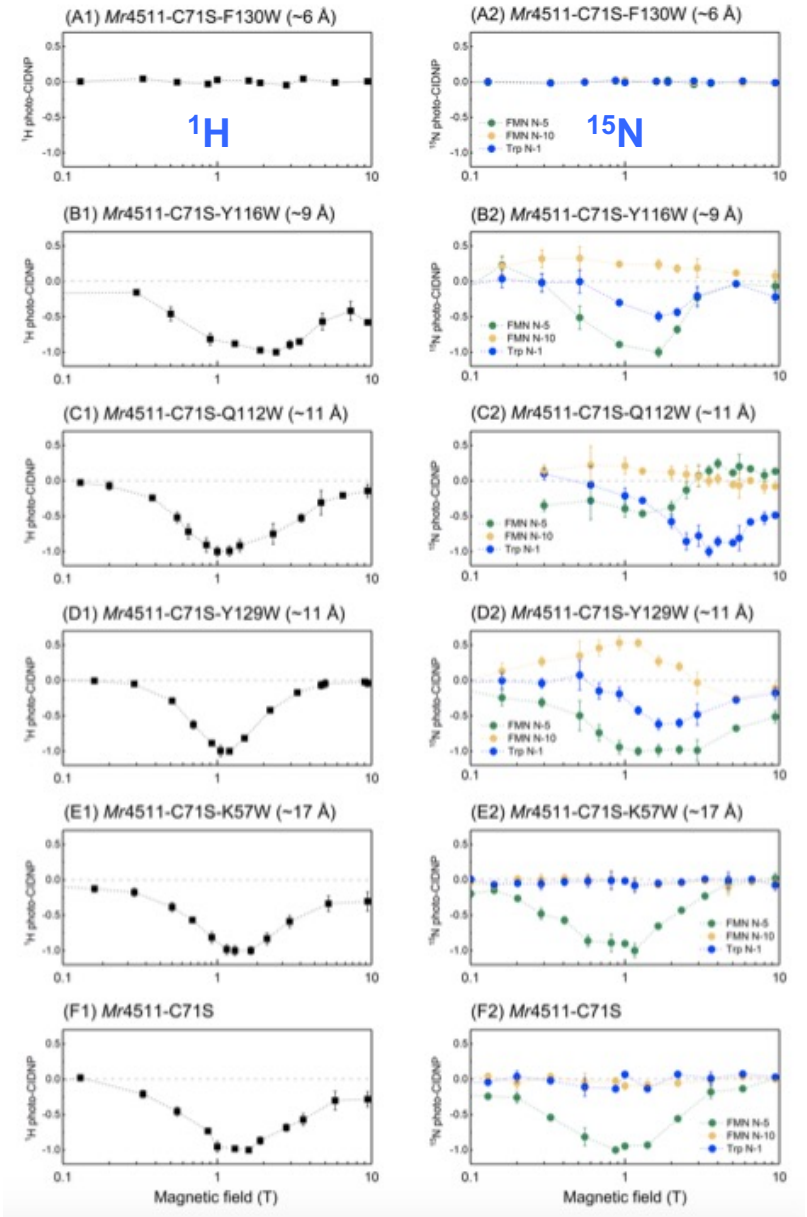


• C450A mutant of **phototropin 1-LOV2** from *Avena sativa* (*As*PHOT1-LOV2-C450A)	Weber (Freiburg)
• C57S mutant of **phototropin-LOV1** from *Chlamydomonas reinhardtii* (*Cr*PHOT-LOV1-C57S)	Kottke (Bielefeld)
• C287S mutant **aureochrome1a-LOV** from *Phaeodactylum tricornutum* (*Pt*AUREO1a-LOV-C287S)	Kottke (Bielefeld)
• C71S mutant of **4511** from *Methylobacterium radiotolerans* (*Mr*4511-C71S)	Losi (Parma) & Gärtner (Leipzig)
• W322F mutant of **animal-like cryptochrome** from *Chlamydomonas reinhardtii* (*Cr*aCRY-W322F)	Kottke (Bielefeld) & Mittag (Jena)

Yonghong Ding et al., Scientific Reports (2020) 10, 18658.

Flavin proteins: Magnetic-field dependence

Liquid-state NMR for ^{1}H and ^{15}N



Distance (Don-Acc)

6 Å

9 Å

11 Å

11 Å

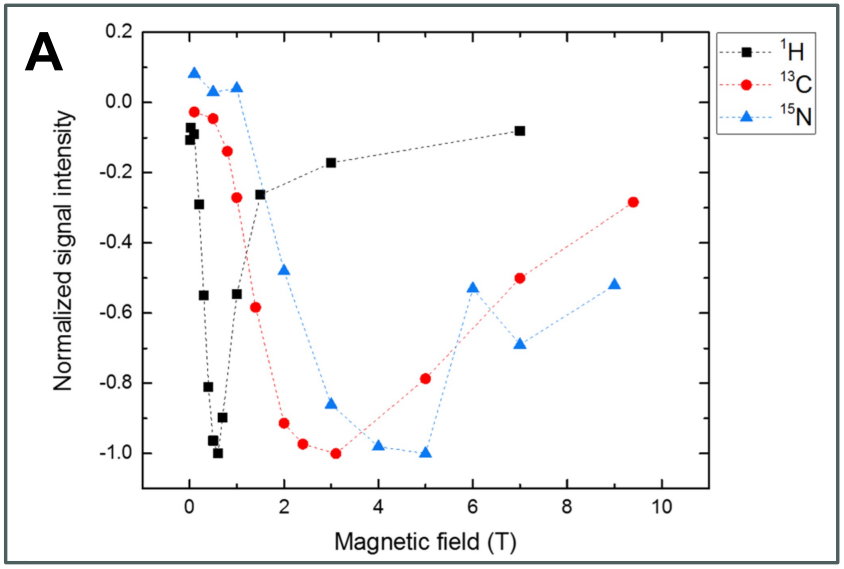
17 Å

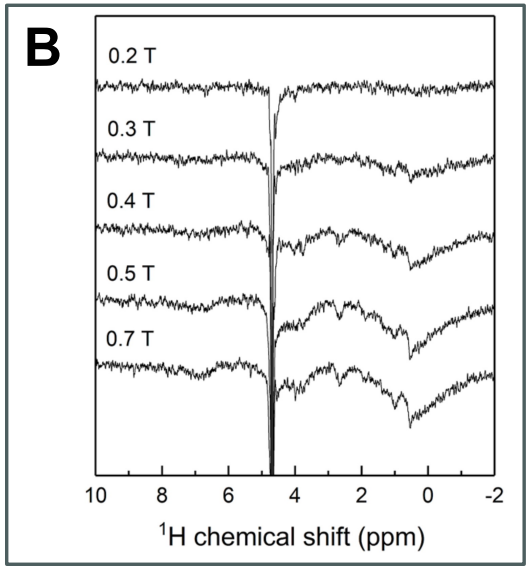
No tryptophan, But tyrosine?

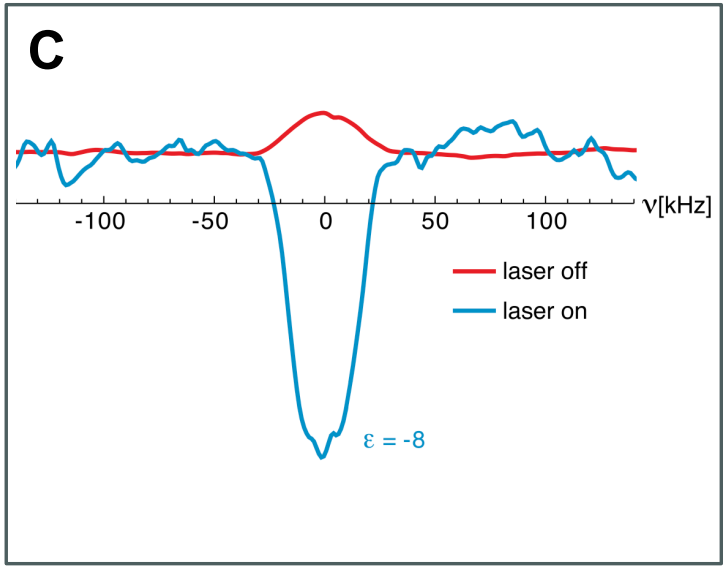
Yonghong Ding et al.,
Scientific Reports (2020) 10, 18658.

Collaboration with Alexandra Yurkovskaya and Konstantin Ivanov, Novosibirsk

The ^{1}H solid-state photo-CIDNP effect







(**A** & **B**) Yonghong Ding et al., Scientific Reports (2020) 10, 18658.

(**C**) Federico De Biasi et al., JACS (2023) 145, 14874.

The ^{1}H solid-state photo-CIDNP effect: towards “CIDNP juice”

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Communication

Light-Induced ^{1}H NMR Hyperpolarization in Solids at 9.4 and 21.1 T

Federico De Biasi, Ganesan Karthikeyan, Máté Visegrádi, Marcel Levien, Michael A. Hope, Paige J. Brown, Michael R. Wasielewski, Olivier Ouari, and Lyndon Emsley*

Cite This: https://doi.org/10.1021/jacs.4c06151
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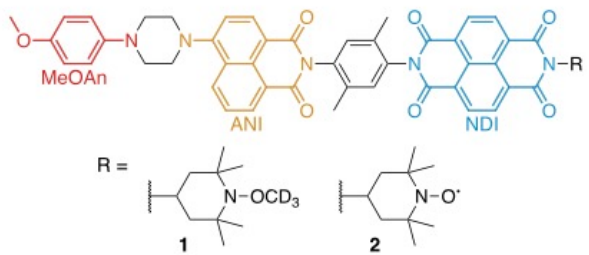

Figure 1. Structures of molecules used in this work. The donor (MeOAn), chromophore (ANI), and acceptor (NDI) moieties in the photoactive part of the structure are shown in red, yellow, and blue, respectively. The linker units are shown in black.

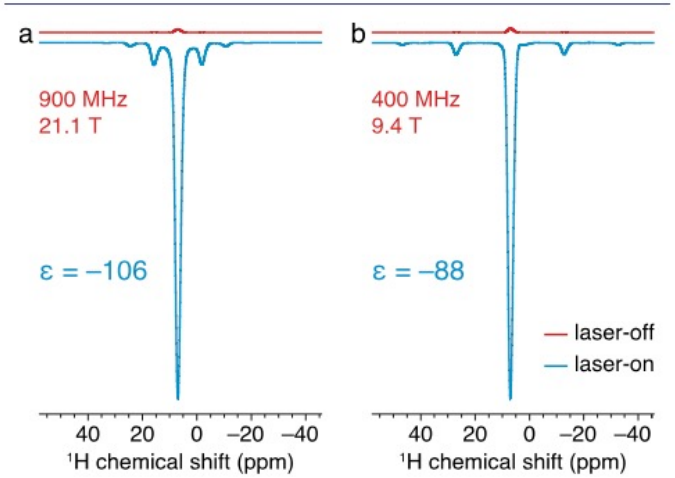

Figure 2. ^{1}H NMR spectra of a frozen solution of 1.5 mM PhotoPol-S in 98.5% OTP-d_{14} recorded at (a) 900 MHz and (b) 400 MHz, with and without continuous 450 nm laser irradiation (blue and red traces, respectively). All spectra were detected with a 70 s recycle delay and 8 kHz MAS using a Hahn echo block (4 rotor periods per half echo delay) to suppress the probe background, and 4 scans per experiment.

The future

- High-field ^{1}H photo-CIDNP MAS NMR on *in-vitro* samples (e.g., for structure determination of proteins)

- Low-field ^{1}H photo-CIDNP MRI on *in-vivo* samples (e.g., as alternative to fluorescence microscopy)

Literature

History of the liquid-state photo-CIDNP effect (1)

Discovery of the CIDEP effect in EPR

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Discovery of the CIDNP effect (in a dark organic radical reaction)

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Observation of photo-CIDNP

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Further development of method

Pulse NMR methods

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History of the liquid-state photo-CIDNP effect (2)

Further development of liquid-state mechanims

High-field CIDNP

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(Pre-)History of the solid-state photo-CIDNP effect

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Solid-state photo-CIDNP mechanisms

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Photo-CIDNP analysis of RCs of *Rb. sphaeroides*

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Photo-CIDNP in other photosynthetic systems

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Experimental progress

i) Two-dimensional photo-CIDNP MAS NMR

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ii) Field-dependent experiments

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iii) Kinetic & time-resolved experiments

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iv) Action spectroscopy

E. Daviso, A. Diller, P. Gast, A. Alia, J. Lugtenburg, M.G. Müller, J. Matysik (2010) Action spectroscopy on dense samples of photosynthetic reaction centers of Rhodobacter sphaeroides WT based on nanosecond laser-flash 13C photo-CIDNP MAS NMR, Appl. Magn. Reson. 38, 105-116.

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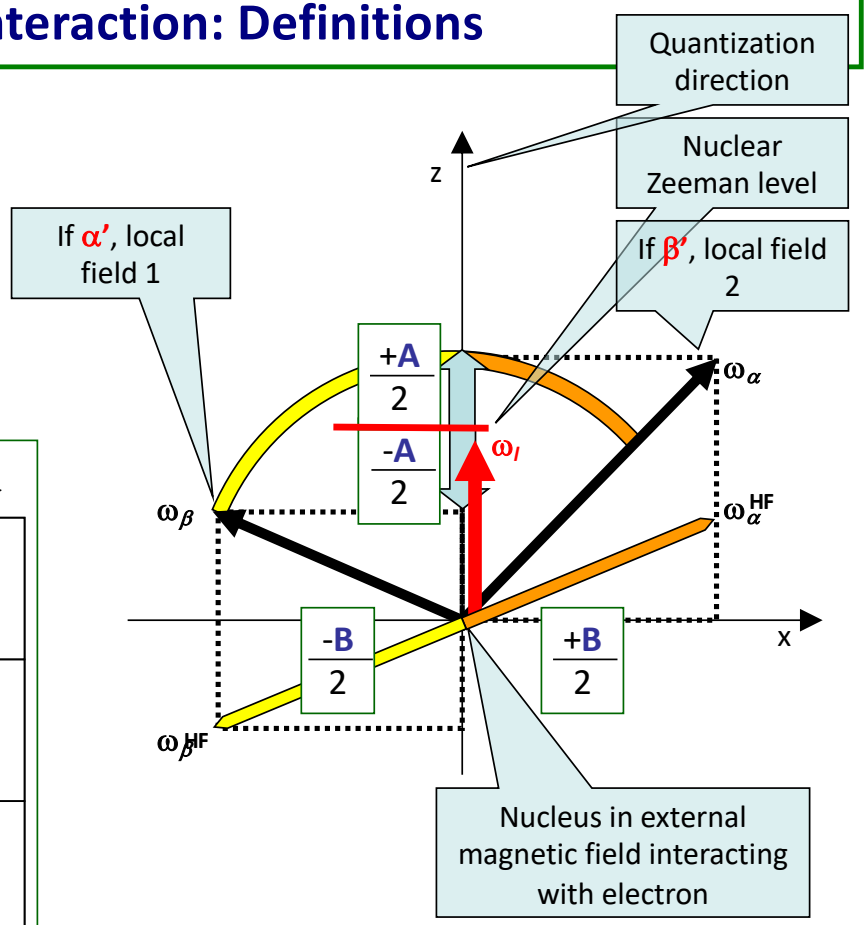
Hyperfine interaction: Definitions

A = secular part of hfi
B = pseudo-secular part of hfi
X = non-secular part of hfi

$\mathbf{A} = (3\cos^2\theta - 1)\mathbf{T} + a_{iso}$
$\mathbf{B} = 3\sin\theta\cos\theta\,\mathbf{T}$
T = anisotropic hfi

	$\lvert\alpha' N_\alpha\rangle$	$\lvert\alpha' N_\beta\rangle$	$\lvert\beta' N_\alpha\rangle$	$\lvert\beta' N_\beta\rangle$
$\langle\alpha' N_\alpha\rvert$	$\frac{+A}{4}$	$\frac{+B}{4}$		
$\langle\alpha' N_\beta\rvert$	$\frac{+B}{4}$	$\frac{-A}{4}$		
$\langle\beta' N_\alpha\rvert$			$\frac{-A}{4}$	$\frac{-B}{4}$
$\langle\beta' N_\beta\rvert$			$\frac{-B}{4}$	$\frac{+A}{4}$



Frequency vectors
ω_I = nuclear frequency
ω_α, ω_β = effective magnetic field experienced by a nucleus caused by α' or β' electron spin

TSM: The "fictitious spin" picture

Jeschke (1997) JCP 106, 10072 & (1998) JACS 120, 4425

Fictitious electron spin S with Zeeman frequency of $\Delta\Omega$ instead of two electrons at Ω_1 and Ω_2. Hamiltonian of the S-T_0 subsystem:

$$\mathcal{H} = \Delta\Omega\, S_Z + \omega_I I_Z + A_{ZZ}\, S_Z I_Z + B_{ZX}\, S_Z I_X + B_{ZY}\, S_Z I_Y + d\, S_X$$

Kaptein

Jeschke

	$\lvert\alpha\alpha\rangle$	$\lvert\alpha\beta\rangle$	$\lvert\beta\alpha\rangle$	$\lvert\beta\beta\rangle$
$\langle\alpha\alpha\rvert$	$P_{\alpha\alpha}$	SQ	SQ	DQ
$\langle\alpha\beta\rvert$	SQ	$P_{\alpha\beta}$	ZQ	SQ
$\langle\beta\alpha\rvert$	SQ	ZQ	$P_{\beta\alpha}$	SQ
$\langle\beta\beta\rvert$	DQ	SQ	SQ	$P_{\beta\beta}$

A = $(3\cos^2\theta - 1)$**T** + a_{iso}
B = $3\sin\theta\cos\theta$ **T**
T = anisotropic hfi

		$\lvert\alpha'\rangle$	$\lvert\beta'\rangle$
		$\lvert\alpha\beta\rangle$	$\lvert\beta\alpha\rangle$
$\langle\alpha'\rvert$	$\langle\alpha\beta\rvert$	$\Delta\Omega/2$	**d**
$\langle\beta'\rvert$	$\langle\beta\alpha\rvert$	**d**	$\Delta\Omega/2$

d = 2J + d'/2
J = exchange coupling
d' = dipole-dipole coupling