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

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京都市, 2024年9月20日
CIDNP 工房

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

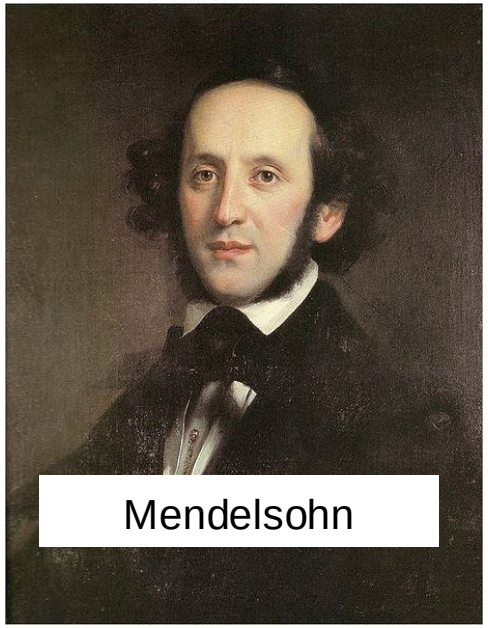
Photo-CIDNP in solids

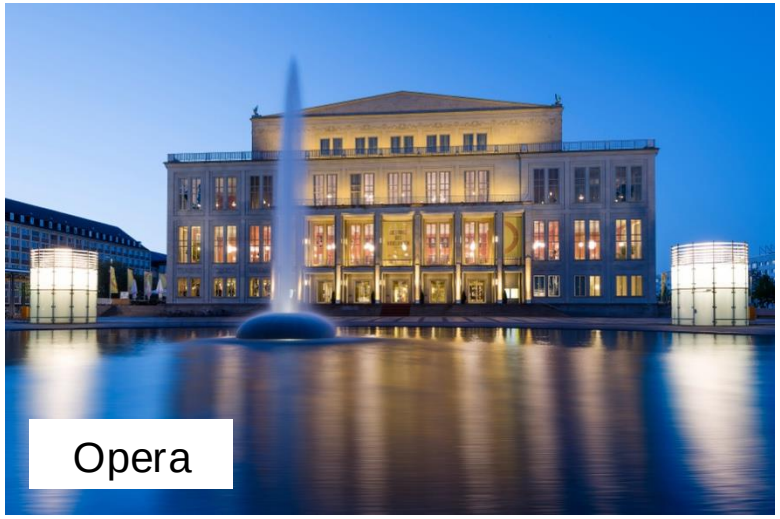
Leipzig: City of Music


Bach


Thomaskirche


Gewandhaus

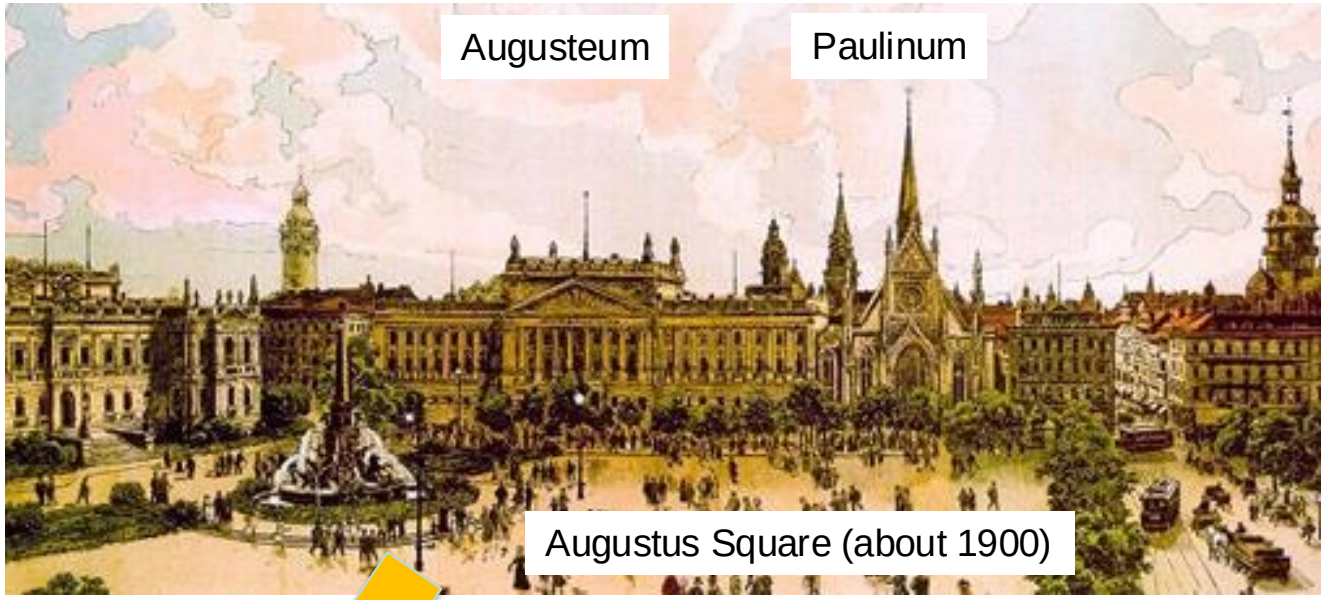

Mendelsohn

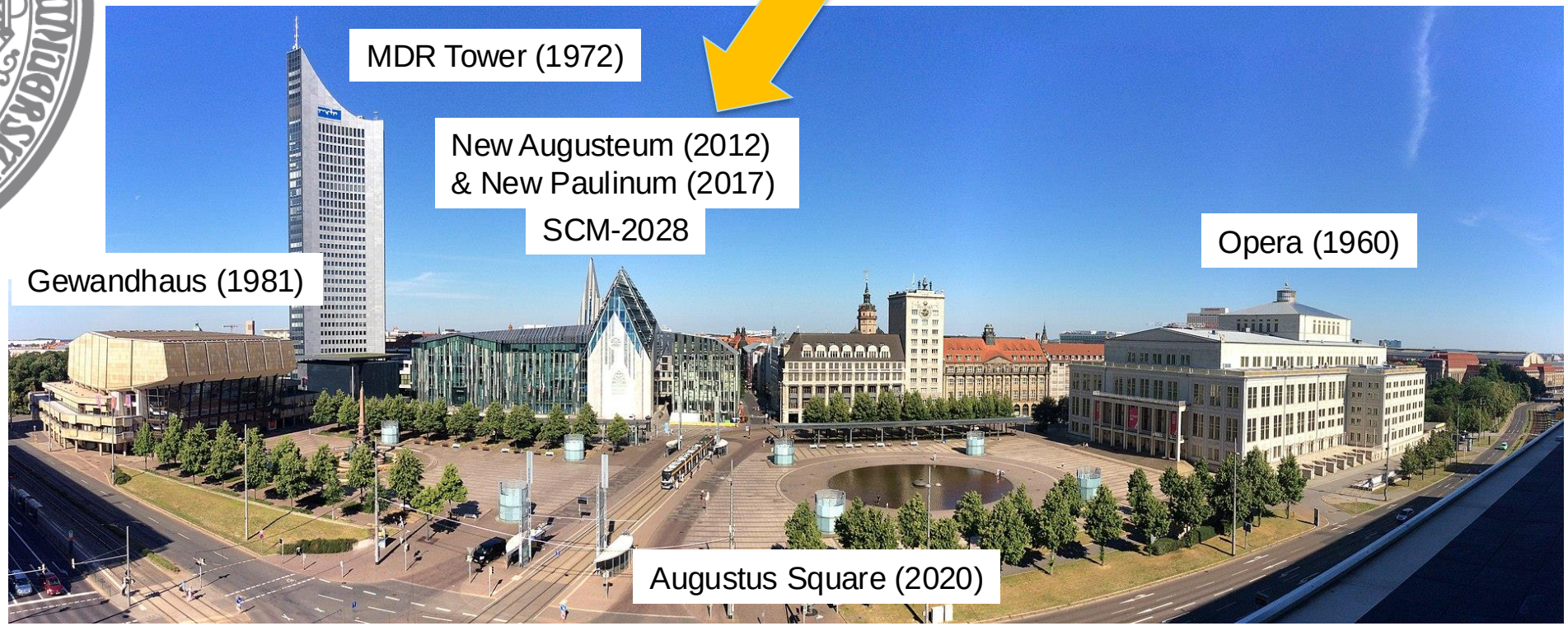

Opera

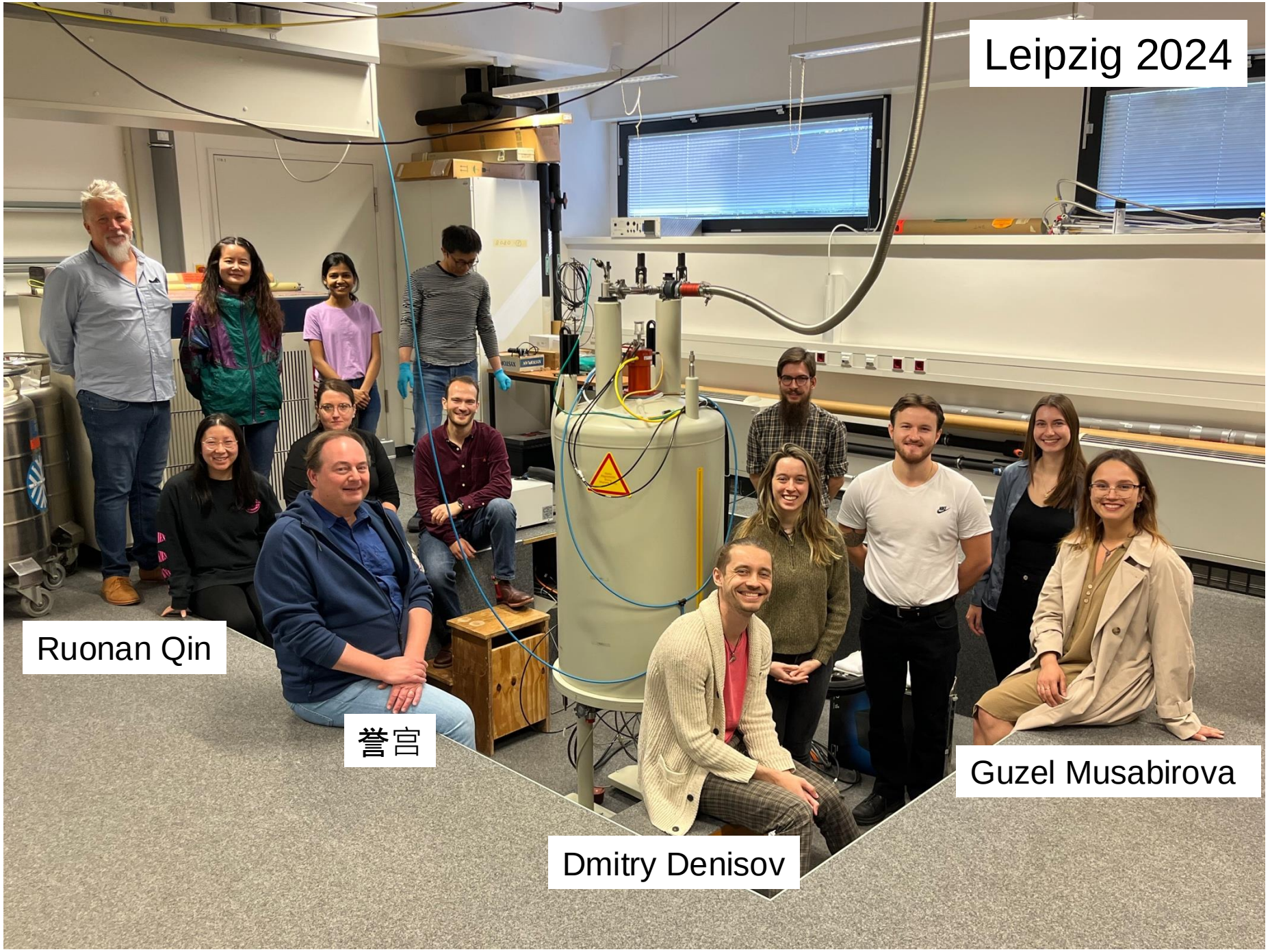

Thomaner-Chor

Universität Leipzig

Founded in 1409 ライプツィヒ大学（ライ大）






Leipzig 2024
Ruonan Qin
誉宫
Guzel Musabirova
Dmitry Denisov

Research consortium HYP*MOL (since Oct. 2023)

HYP*MOL

HYPERPOLARIZATION
IN MOLECULAR SYSTEMS

POLARIZATION | TRANSPORT | REACTIVITY

HYP*MOL on LINKED-IN

Reviews on the solid-state photo-CIDNP effect

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

Applied Magnetic Resonance

REVIEW

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

CHEMICAL REVIEWS

pubs.acs.org/CR

Review

Spin Hyperpolarization in Modern Magnetic Resonance

James Eills,* Dmitry Budker, Silvia Cavagnero, Eduard Y. Chekmenev, Stuart J. Elliott, Sami Jannin, Anne Lesage, Jörg Matysik, Thomas Meersmann, Thomas Prisner, Jeffrey A. Reimer, Hanming Yang, and Igor V. Koptyug*

Cite This: *Chem. Rev.* 2023, 123, 1417–1551

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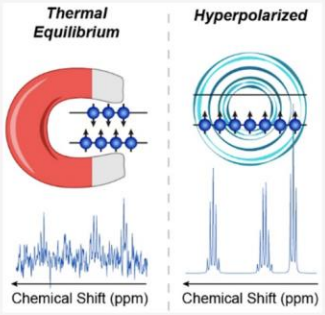
ABSTRACT: Magnetic resonance techniques are successfully utilized in a broad range of scientific disciplines and in various practical applications, with medical magnetic resonance imaging being the most widely known example. Currently, both fundamental and applied magnetic resonance are enjoying a major boost owing to the rapidly developing field of spin hyperpolarization. Hyperpolarization techniques are able to enhance signal intensities in magnetic resonance by several orders of magnitude, and thus to largely overcome its major disadvantage of relatively low sensitivity. This provides new impetus for existing applications of magnetic resonance and opens the gates to exciting new possibilities. In this review, we provide a unified picture of the many methods and techniques that fall under the umbrella term "hyperpolarization" but are currently seldom perceived as integral parts of the same field. Specifically, before delving into the individual techniques, we provide a detailed analysis of the underlying principles of spin hyperpolarization. We attempt to uncover and classify the origins of hyperpolarization, to establish its sources and the specific mechanisms that enable the flow of polarization from a source to the target spins. We then give a more detailed analysis of individual hyperpolarization techniques: the mechanisms by which they work, fundamental and technical requirements, characteristic applications, unresolved issues, and possible future directions. We are seeing a continuous growth of activity in the field of spin hyperpolarization, and we expect the field to flourish as new and improved h
https://pubs.acs.org/doi/10.1021/acs.chemrev.2c00534?fig=tgr1&ref=p
are implemented. Some key areas for development are in prolonging polarization lifetimes, making hyperpolarization techniques more generally applicable to chemical/biological systems, reducing the technical and equipment requirements, and creating more efficient excitation and detection schemes. We hope this review will facilitate the sharing of knowledge between subfields within the broad topic of hyperpolarization, to help overcome existing challenges in magnetic resonance and enable novel applications.



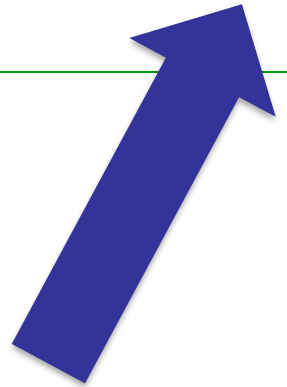
(Photo-) CIDNP

(Photo-)chemically induced dynamic nuclear polarization

(Photo-) CIDNP

(Photo-) CIDNP is based
on spin-correlated radical pairs (SCRPs)

ONP

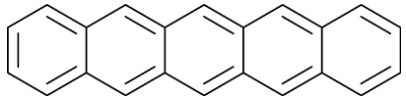


Optical nuclear polarization (ONP) is based on molecular triplet states

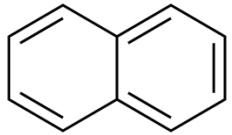
Papers by Schwörer, van der Waals, Stehlik … around 1980; nowadays NV centers

ONP

Pentacen

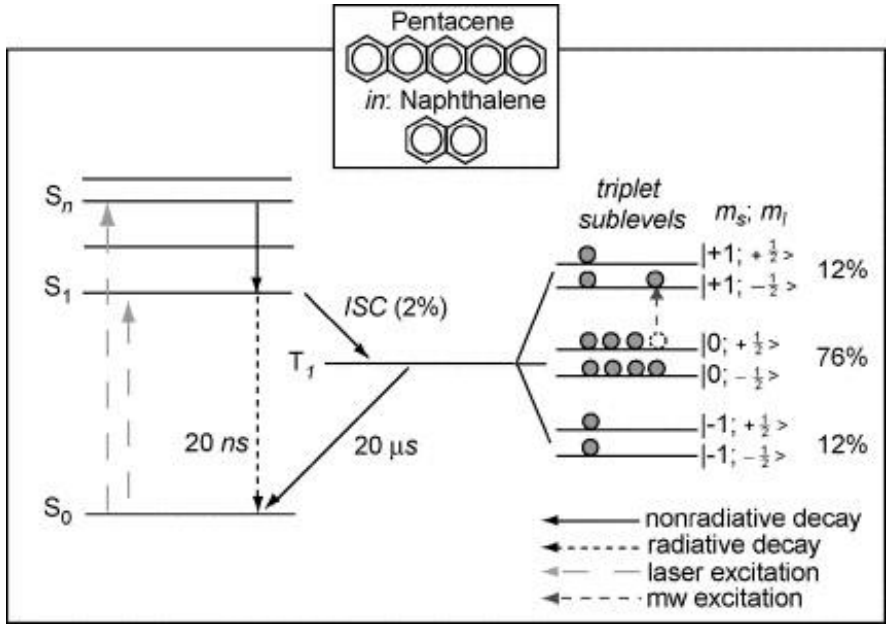


Naphthalene



(i) Strong lamp/laser

Triplet state is photochemically induced in molecular crystal: high electron spin order.



(ii) Stray field of NMR magnet

Sample is put into a weak magnet field (mT) comparable with the hyperfine interaction (hyperfine matching). Now, **polarization flows from the electrons to the nuclei**.

(iii) NMR measurement in NMR magnet

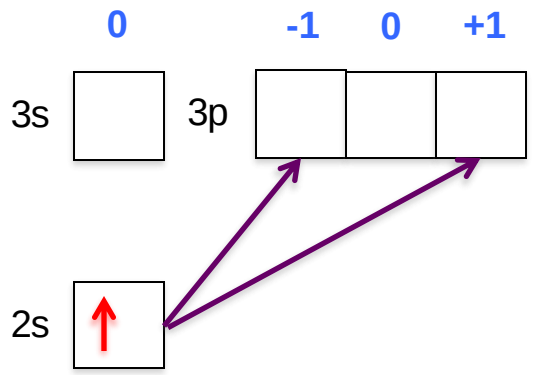
In the final step, solid-state NMR is measured: **^{13}C nuclear signals are enhanced due to polarization transfer** from the electrons. Long T_1 needed.

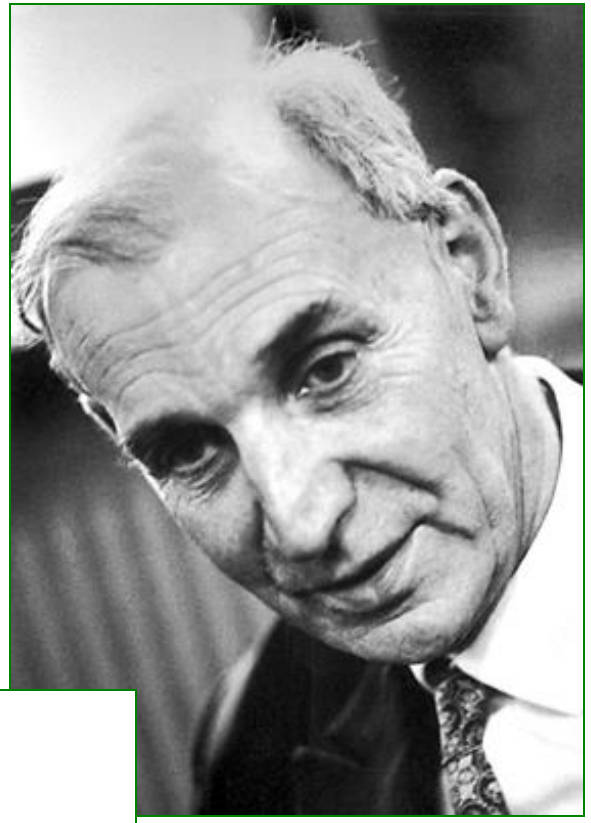
Optical pumping

(Spin-exchange) optical pumping (SEOP) is based on circularly polarized light

Optical pumping

Selection with **circularily** polarised light





Alfred Kastler
* 1902 in Gebweiler, Elsass, Germany
† 1984 in Bandol, Cote d´Azur, France
1966 Nobelpreis für Physik.

Kastler, A. (1950) J. Phys. Radium 11, 255.

Optical pumping

Spin-exchange optical pumping (SEOP) is based on circularly polarized light

Happer, W. (1972) Rev. Mod. Phys. 44, 169.

The (photo-) **CIDNP** effect

Kernresonanz-Emissionslinien während rascher Radikalreaktionen

I. Aufnahmeverfahren und Beispiele

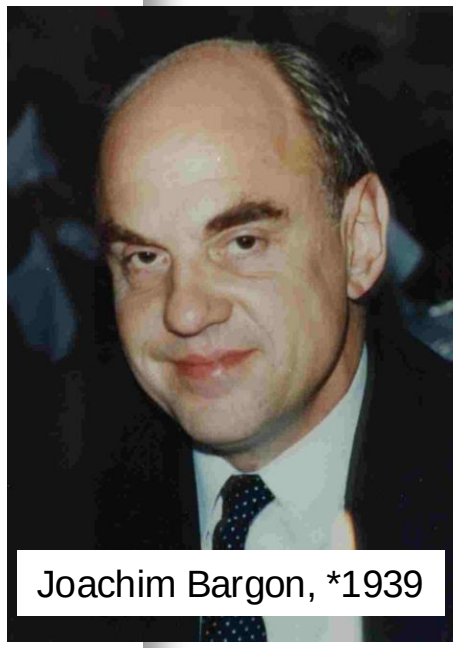
J. Bargon, H. Fischer und U. Johnsen

Deutsches Kunststoff-Institut Darmstadt

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

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.

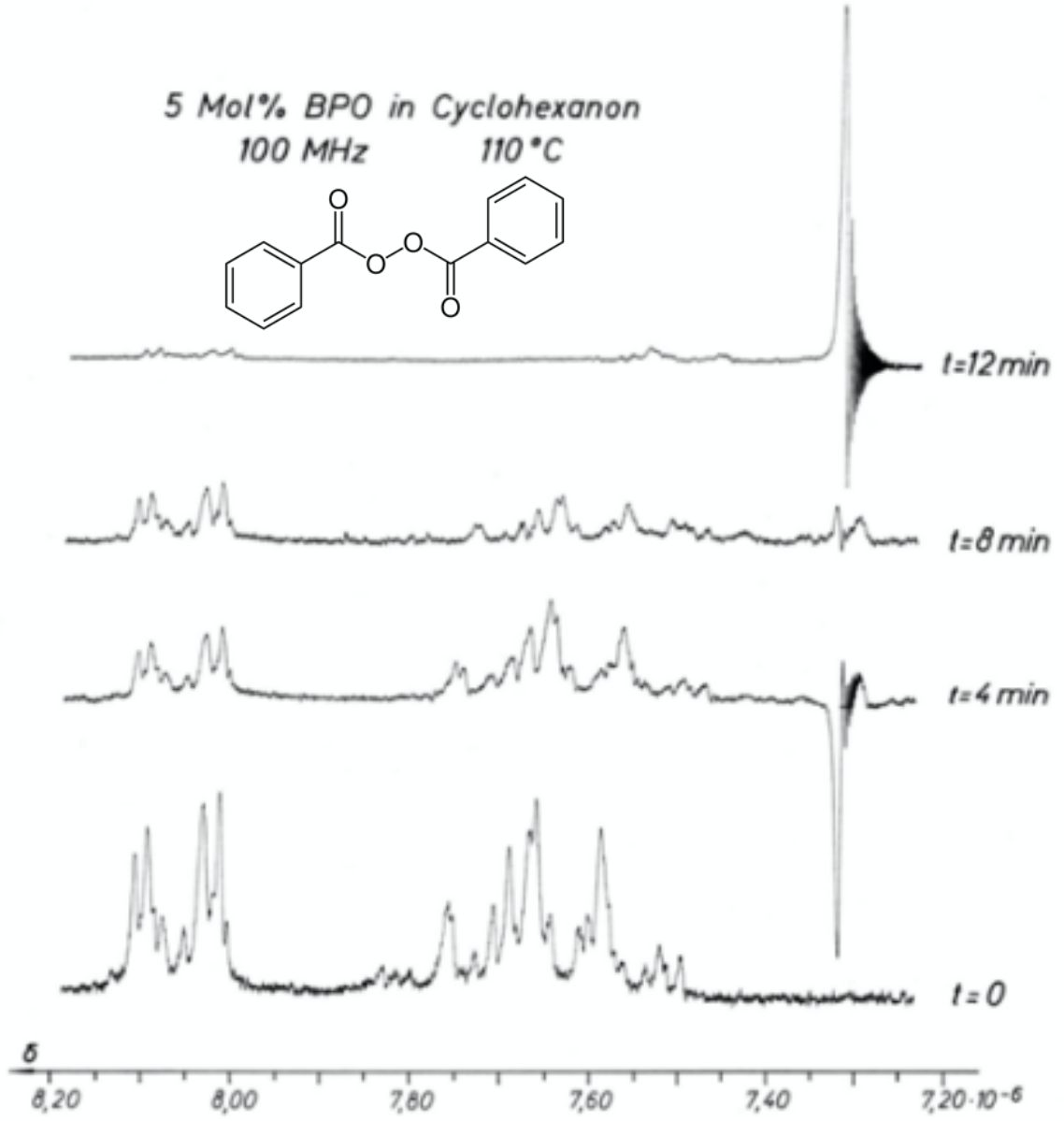
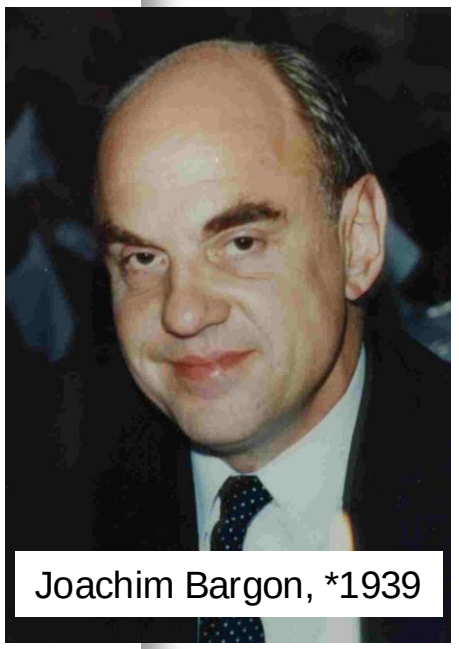


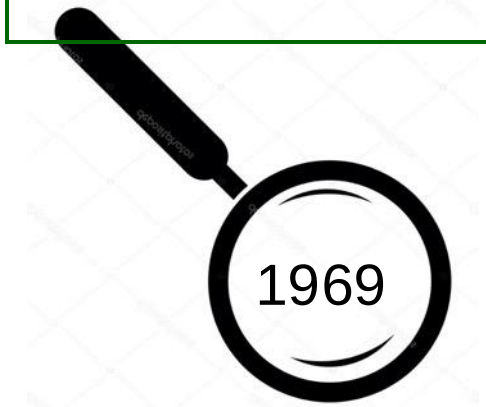
Abb. 2. Kernresonanzspektren während des thermischen Zerfalls von Dibenzoylperoxid nach verschiedenen Reaktionszeiten (Meßfrequenz 100 MHz).

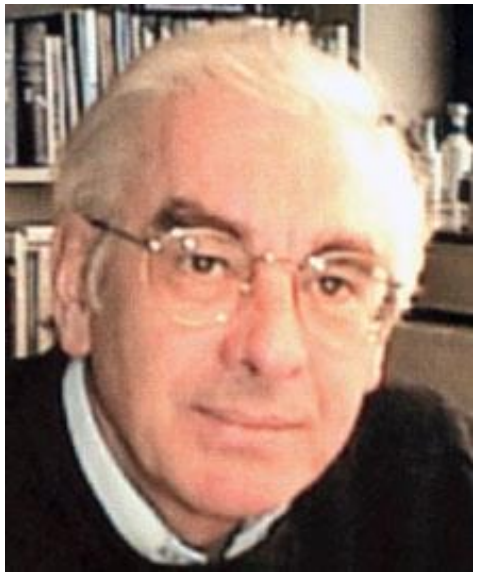
1967



Joachim Bargon, *1939

The Radical-Pair Mechanism (RPM)





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

Radical-pair mechanism (RPM)

Excited state

D*

A

hν

Ground state

D

A

Spin-correlated radic pair

Singlet state

D^+

A^-

Singlet-triplet inter-conversion

Triplet state

D^+

A^-

Recombination reaction

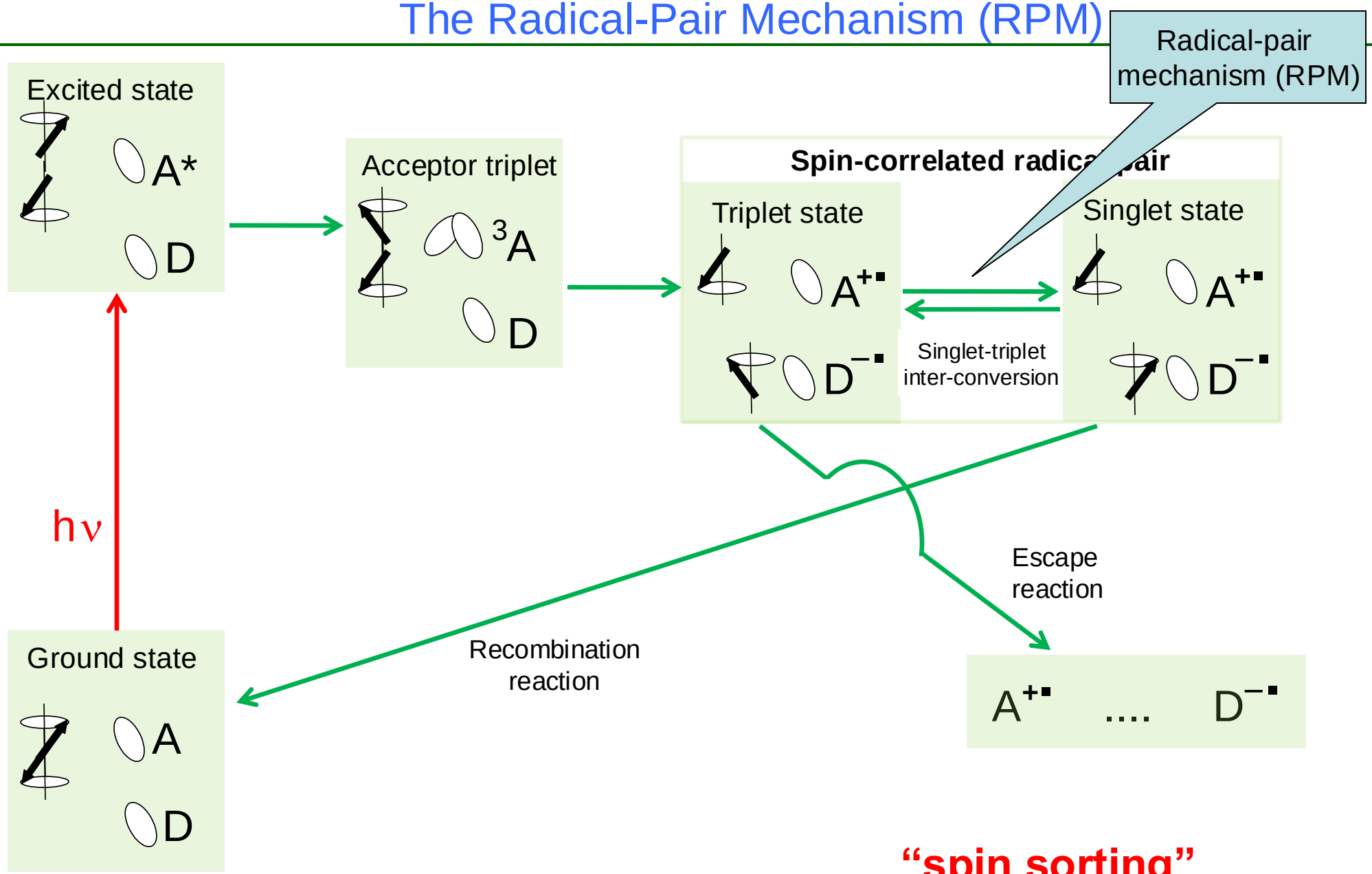
Escape reaction

D^+ .... A^-

"spin sorting"

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

The Radical-Pair Mechanism (RPM)



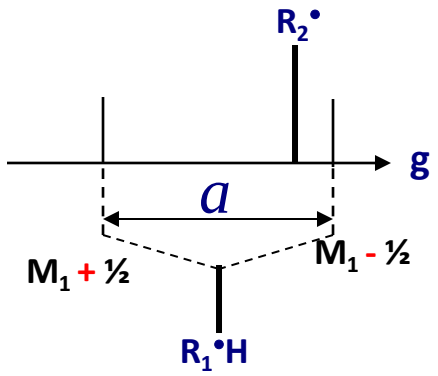
"spin sorting"

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

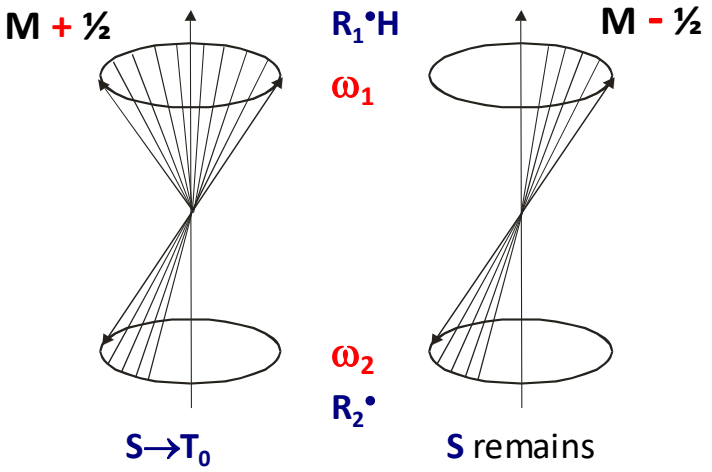
Spin-sorting

Reaction dynamics at high fields

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



hyperfine coupling constant a

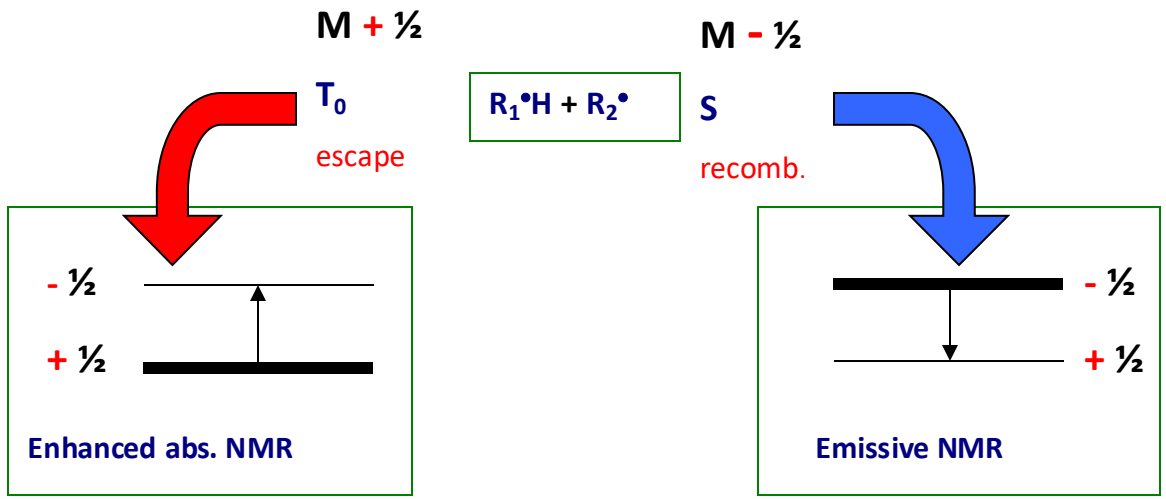


$$\Delta\omega = (g_1 - g_2)\,\frac{\beta B_0}{h}\,\pm ½\, a_H$$

Nuclear spins control reaction path

Spin-sorting

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 *classical* RPM (1969)

- was the birth of Spin-Chemistry
- is counter-intuitive
- Hamiltonian operator:

$$\mathcal{H} = \Delta\Omega\, S_Z + \omega_I\, I_Z + a_{iso}\, S_Z I_Z$$

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

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

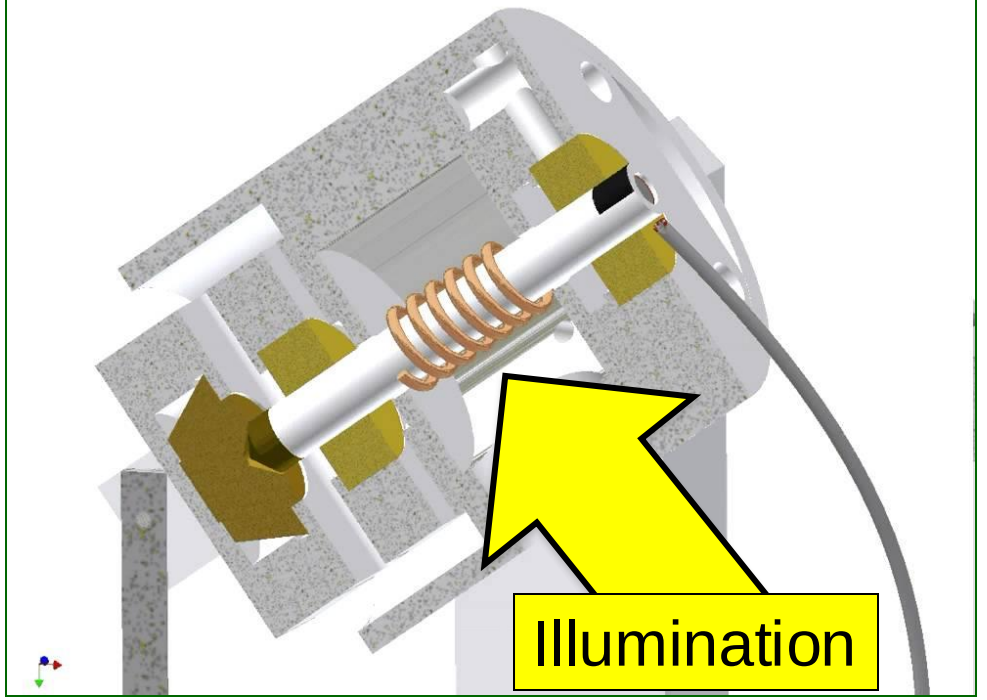
Olga B. Morozova[a, b] and Konstantin L. Ivanov*[a, b]

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

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

Photo-CIDNP MAS NMR **method**

Magic-angle spinning



The solid-state photo-CIDNP effect: 1994 discovered

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

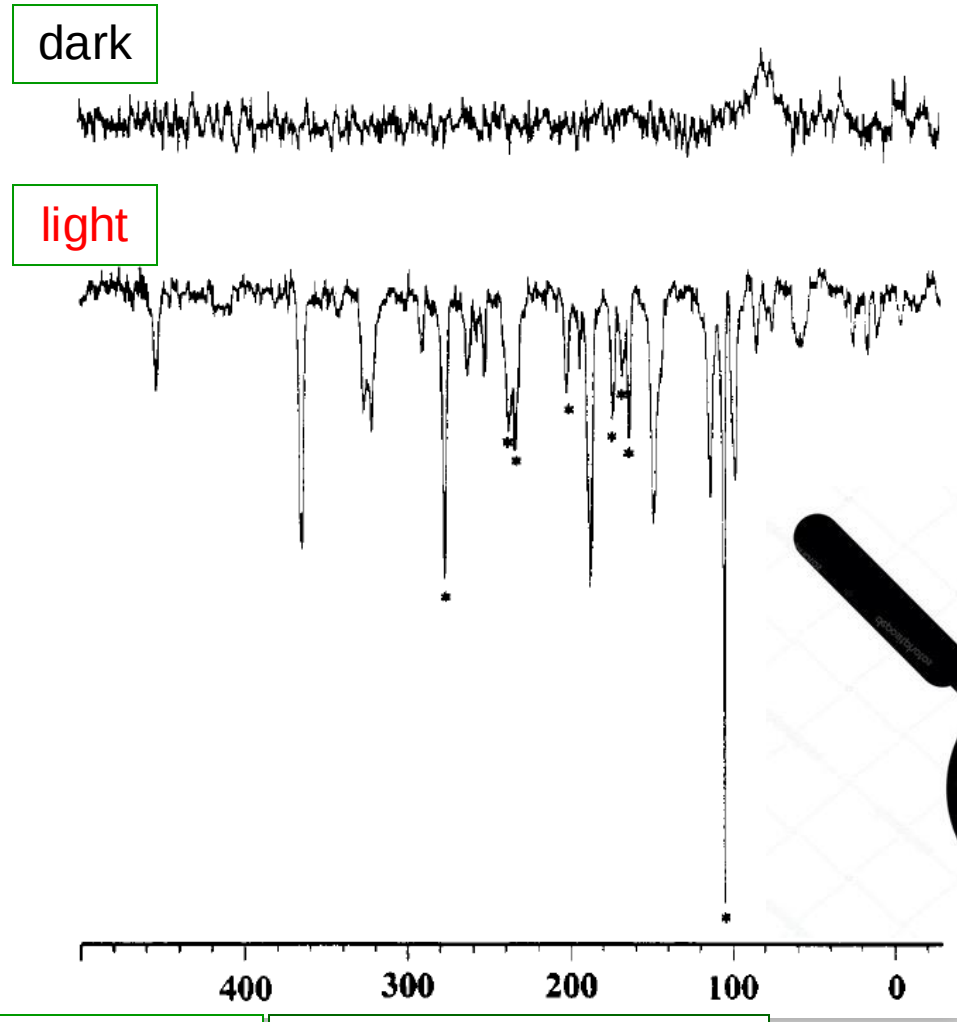
Photochemically Induced Dynamic Nuclear Polarization in the Solid-State ^{15}N Spectra of Reaction Centers from Photosynthetic Bacteria *Rhodobacter sphaeroides* R-26

Martín G. Zysmilich and Ann McDermott*

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



1994

9.4 T, 3.6 kHz MAS

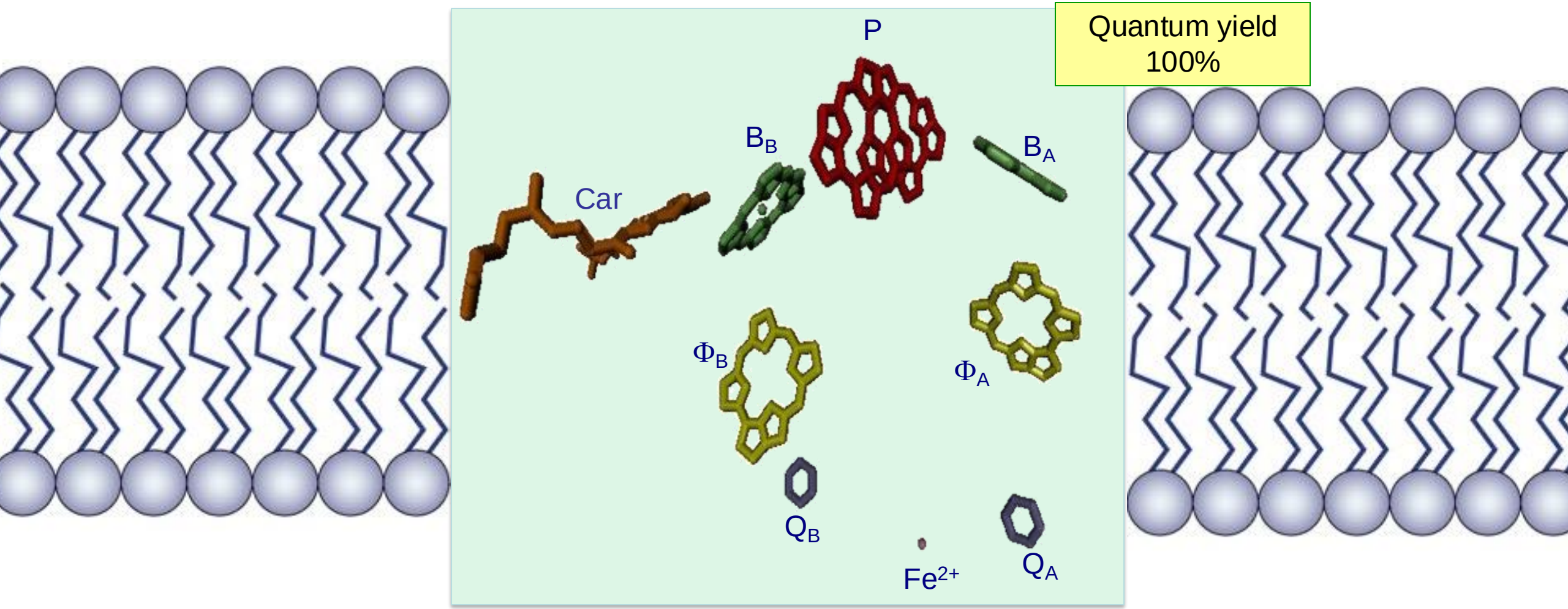
^{15}N chemical shift

The purple bacterial Reaction Center (RC) protein

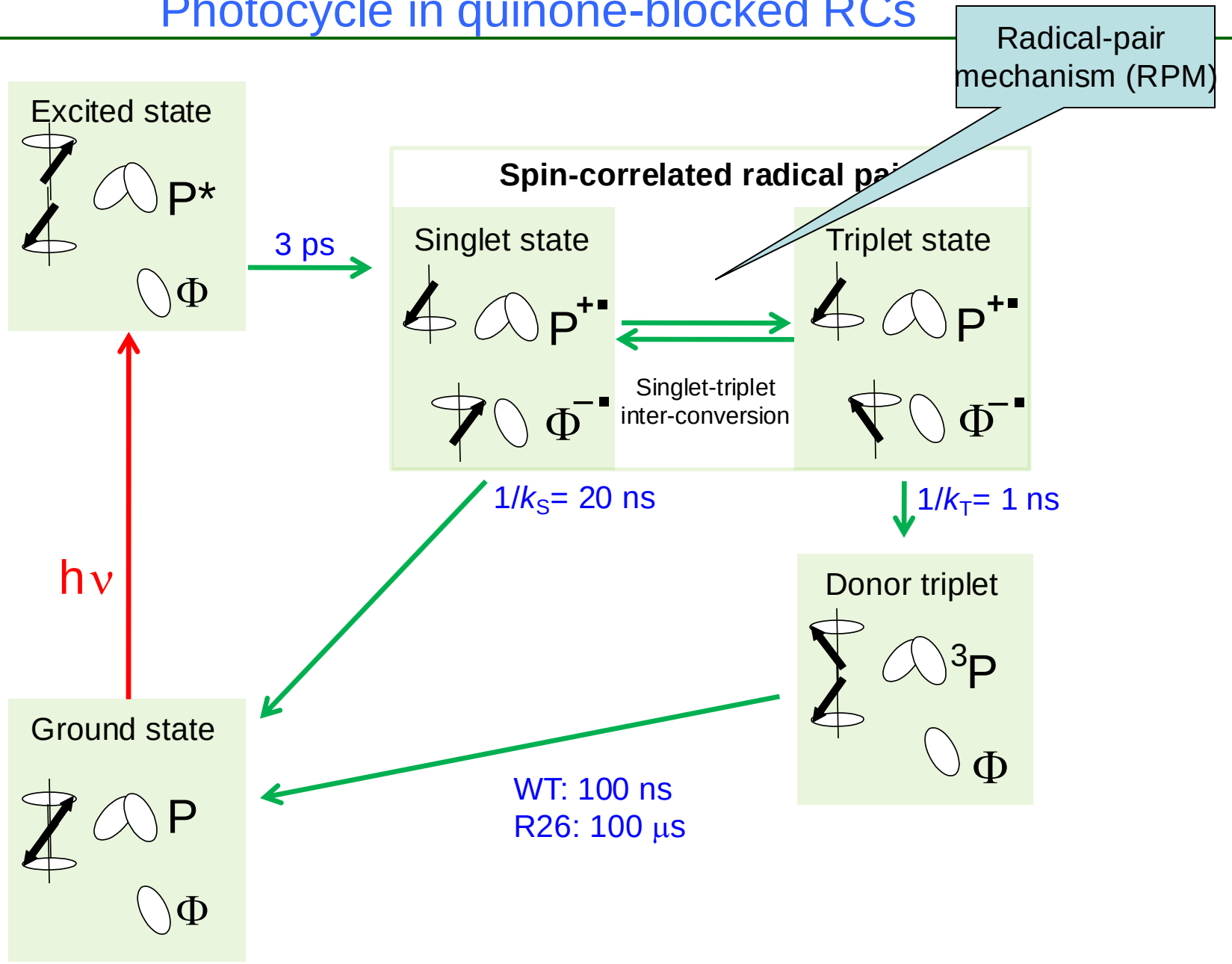
Rhodobacter sphaeroides WT
PDB entry 1M3X

Asymmetric electron transfer

Quantum yield 100%

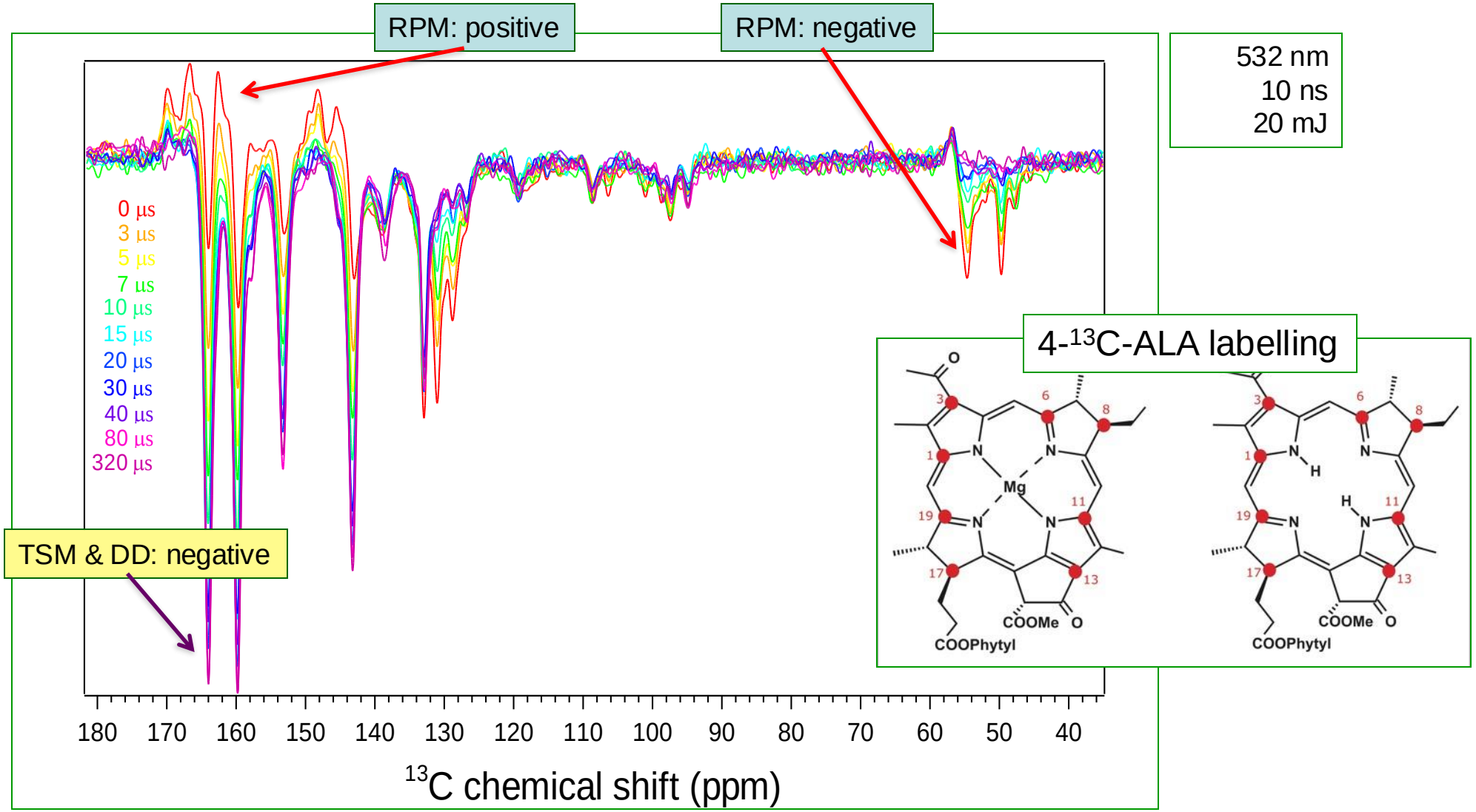


Photocycle in quinone-blocked RCs



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

Nanosecond ^{13}C photo-CIDNP MAS NMR

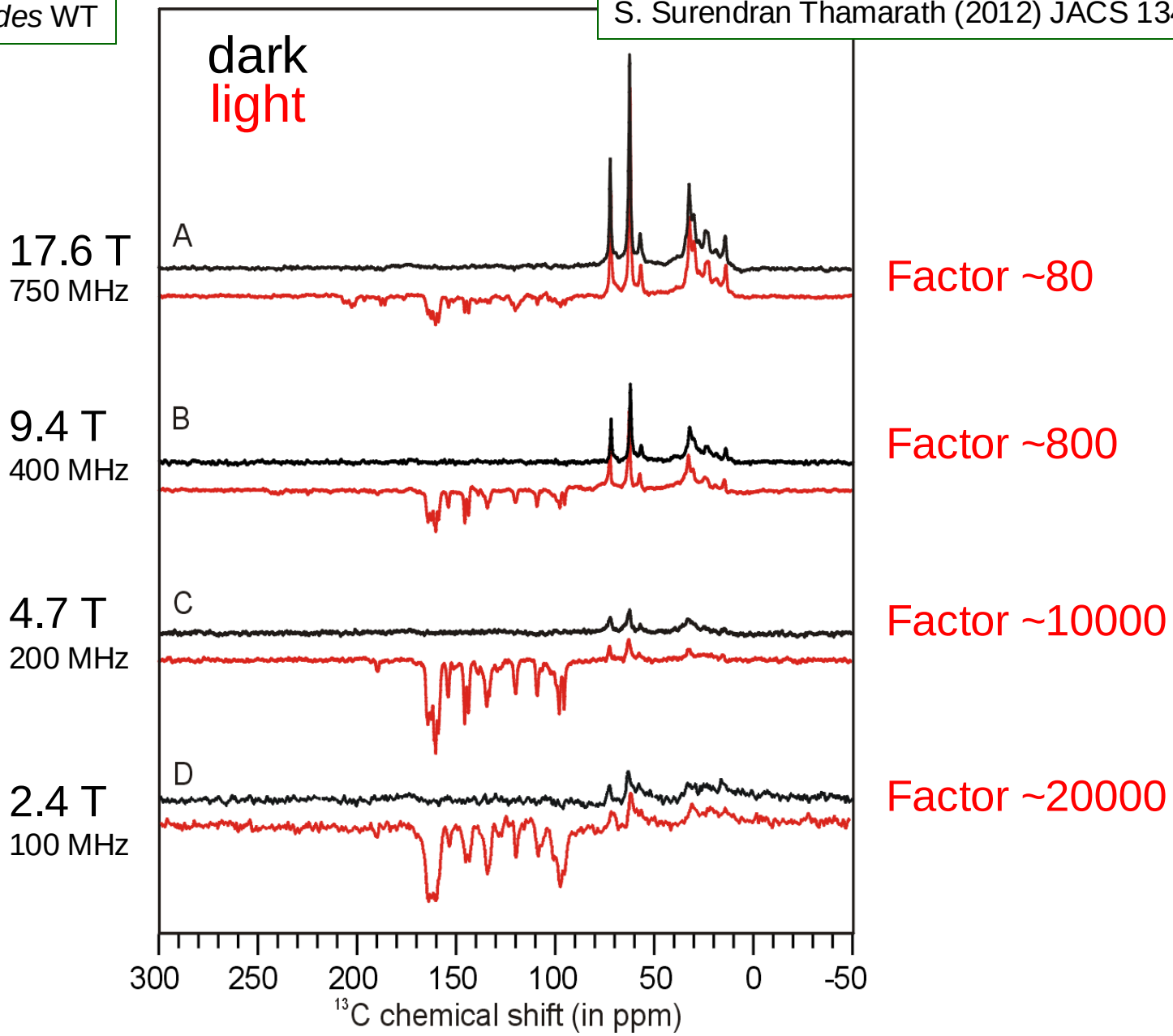


E. Daviso et al. (2008) JMR 190, 170-178; E. Daviso et al. (2009) JPCC 113, 10269-10278.

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

R. sphaeroides WT

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



Factor ~80

Factor ~800

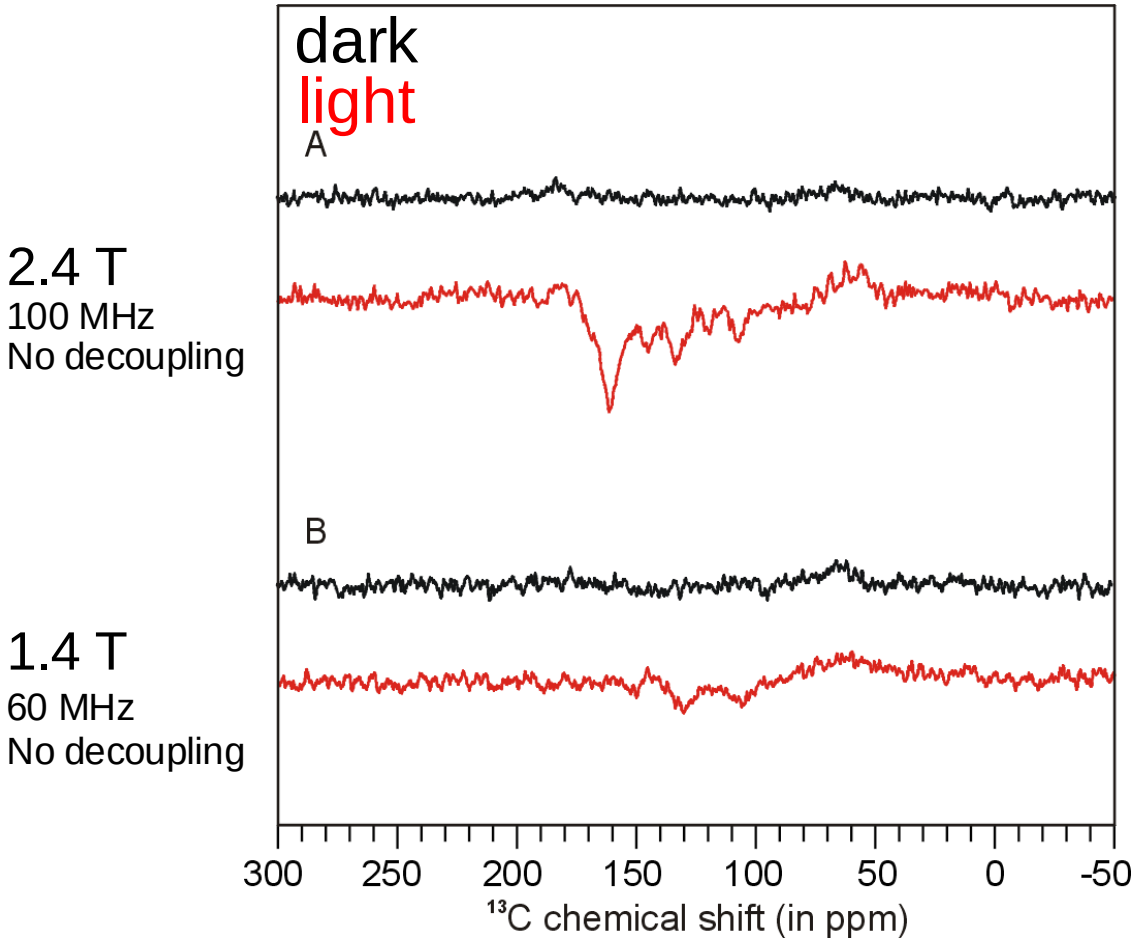
Factor ~10000

Factor ~20000

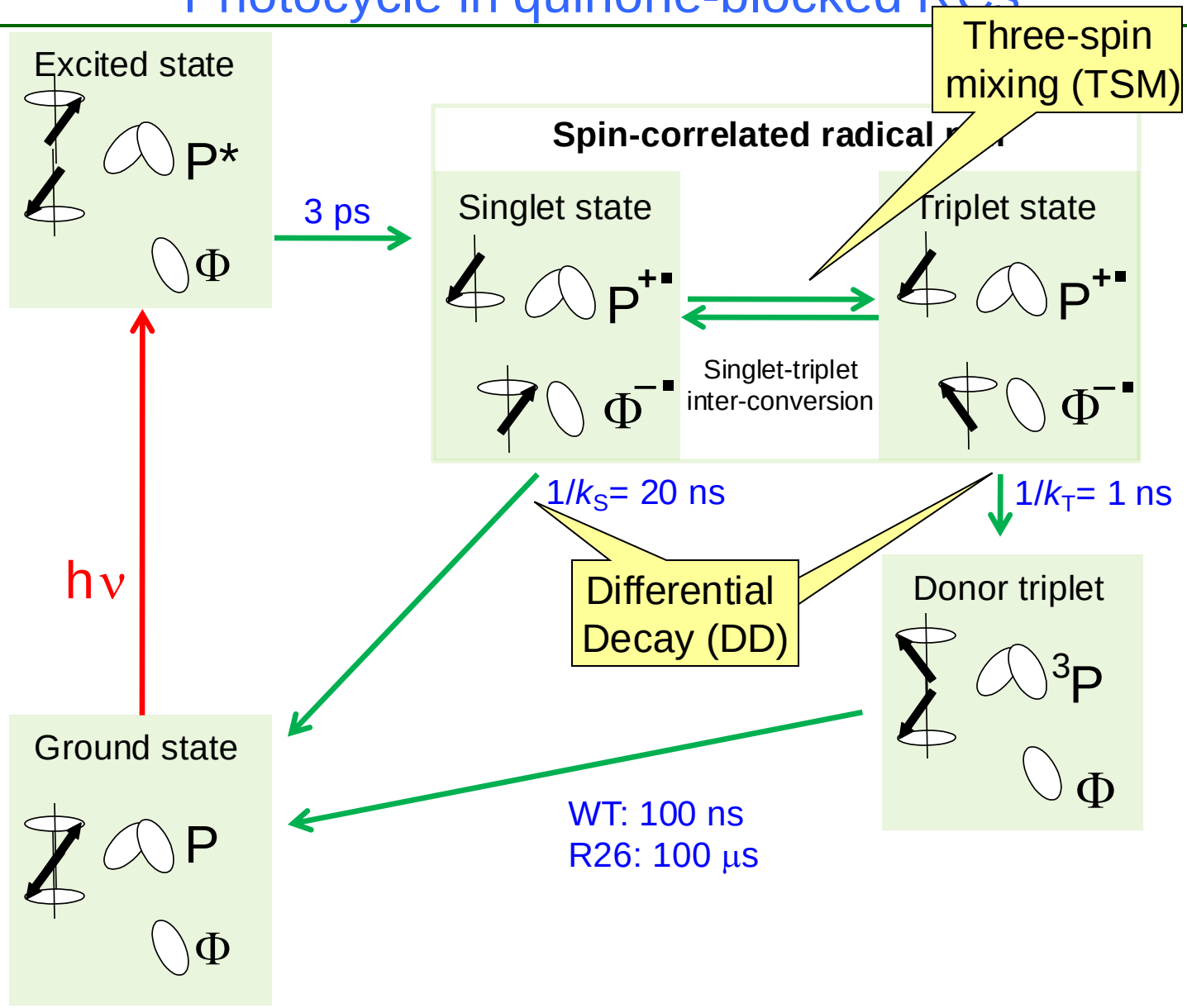
The solid-state photo-CIDNP effect: Field-dependence

R. sphaeroides WT

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



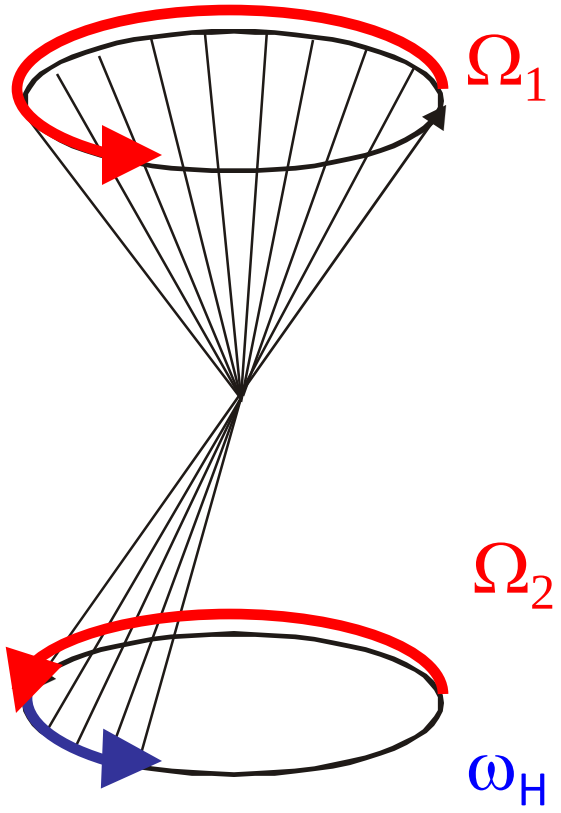
Photocycle in quinone-blocked RCs



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

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

1st condition: **Resonance**

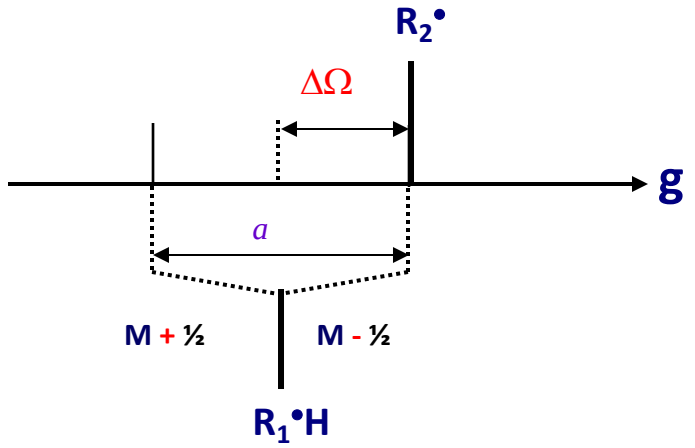


Ω = electron Zeeman frequency

ω = nuclear Zeeman frequency

2nd condition: **Hyperfine matching**

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



a = hf coupling constant

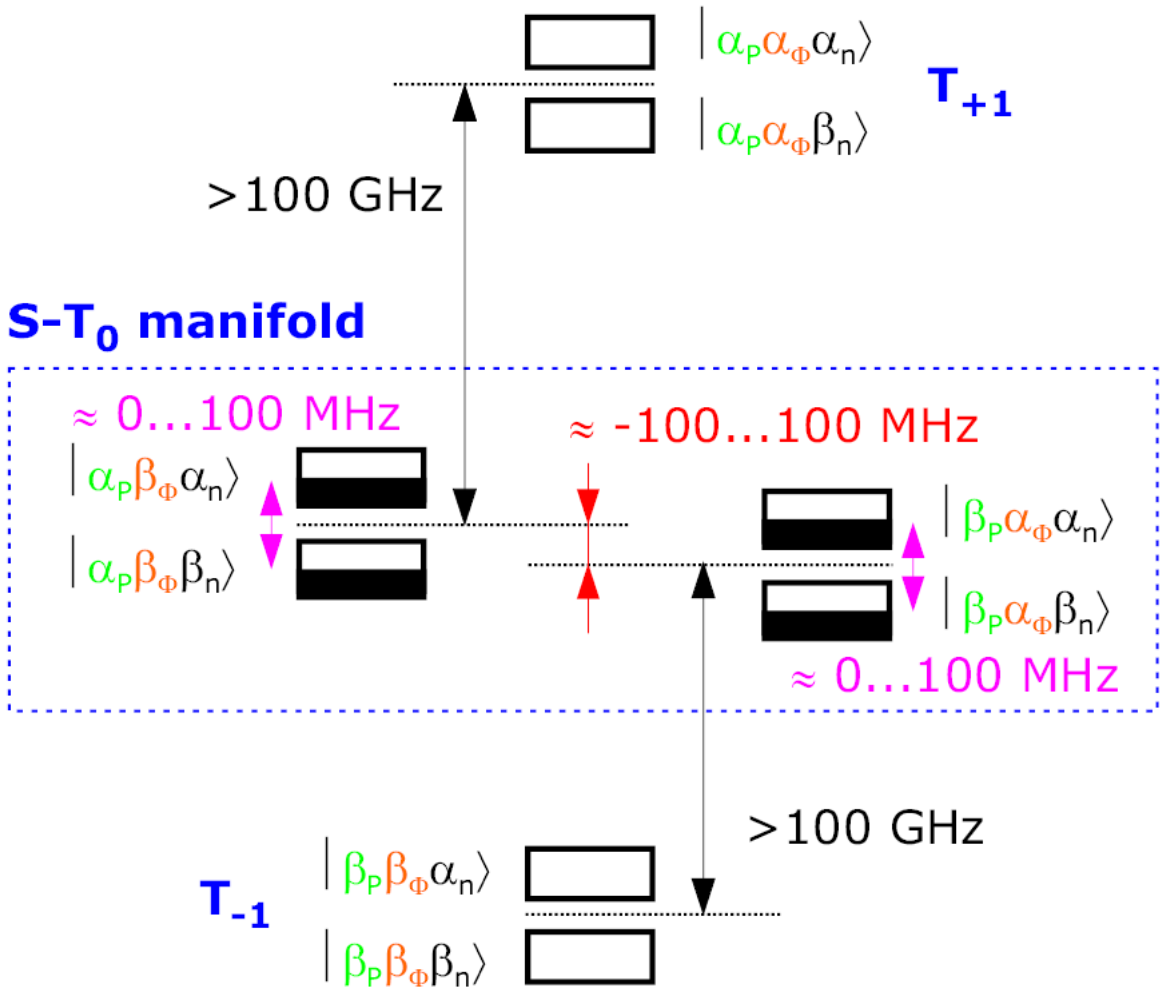
Double matching condition:

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

Jeschke (1997) J. Chem. Phys. 106, 10072

Jeschke (1998) JACS 120, 4425

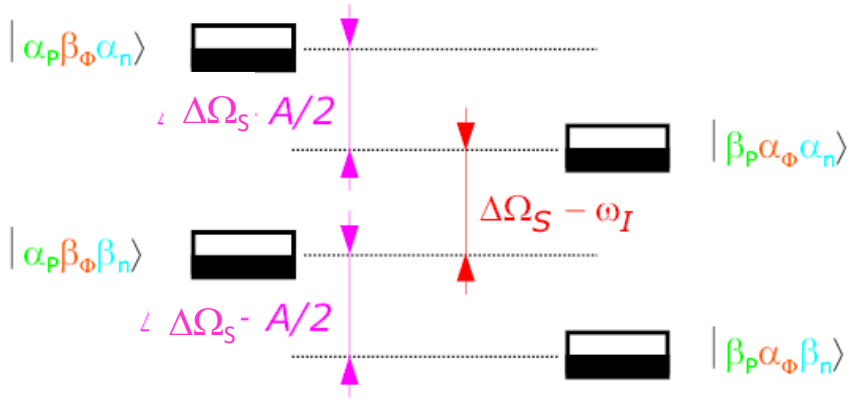
Evolution of the spin-correlated radical pair



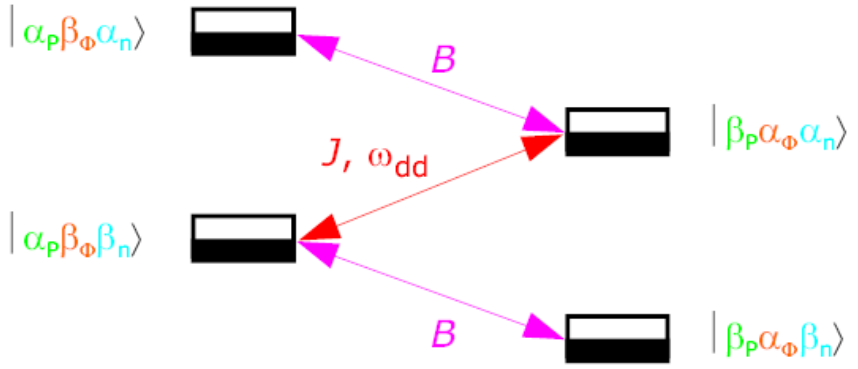
Electron-electron-nuclear three-spin mixing (TSM)

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



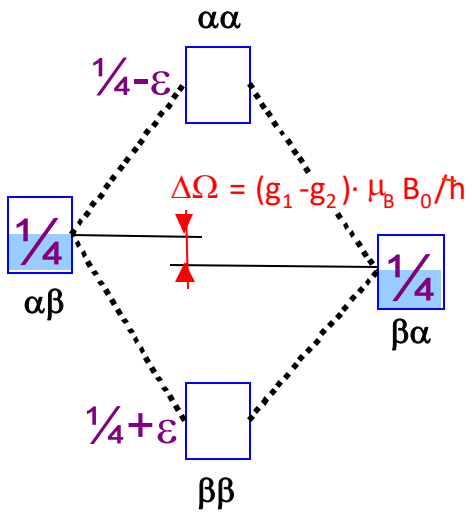
Mixing terms



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↓

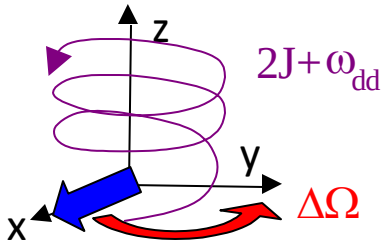
2. Spin coupling polarises the two radicals

	|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

	|αβ$I_α$>	|βα$I_β$>	|βα$I_α$>	|αβ$I_β$>
<αβ$I_α$|	+A/4	+B/4		
<βα$I_β$|	+B/4	-A/4		
<βα$I_α$|			-A/4	-B/4
<αβ$I_β$|			-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|

$P_{Nα}$↑ $Φ_{Nβ}$↓

Three-spin mixing (TSM)

Gunnar 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

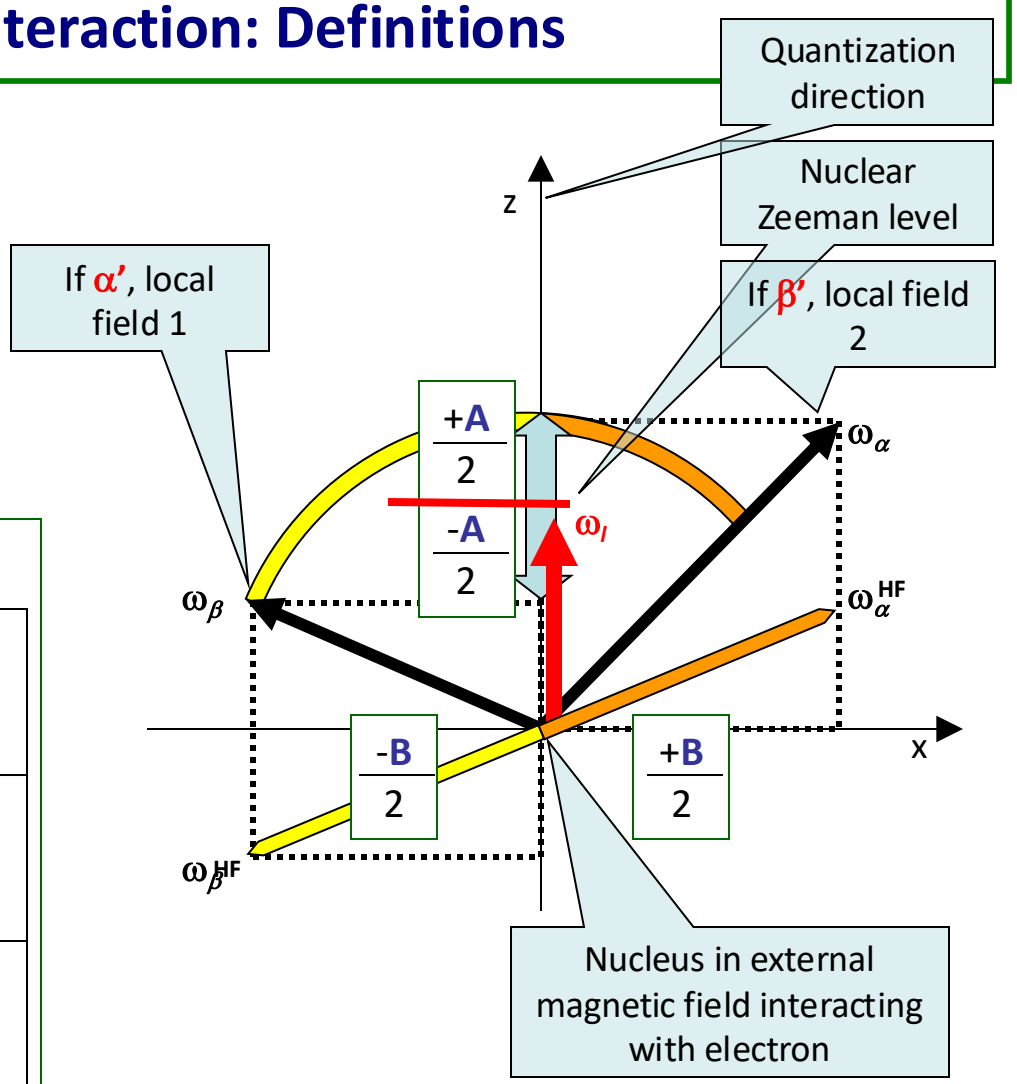
Jeschke

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

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

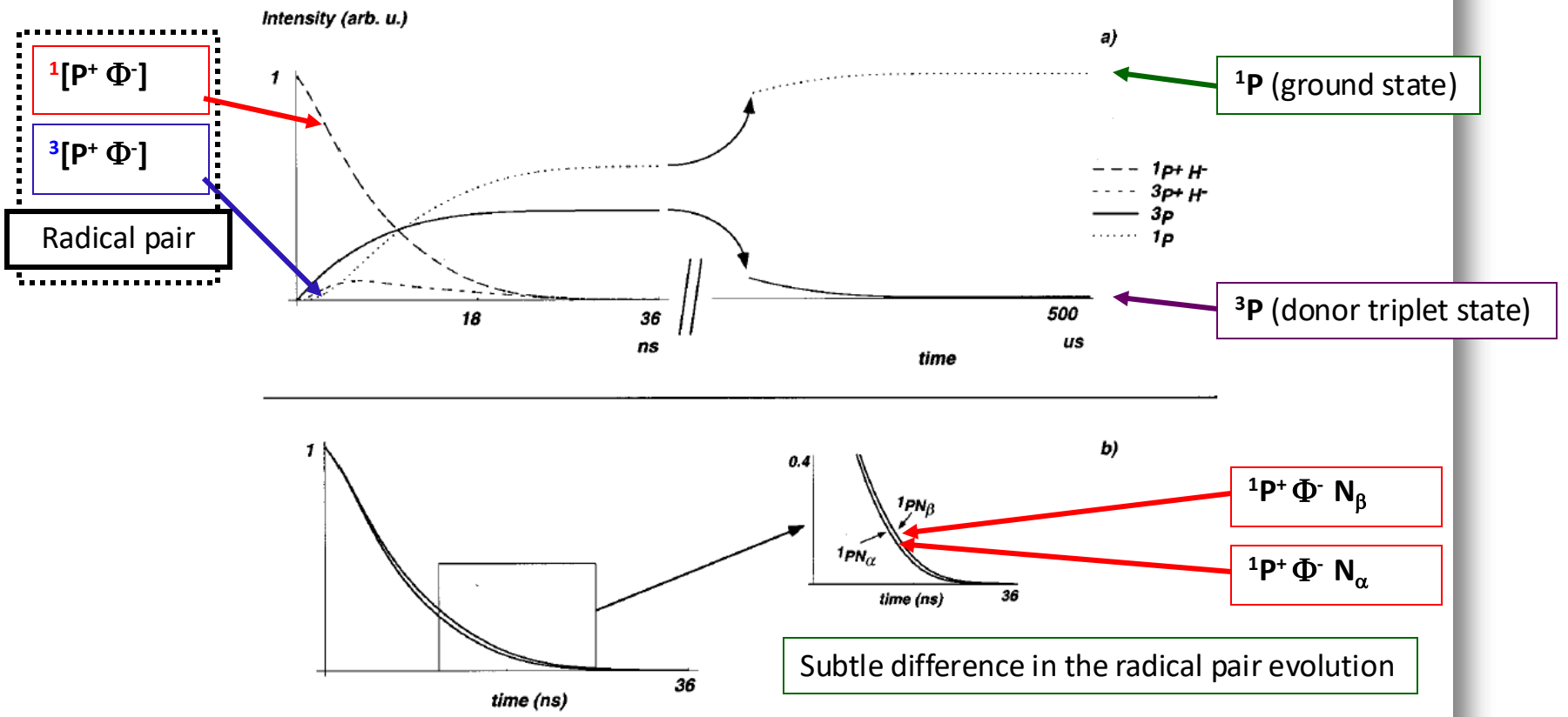


Frequency vectors
ω_I = nuclear frequency
ω_α, ω_β = effective magnetic field experienced by a nucleus caused by α' or β' electron spin

Differential decay (DD)

Photoinduced Nuclear Polarization

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



$^1[P^+ \Phi^-]$

$^3[P^+ \Phi^-]$

Radical pair

^1P (ground state)

^3P (donor triplet state)

$^1P^+ \Phi^- N_\beta$

$^1P^+ \Phi^- N_\alpha$

Subtle difference in the radical pair evolution

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

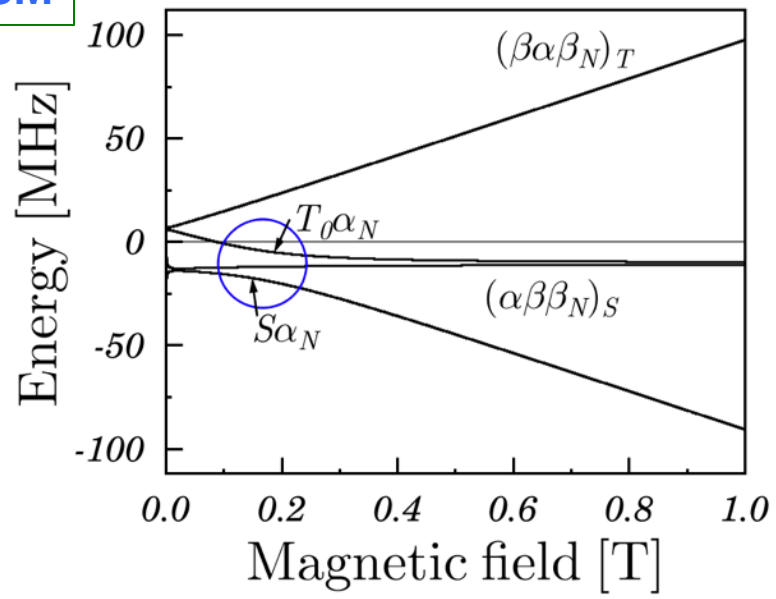


FIG. 8. Field dependence of energy levels in the TSM case; the relevant LAC is indicated. Parameters used in calculation: $g_1 = 2$ and $g_2 = 2.0067$; the nucleus is a proton; $A = 1$ mT; $d = 0.5$ mT; $b = 0, k_S = k_T = 0.1$ ns^{-1}, $k_{sc} = 0.002$ ns^{-1}. The notation $(\alpha\beta\beta_N)_S$ 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

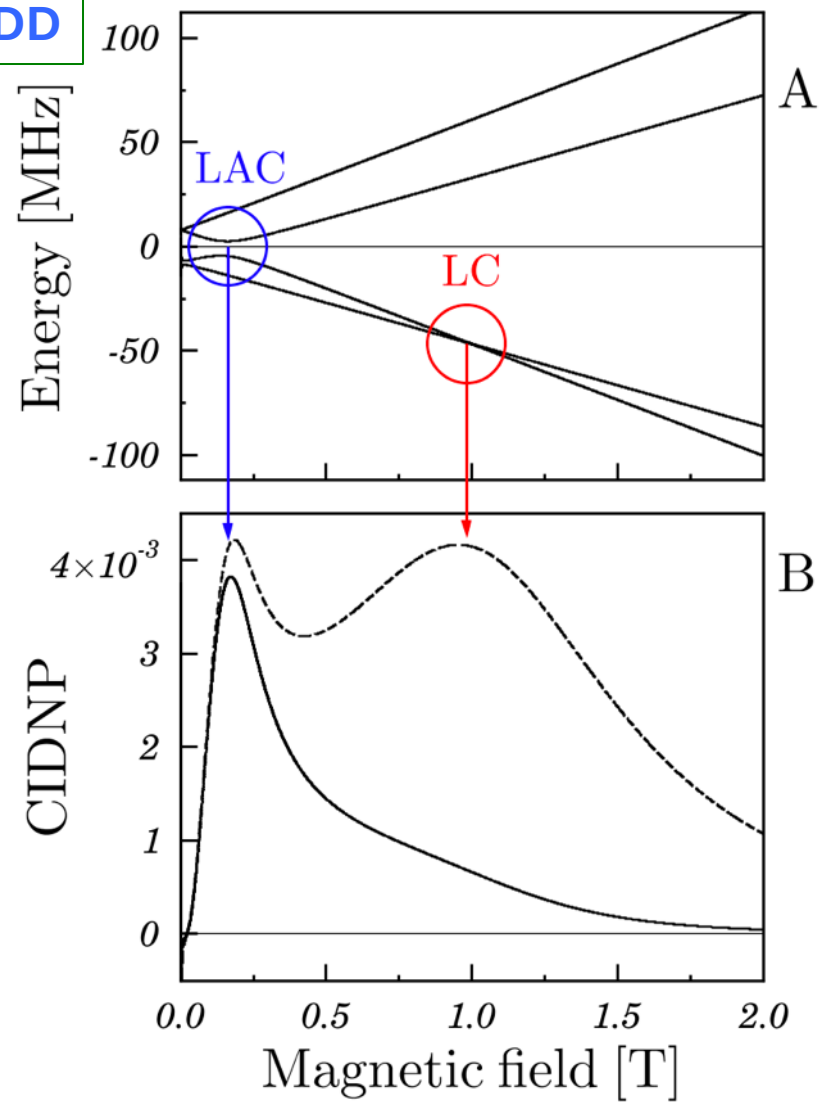
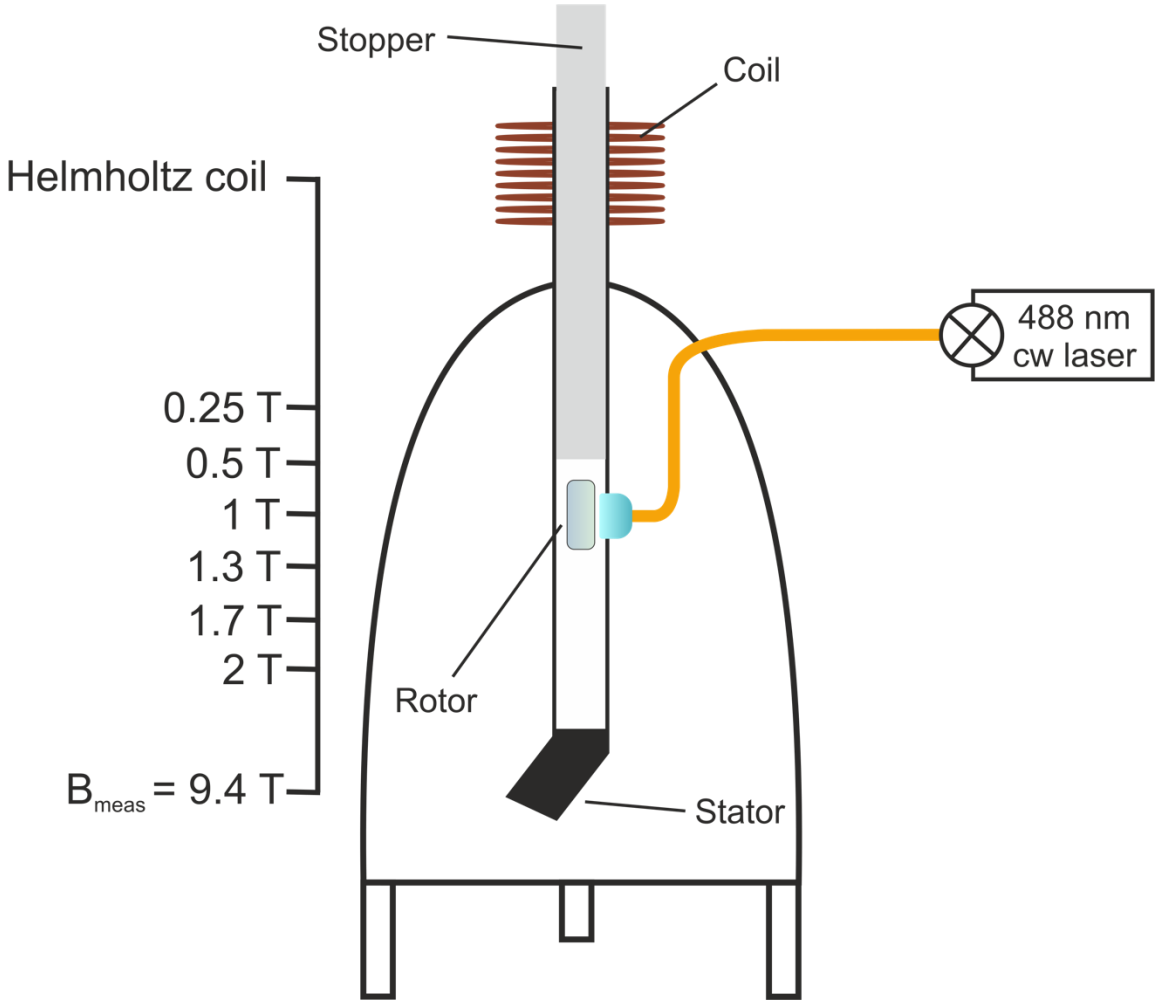


FIG. 5. Field dependence of energy levels (a) and field dependence of CIDNP (b). Parameters used in calculation: $g_1 = 2$ and $g_2 = 2.001$; the nucleus is a proton; $A = 1$ mT; $d = 0$; $k_S = 2k_T = 0.08$ ns^{-1}, $b = 0.5$ mT, $k_{sc} = 0.002$ ns^{-1} (dashed line), $k_{sc} = 0$ (solid line); the 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 Shuttle MAS NMR system



- Illumination at the desired field strength
- Measurement at high field under MAS
- Shuttle cycle takes $t_{illumination}$ + 8 sec

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

R. sphaeroides WT

• Enhancement curve is very broad

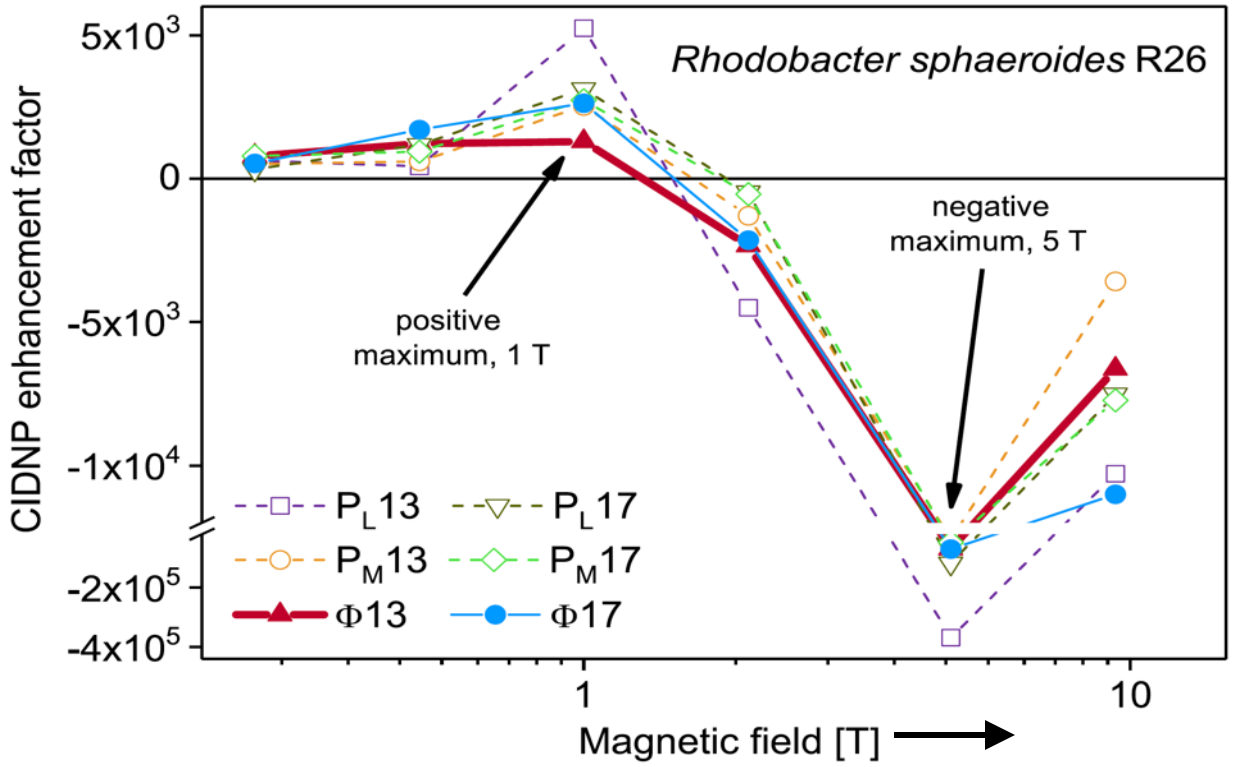


FIG. 1. Experimental CIDNP field dependence obtained for the photosynthetic reaction center of the purple bacterium *Rhodobacter sphaeroides* R26. The field dependence of the **C13Φ** nucleus is highlighted. See text for further explanation.

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

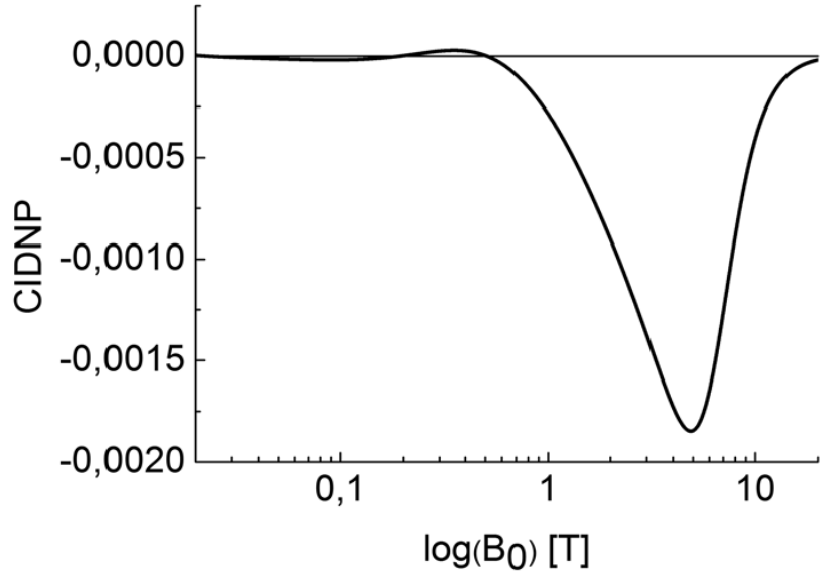
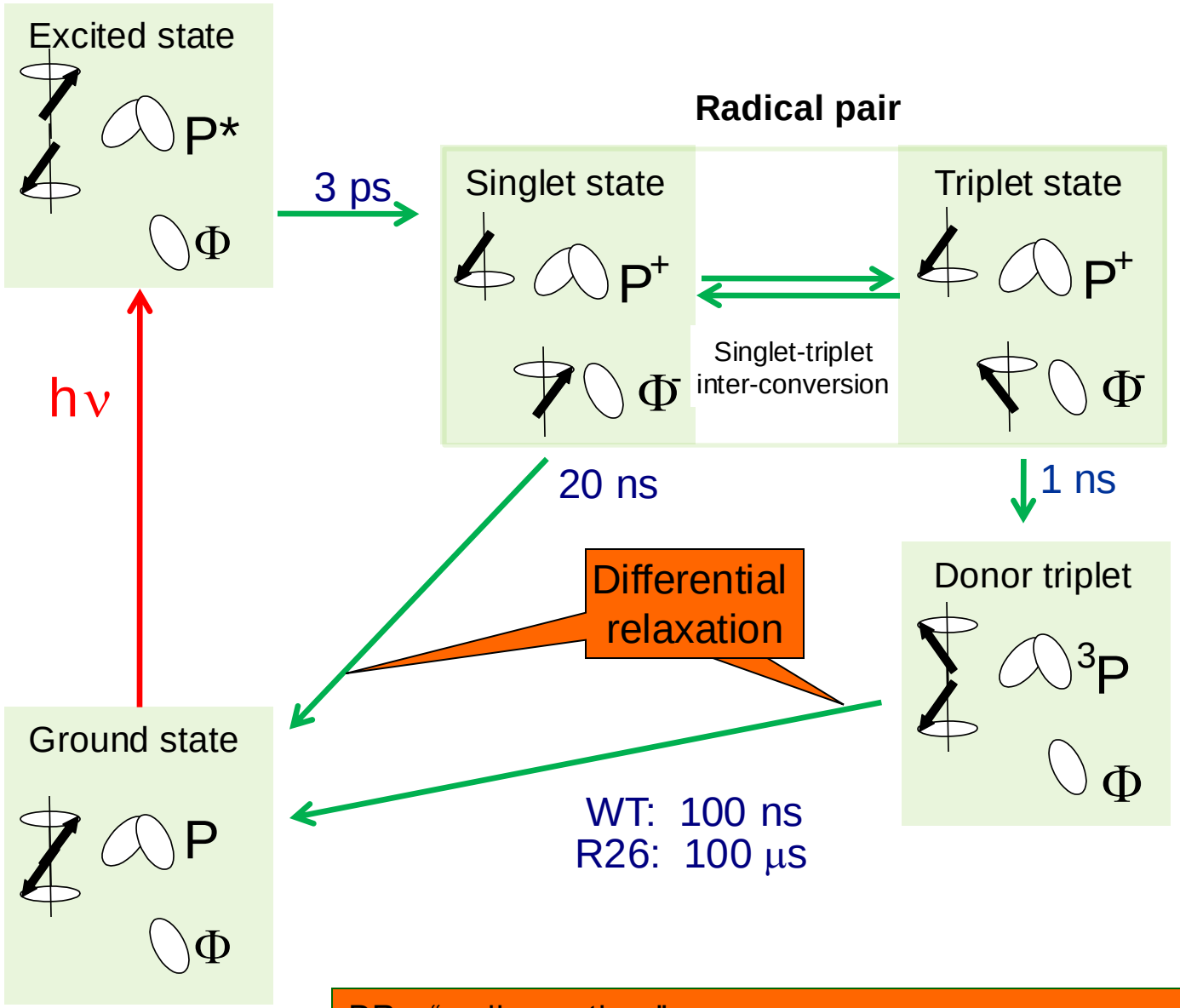


FIG. 8. CIDNP field dependence of a photosynthetic reaction center protein of *Rhodobacter sphaeroides* averaged over all possible orientations. Simulation parameters: nucleus is the ^{13}C nucleus **C13Φ**; k_S = 0.015 ns^{-1}, k_T = 0.4 ns^{-1}, ξ = 0.98.

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.

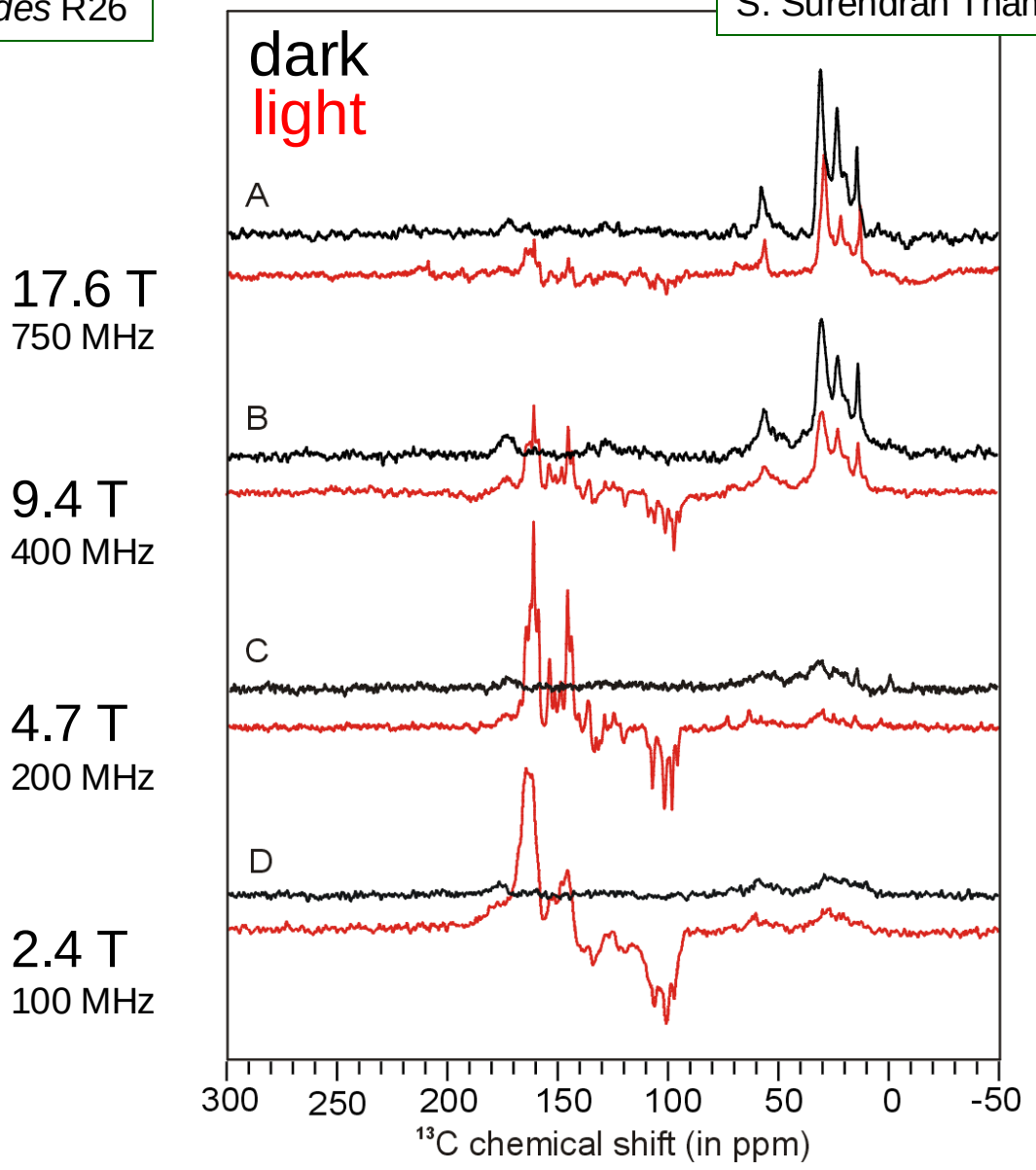
The solid-state photo-CIDNP effect

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

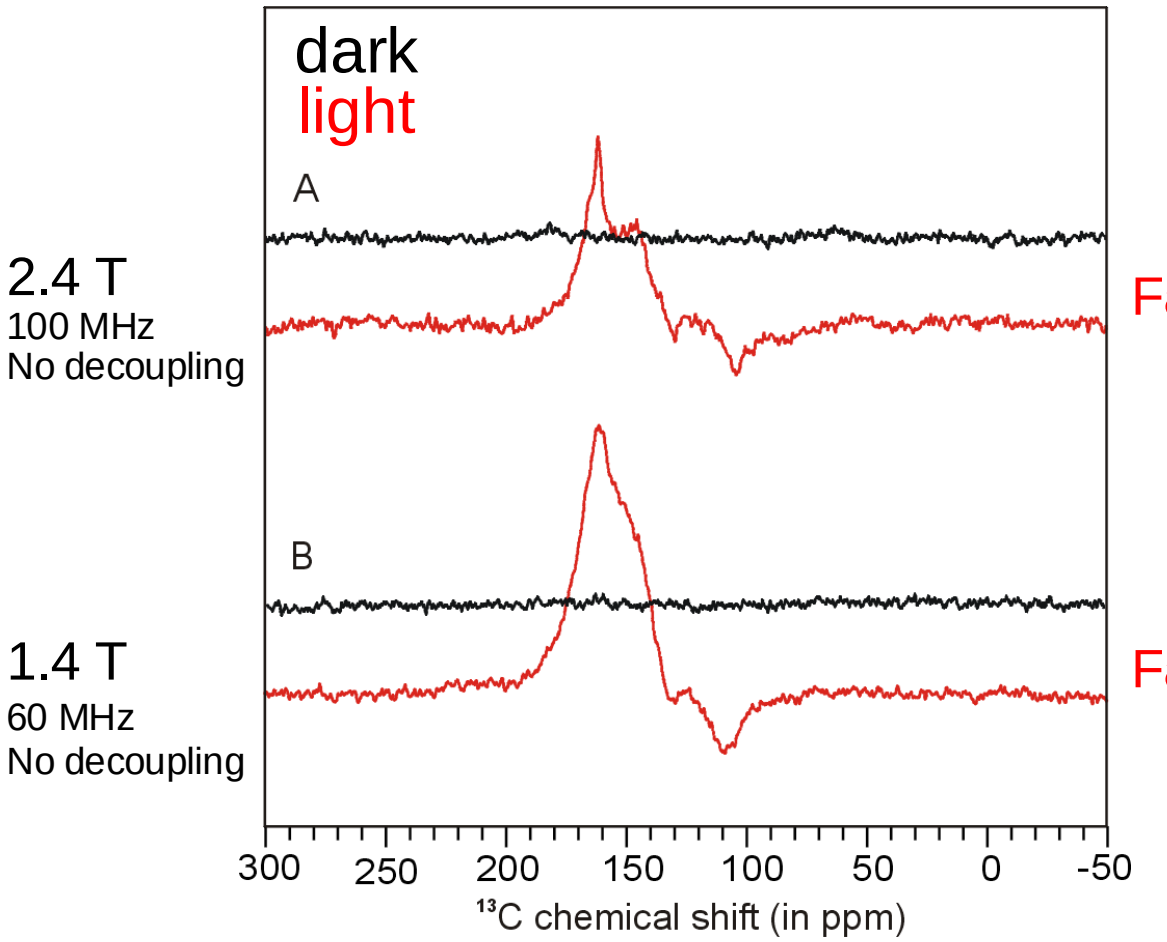
The solid-state photo-CIDNP effect

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

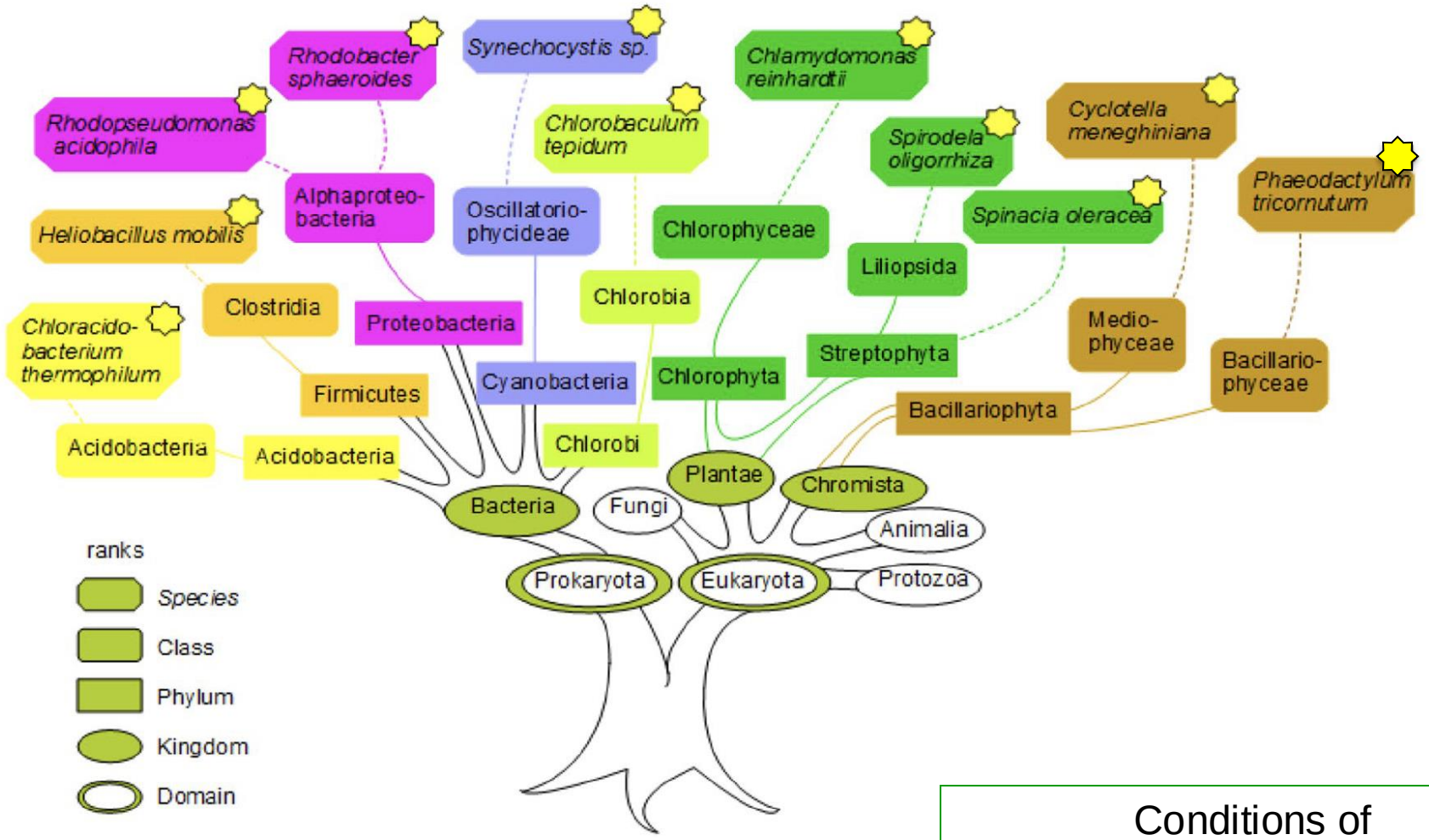
Bela Bode et al. (2013) “The solid-state photo-CIDNP effect and its analytical application”, In: Hyperpolarization methods in NMR spectroscopy (Lars Kuhn, ed.) Springer, pp. 105-121 (Review).

Part 1 Photosynthetic Reaction Centers

Part 2 Flavoproteins

Part 3 Artificial electron-transfer diads

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

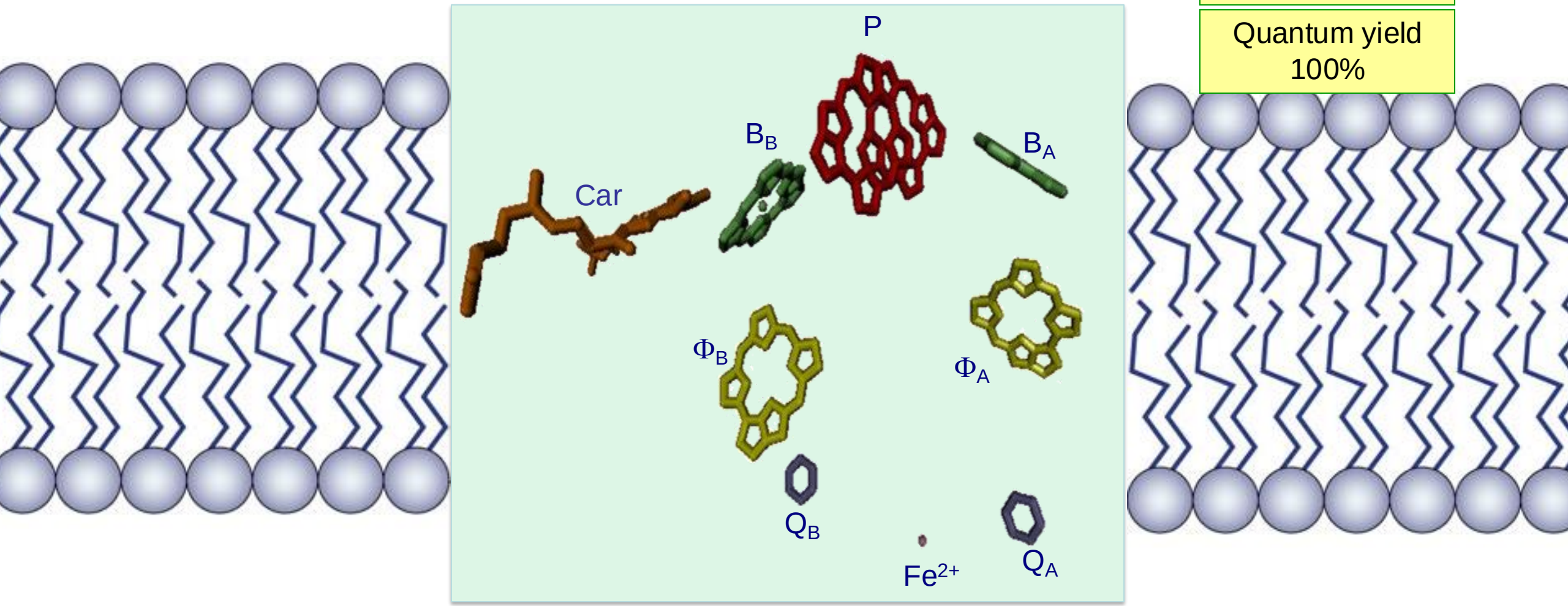
Part 1 Photosynthetic Reaction Centers

Analytical applications:
Purple bacterial RC
of *Rhodobacter sphaeroides*.

The purple bacterial Reaction Center (RC) protein

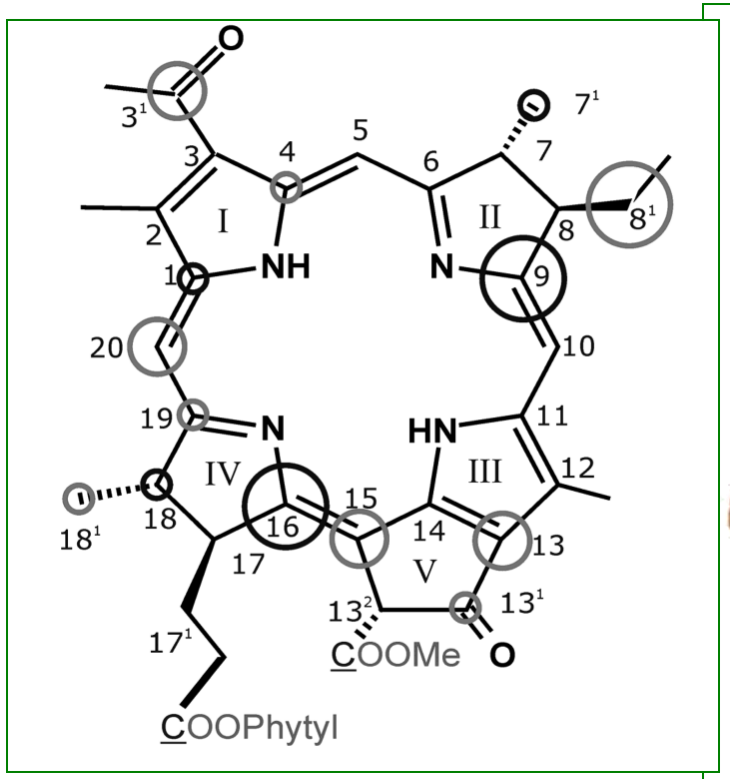
Asymmetric electron transfer

Quantum yield 100%

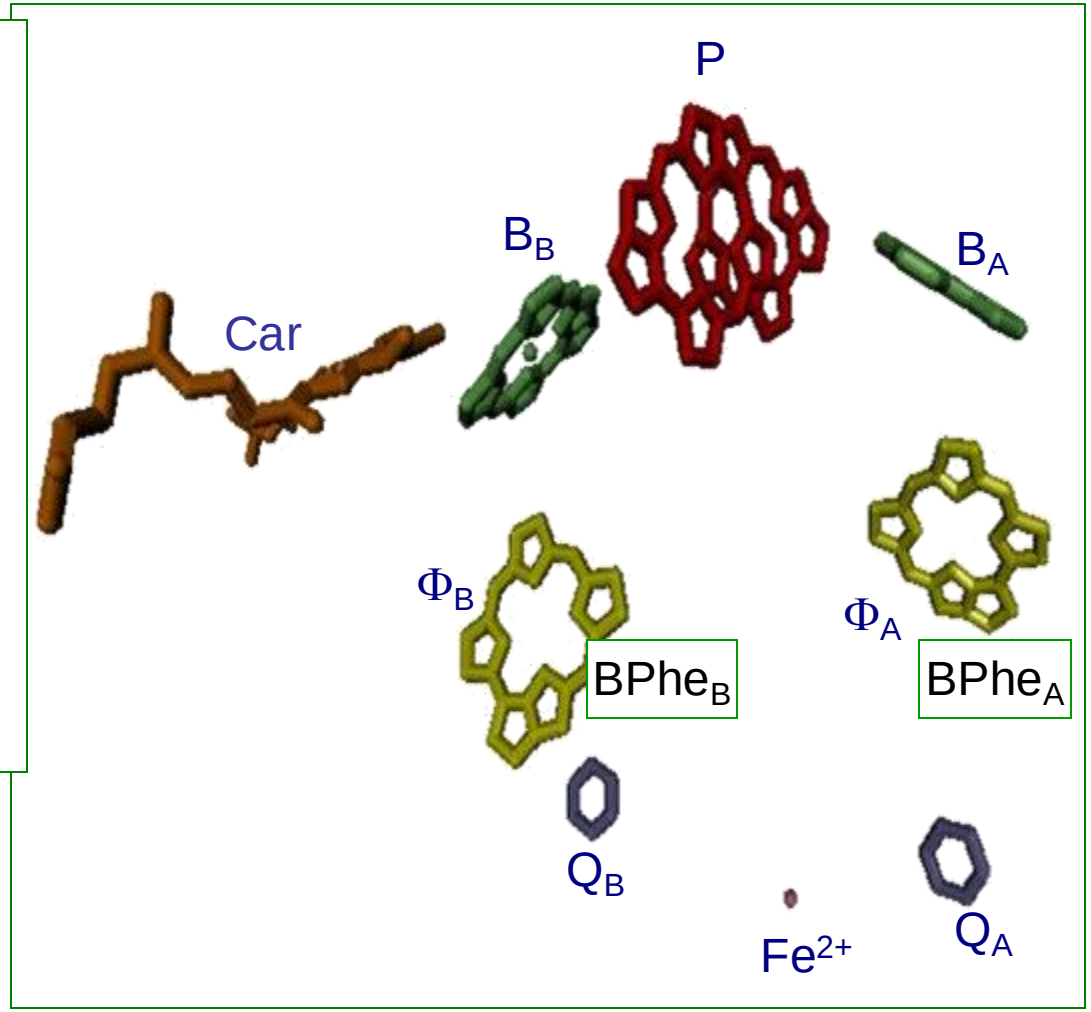


Rhodobacter sphaeroides WT
PDB entry 1M3X

Acceptor BPhe is not specially tuned



O = +1 ppm O = -1 ppm

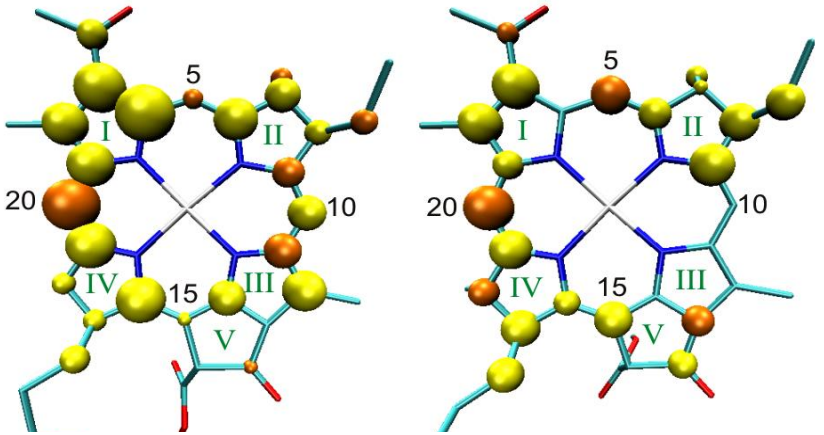


- The chemical shifts of the $BPhe_A$ are normal.

Sai Sankar Gupta et al. (2013) JPCB 117, 3287.

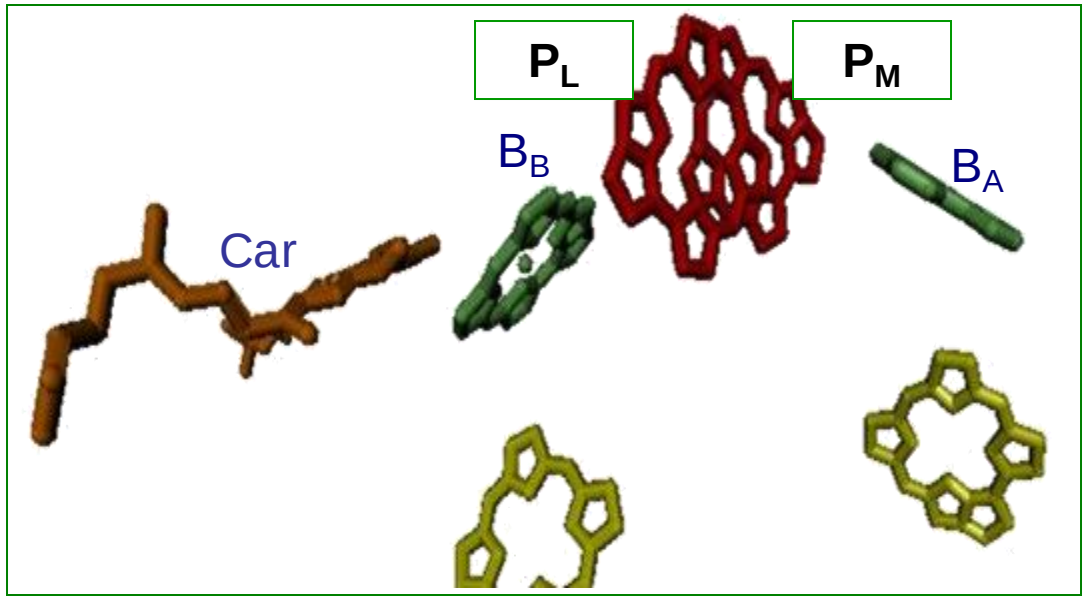
Electronic structure of the Special Pair

Relative electron density distribution



Experiment

- Predominantly upfield shifts: Excess of negative charge: $P_L^{\delta-}$ $P_M^{\varepsilon-}$
- Asymmetric in ground state
- P_L is special
- Electron density is concentrated in overlapping region of special pair



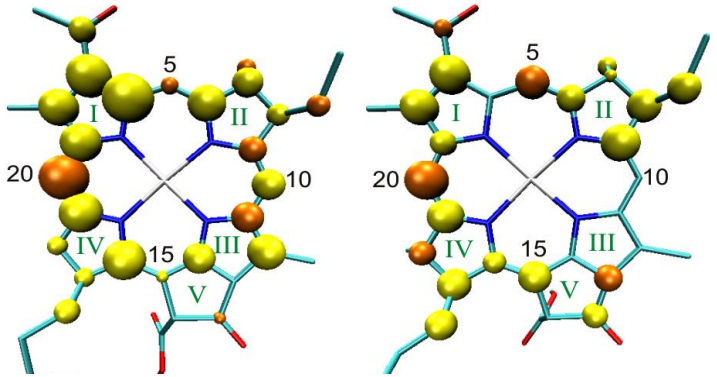
Daviso et al. PNAS (2009) 106, 22281.

Electronic structure of the Special Pair

P_L	P_M

Relative electron density distribution

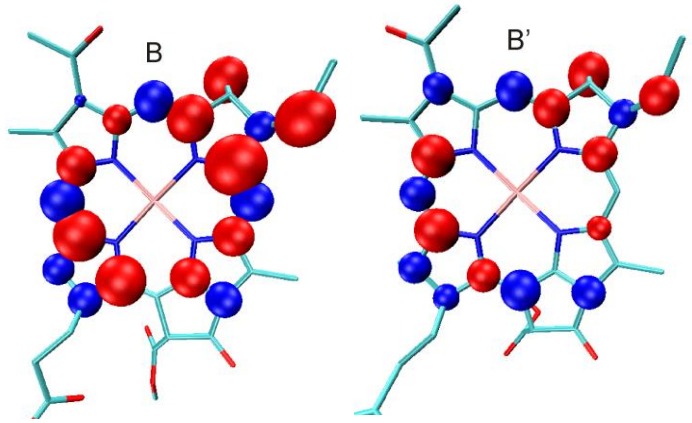
(Ground state)



Experiment

Relative electron ***spin*** density distribution

(Radical cation)



Experiment

- Asymmetric in radical cation state (3:2)
- Overlapping region of special pair is emptied → electric polarization effect

Daviso et al. PNAS (2009) 106, 22281.

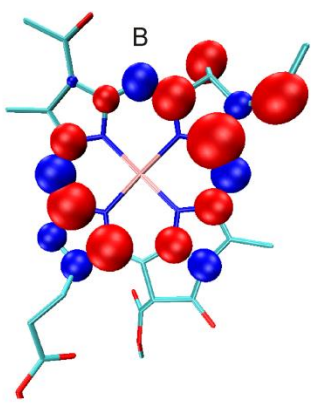
Electronic structure of the Special Pair

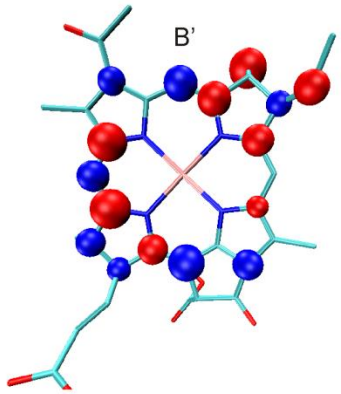
P_L | P_M

- Electronic properties are inherent.

Relative electron ***spin*** density distribution

(Radical cation)

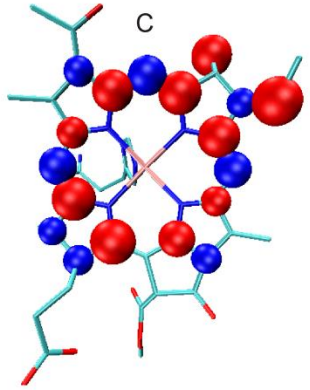


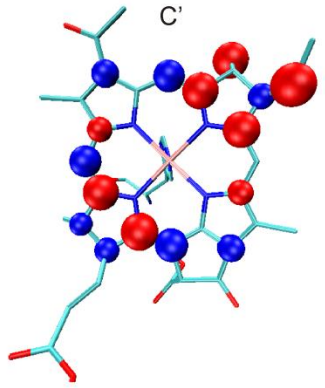


Experiment

Relative electron ***spin*** density distribution

(Radical cation)





Calculation

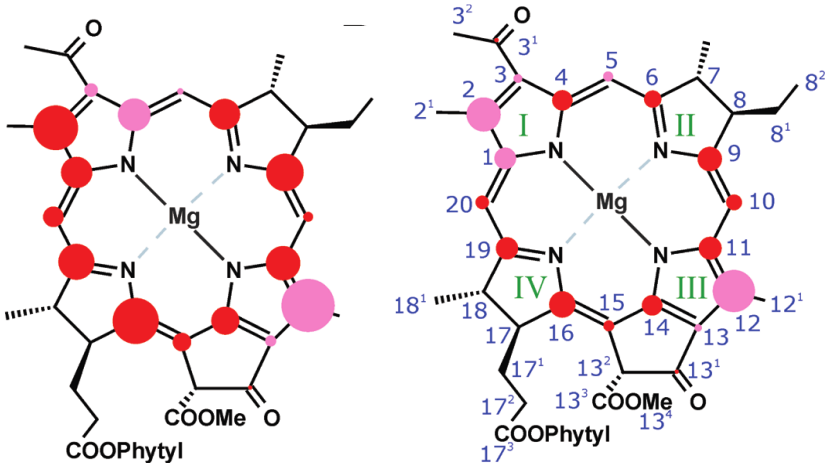
Daviso et al. PNAS (2009) 106, 22281.

Electronic structure of the Special Pair

P_L	P_M

Relative electron ***spin*** density distribution

(Donor triplet state ^3P)



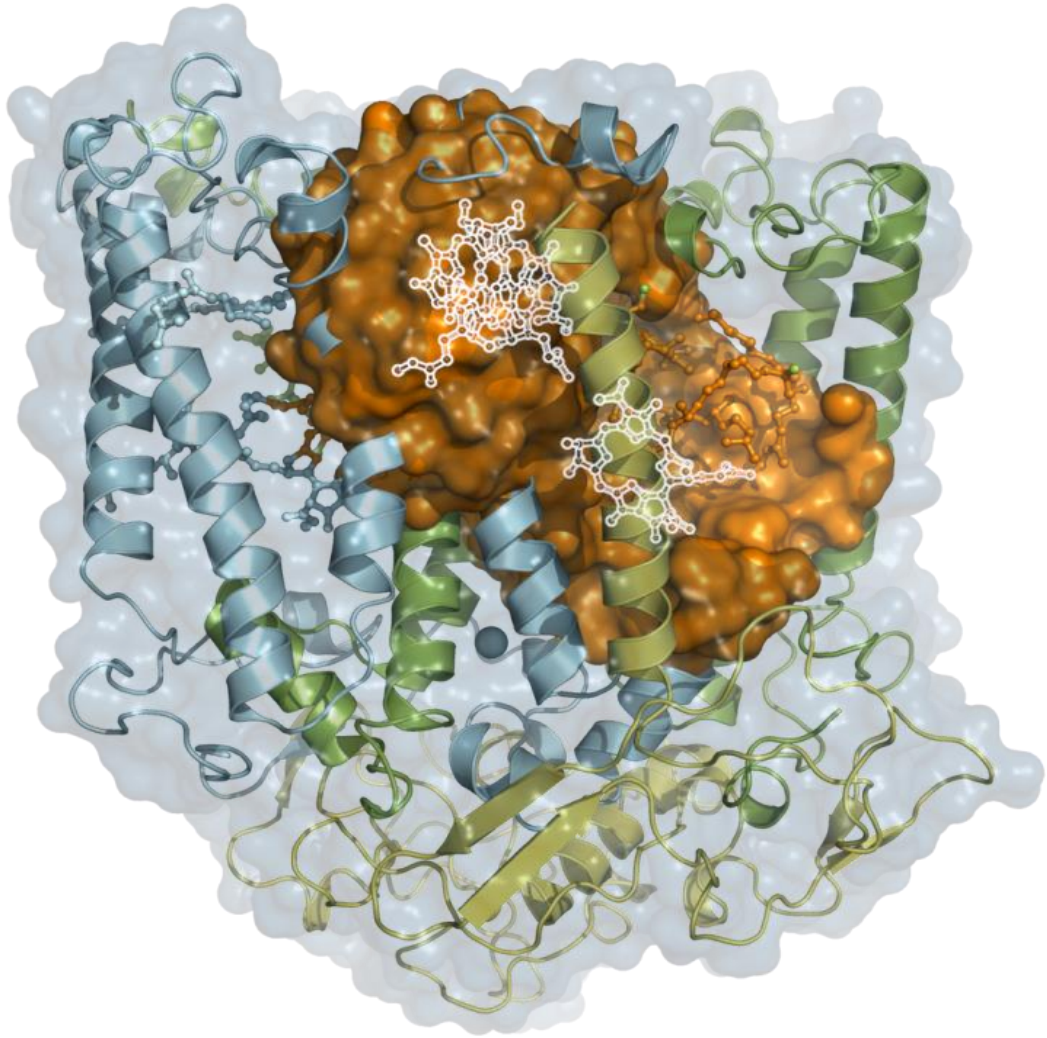
Red: Exp. & Calc.

Pink: Calc.

- ^3P electron spin density: Symmetrically distributed
- LUMO shifted towards P_M

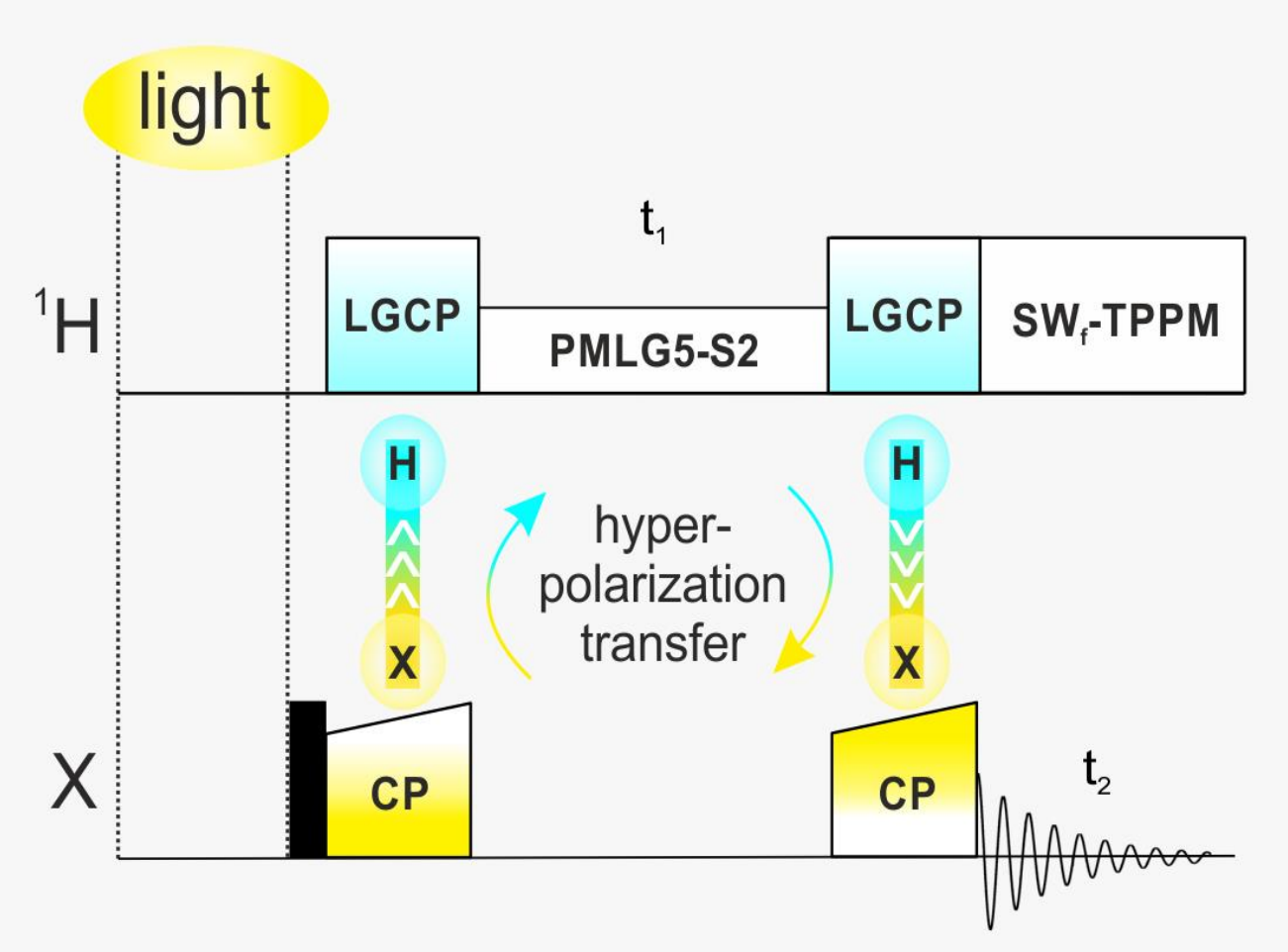
Surendran-Thamarath et al. JACS (2012) 134, 5921.

“Spin-Torch” X→^{1}H→X



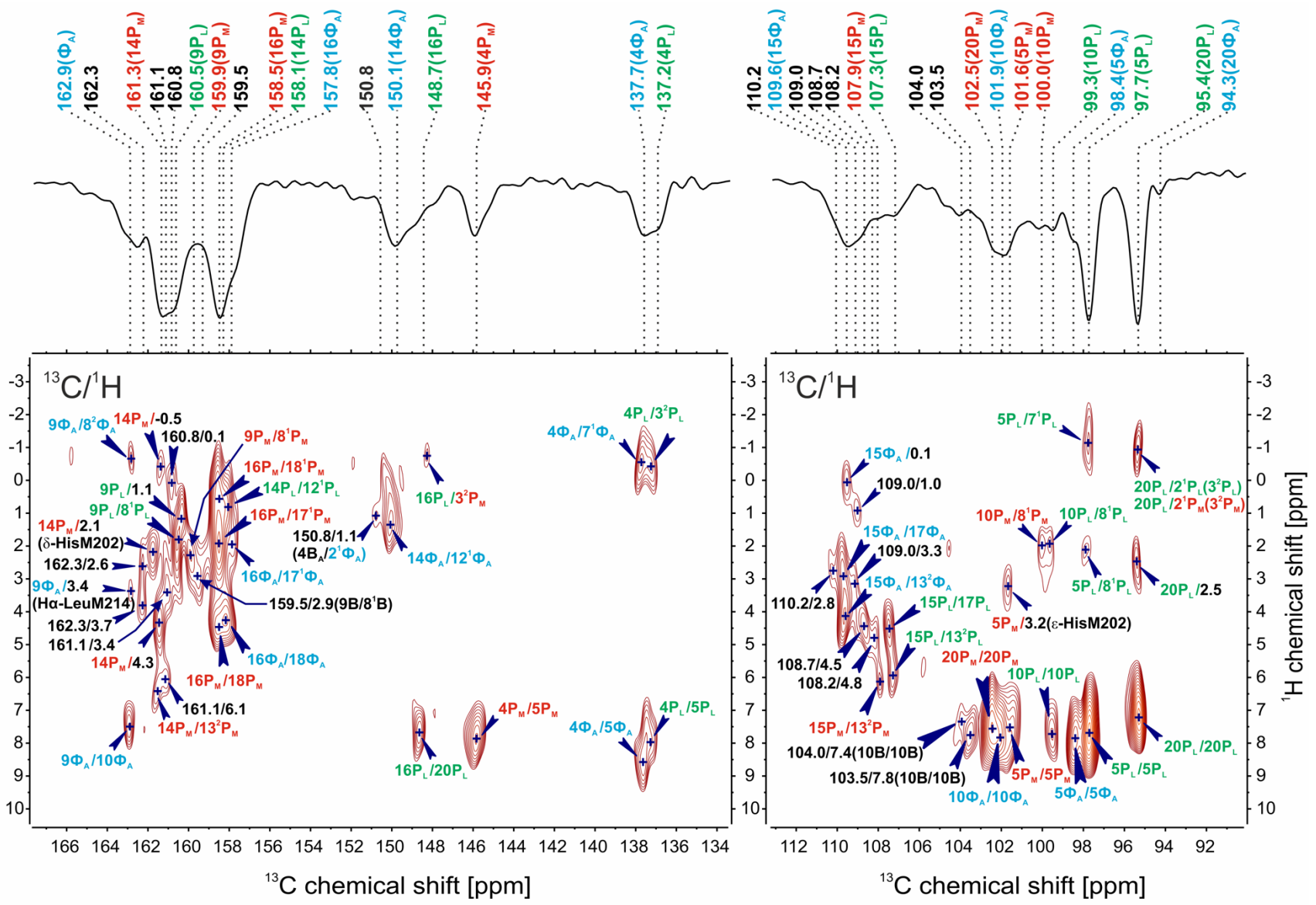
P. Bielytskyi et al., to be published. Collaboration with P.K. Madhu, TIFR.

“Spin-Torch” X→^{1}H→ ^{1}H→ X



P. Bielytskyi et al., to be published. Collaboration with P.K. Madhu.

“Spin-Torch” X→^{1}H→ ^{1}H→ X



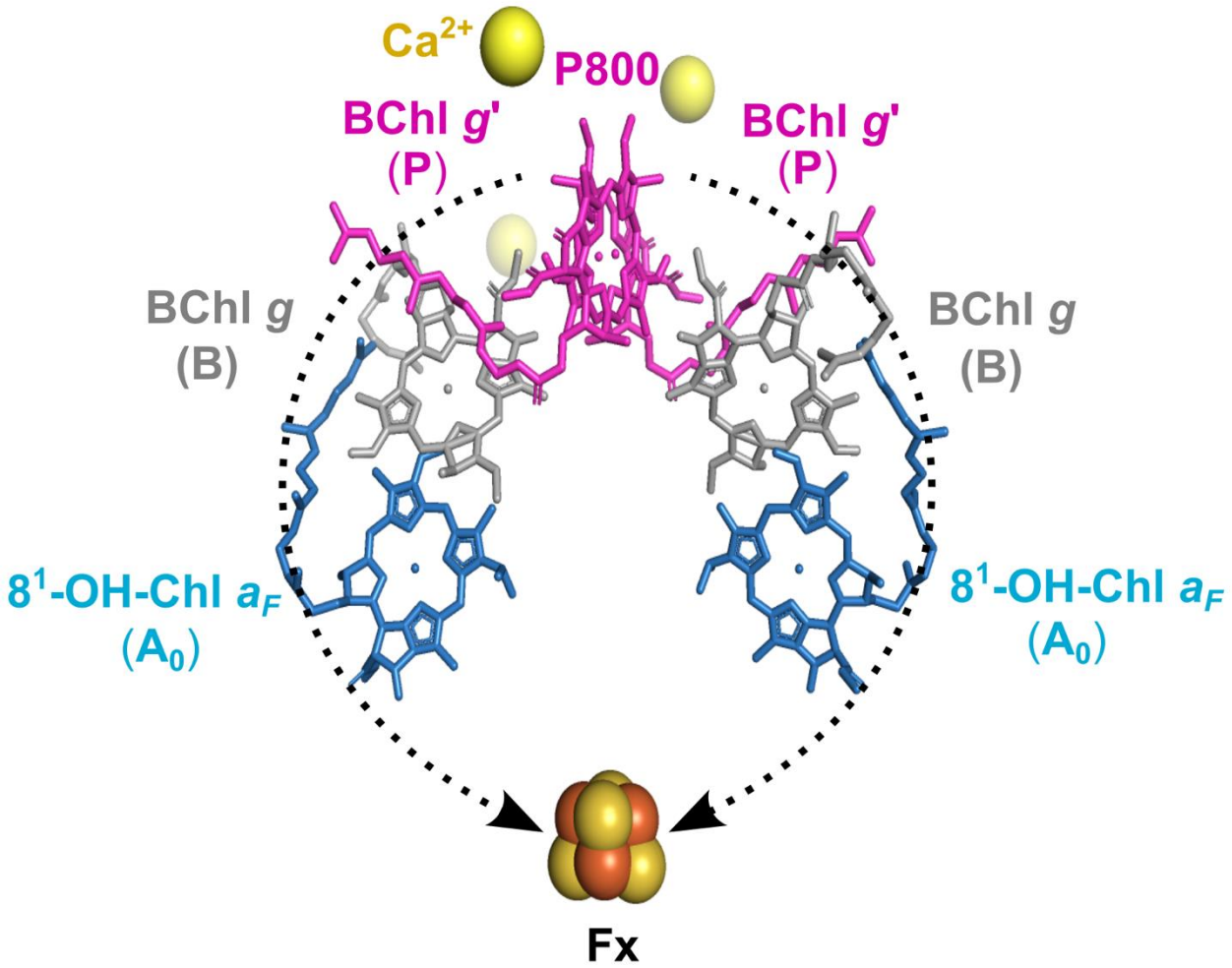
Tentative assignments. P. Bielytskyi et al., to be published. Collaboration with P.K. Madhu.

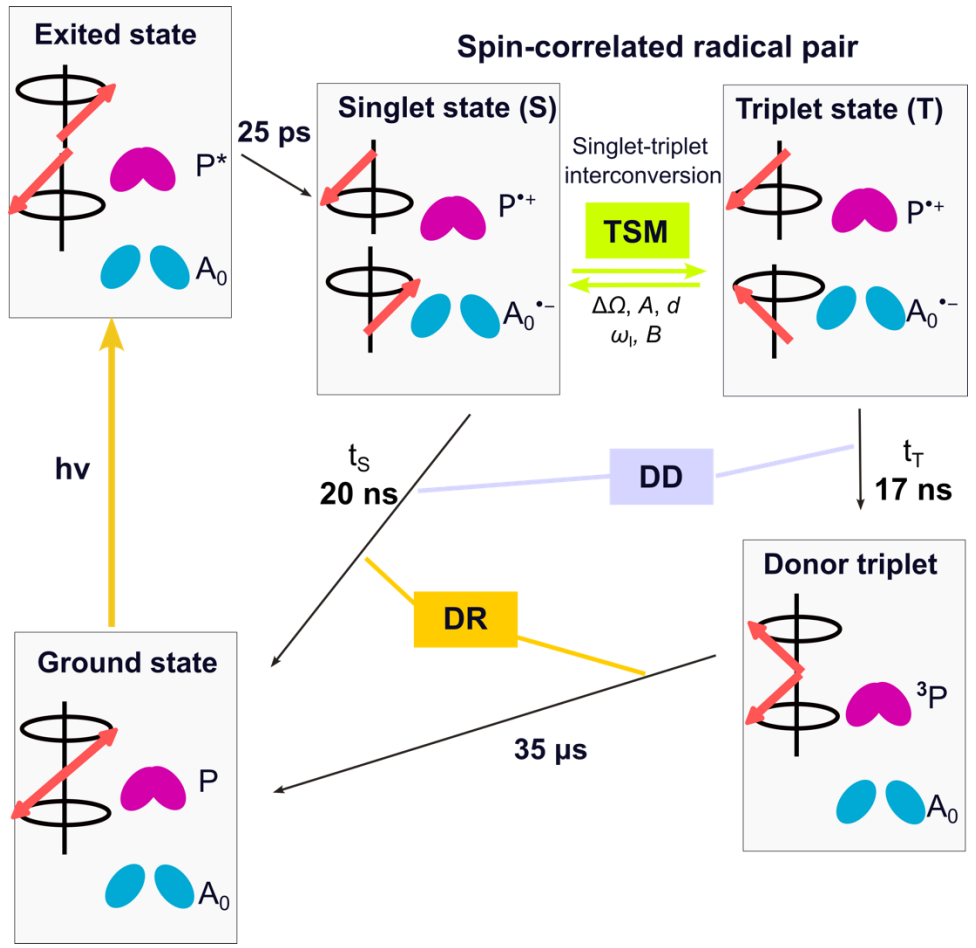
Part 1

Photosynthetic Reaction Centers

Analytical applications:
Heliobacterial RC

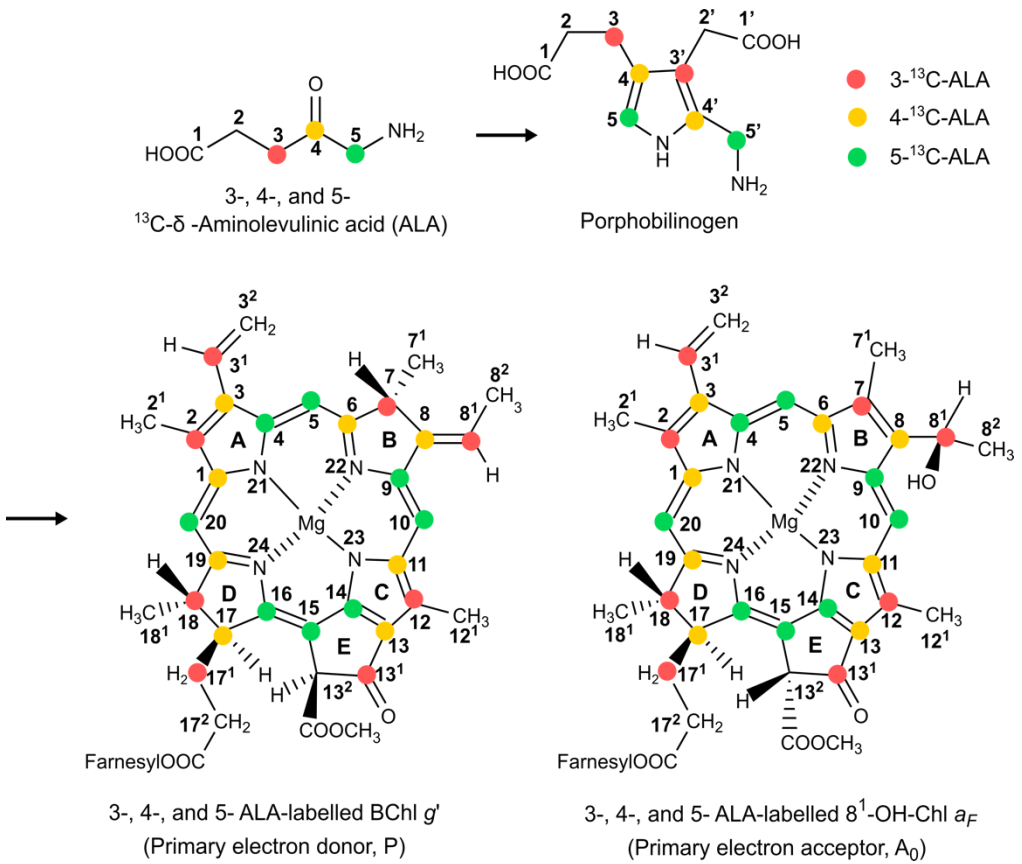
Heliobacterial RCs

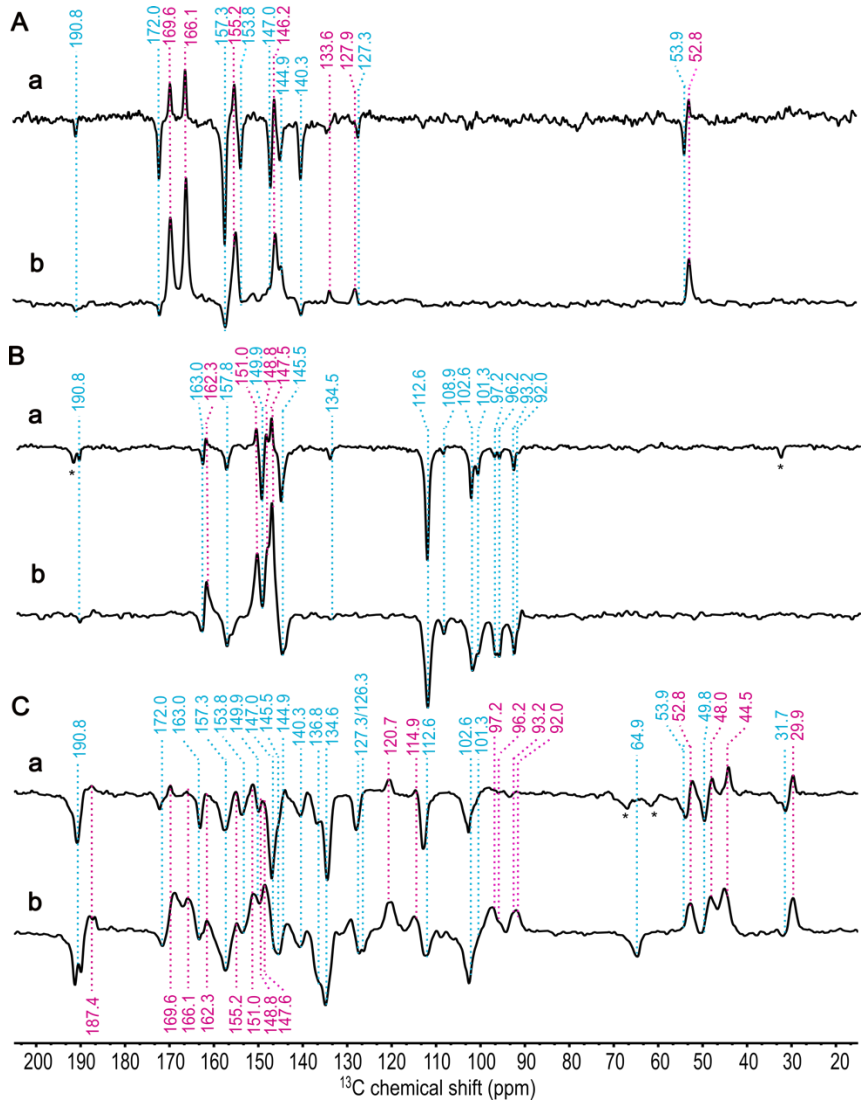




Heliobacterial RC
PDB: 5V8K

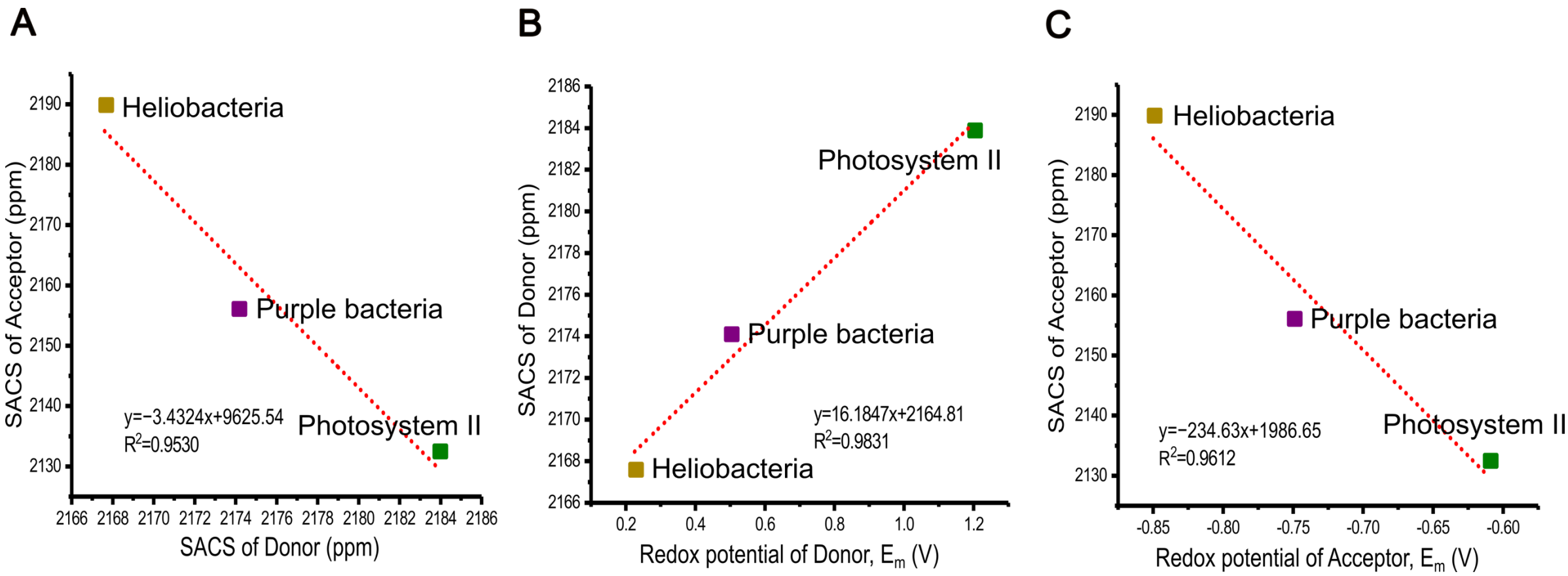
Heliobacterial RCs





Yunmi Kim, et al. (2024) Molecules 29, 1021.

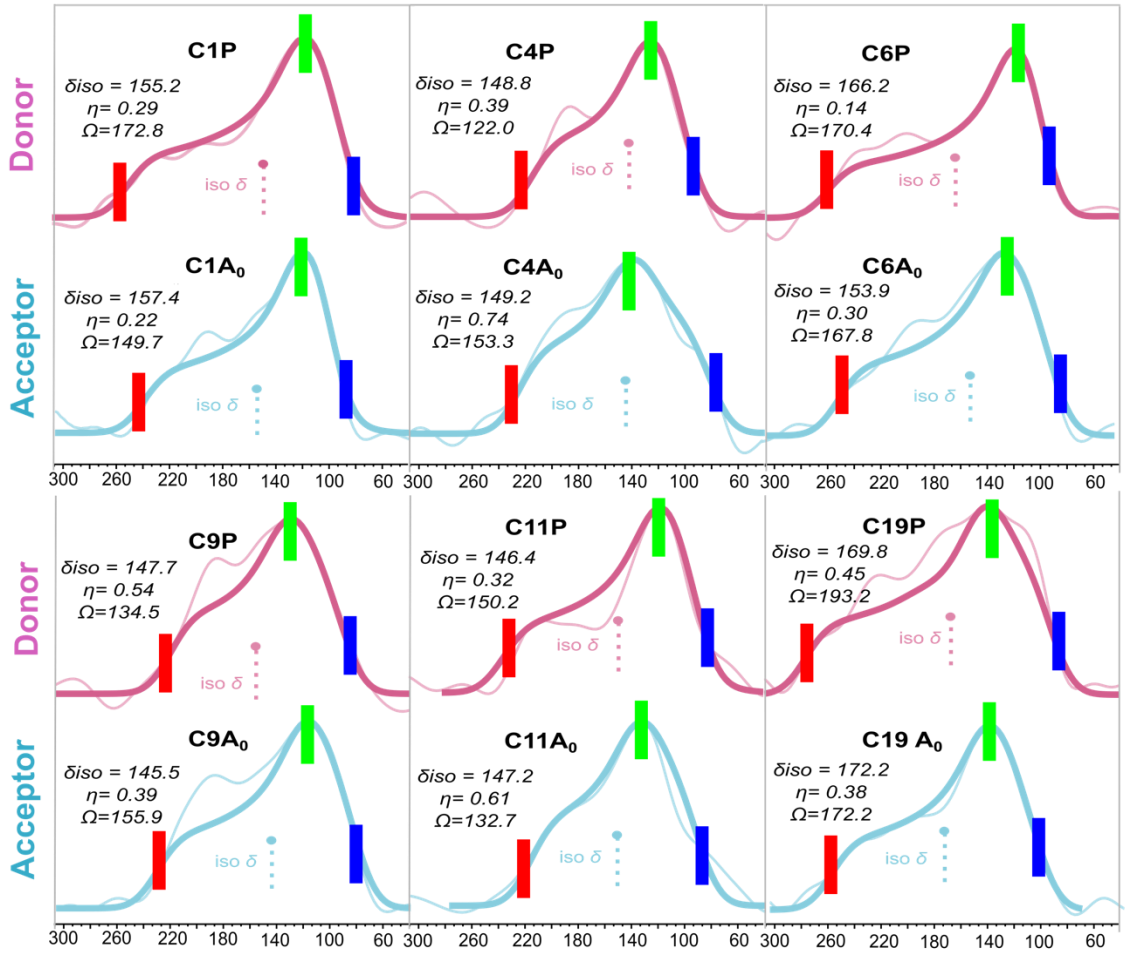
Sum of aromatic chemical shifts (SACSs): Comparing RCs

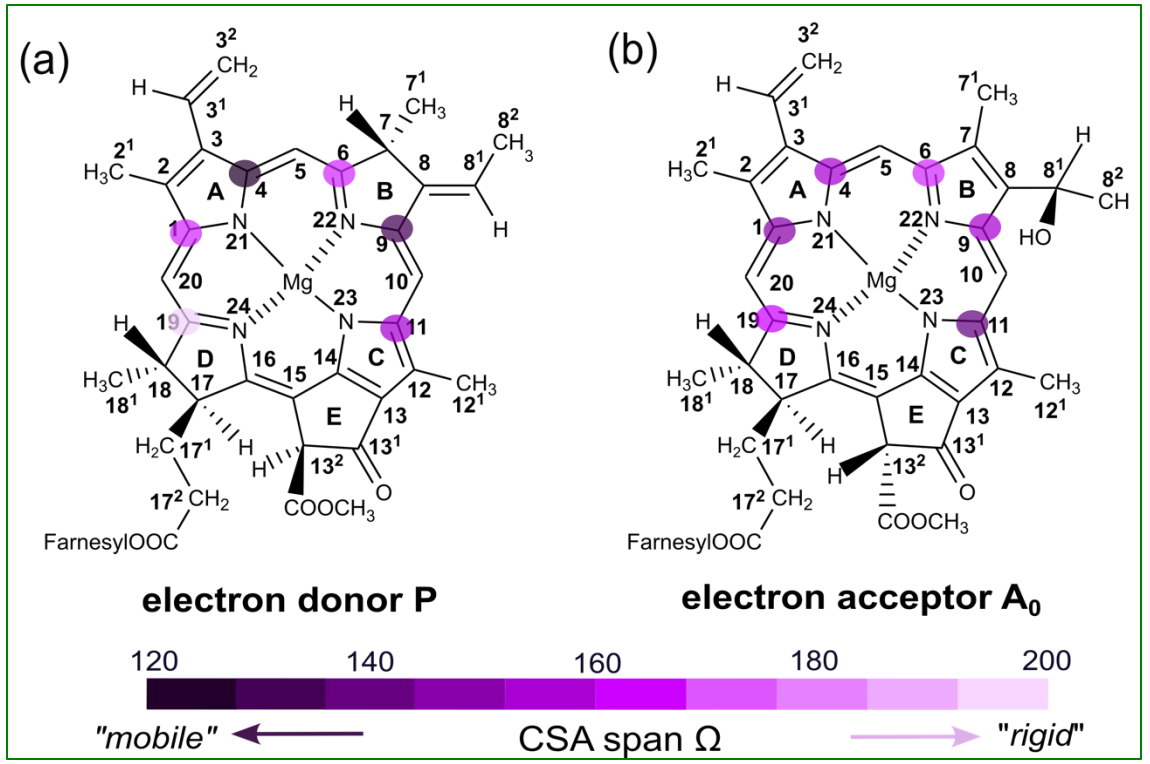


Yunmi Kim, et al. (2024) Molecules 29, 1021.

Heliobacterial RCs: Local dynamics (ns to μs)

^{13}C photo-CIDNP SUPER MAS NMR: Line shapes

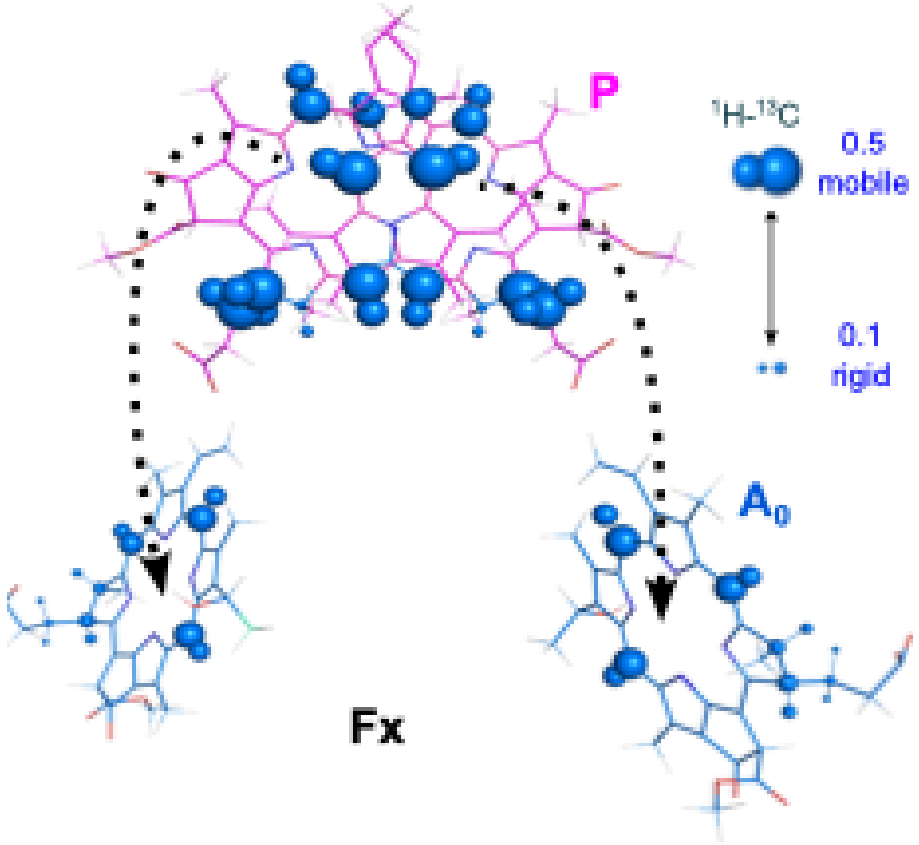




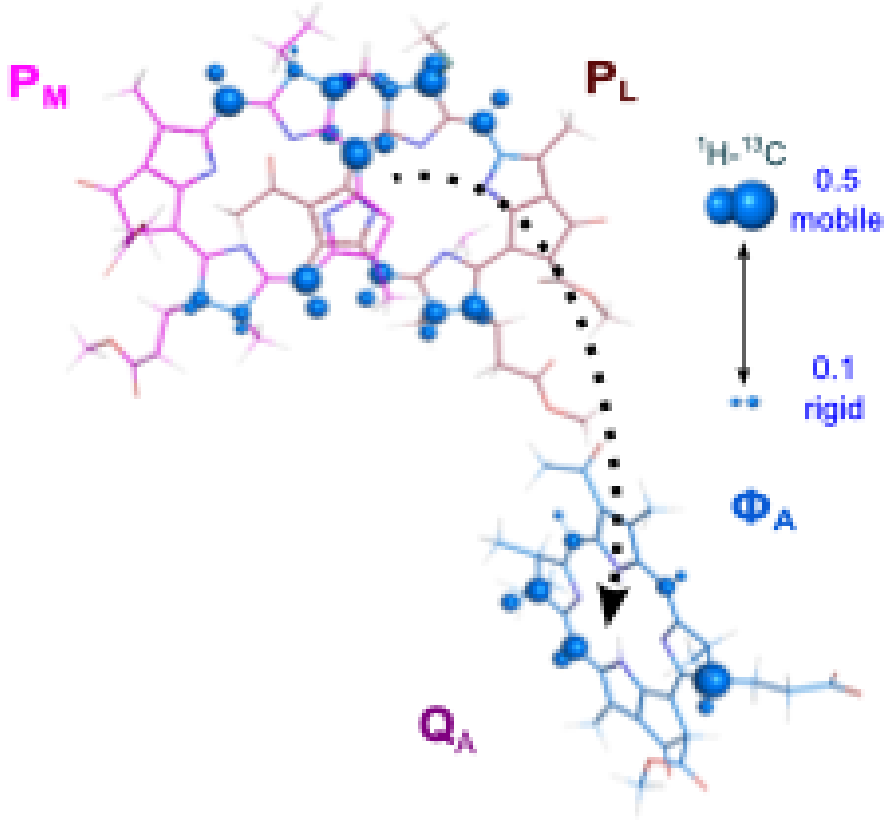
Yunmi Kim, et al. (2024) under review.

Heliobacterial RCs: Local dynamics (ns to μs)

Helio RCs



purple RCs

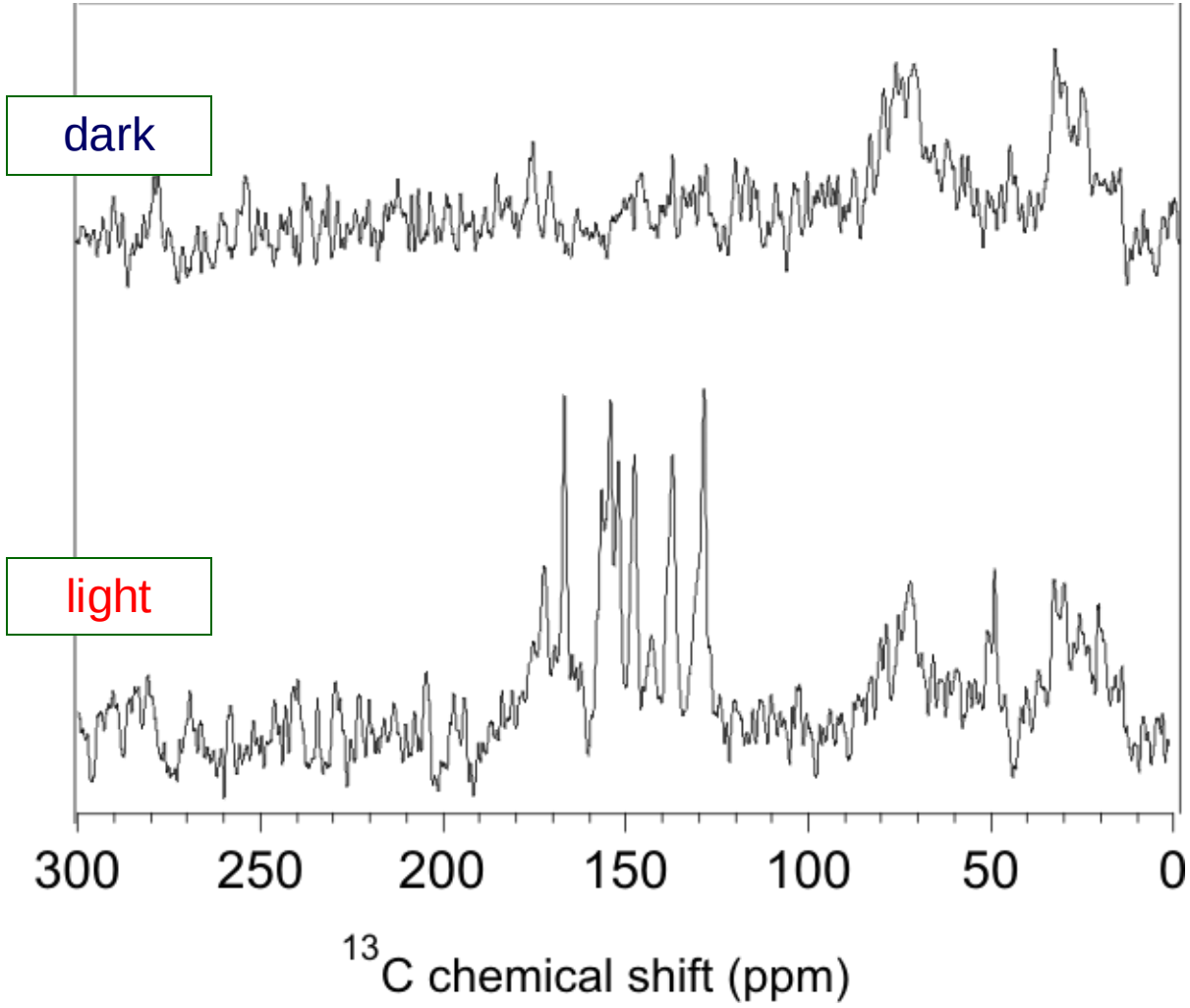


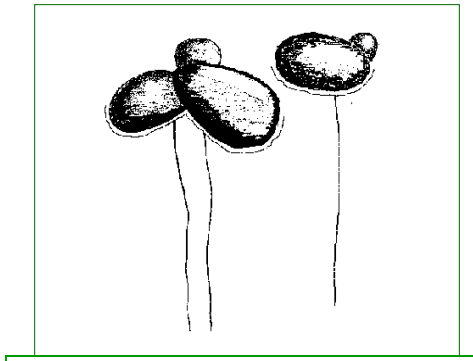
Yunmi Kim, et al. (2024) under review.

Part 1 Photosynthetic Reaction Centers

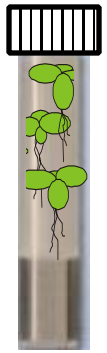
Analytical applications:
Photosystem II of plants.

The solid-state photo-CIDNP effect in entire plants





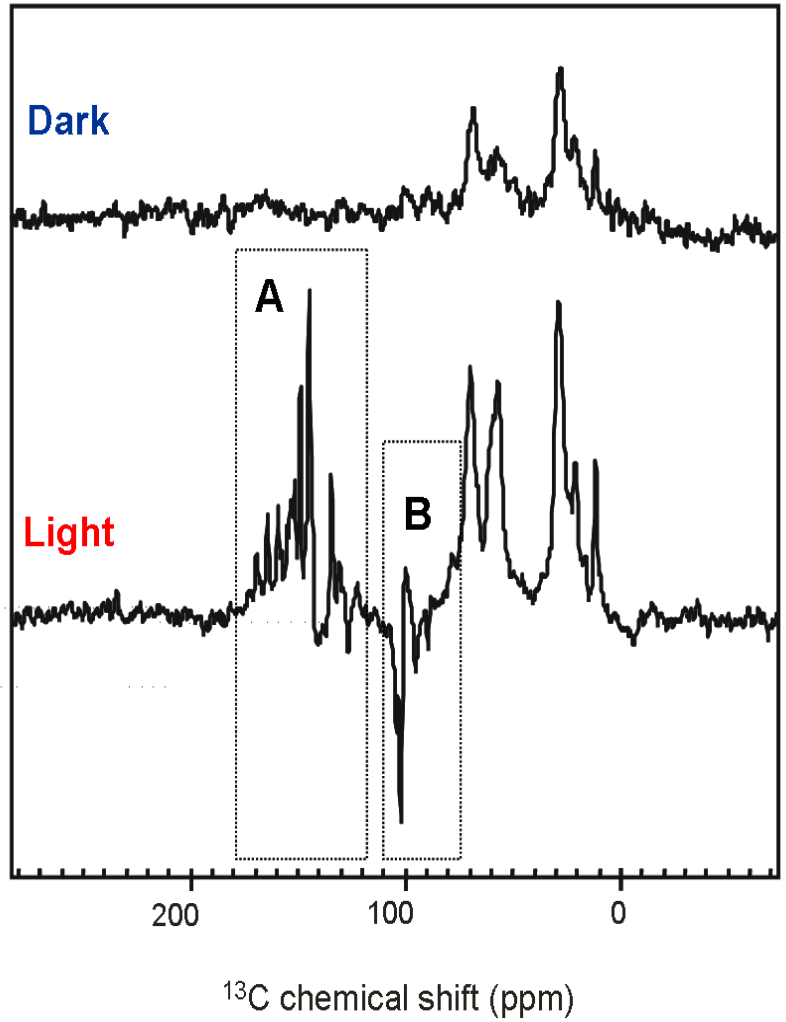
Spirodela (duckweed)

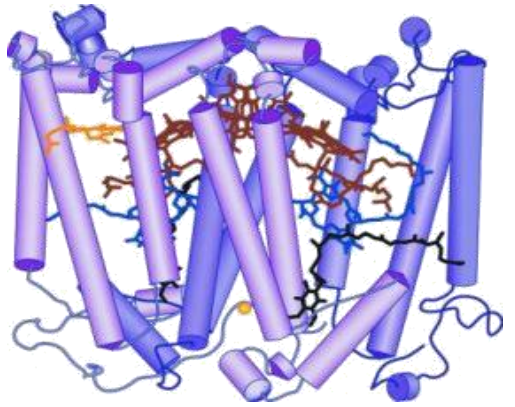


Sapphire
4mm
70μL

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).

^{13}C Photo-CIDNP MAS NMR on D1D2



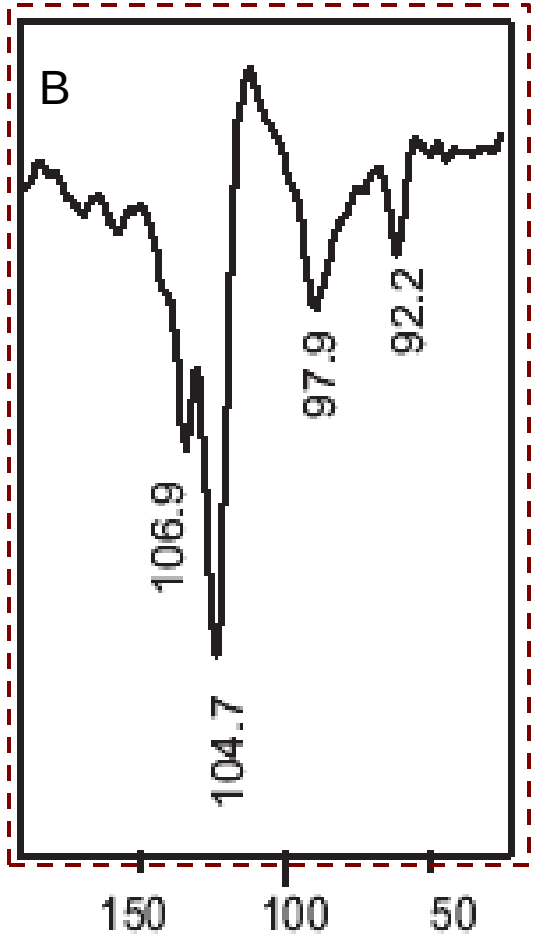


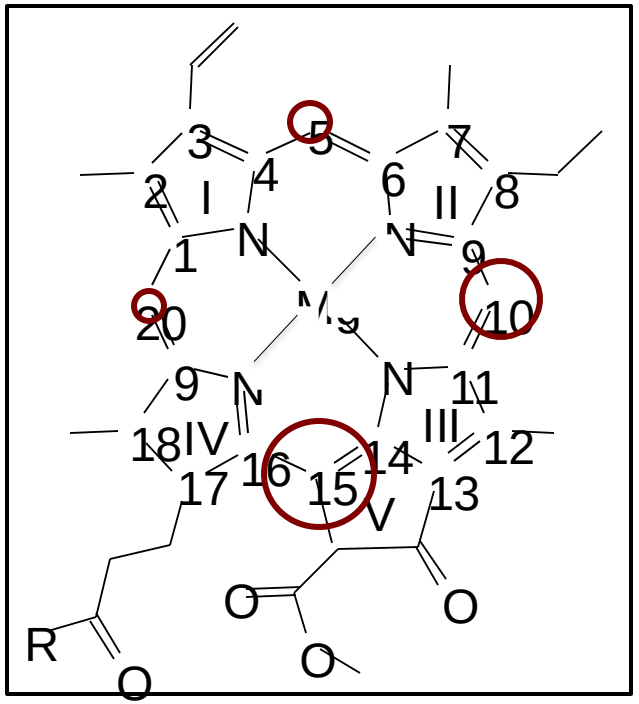
No isotope labeling

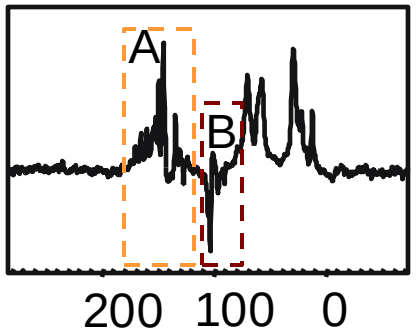
There is photo-CIDNP!

Matysik et al. (2000) PNAS, 104, 12767

^{13}C Photo-CIDNP MAS NMR on D1D2

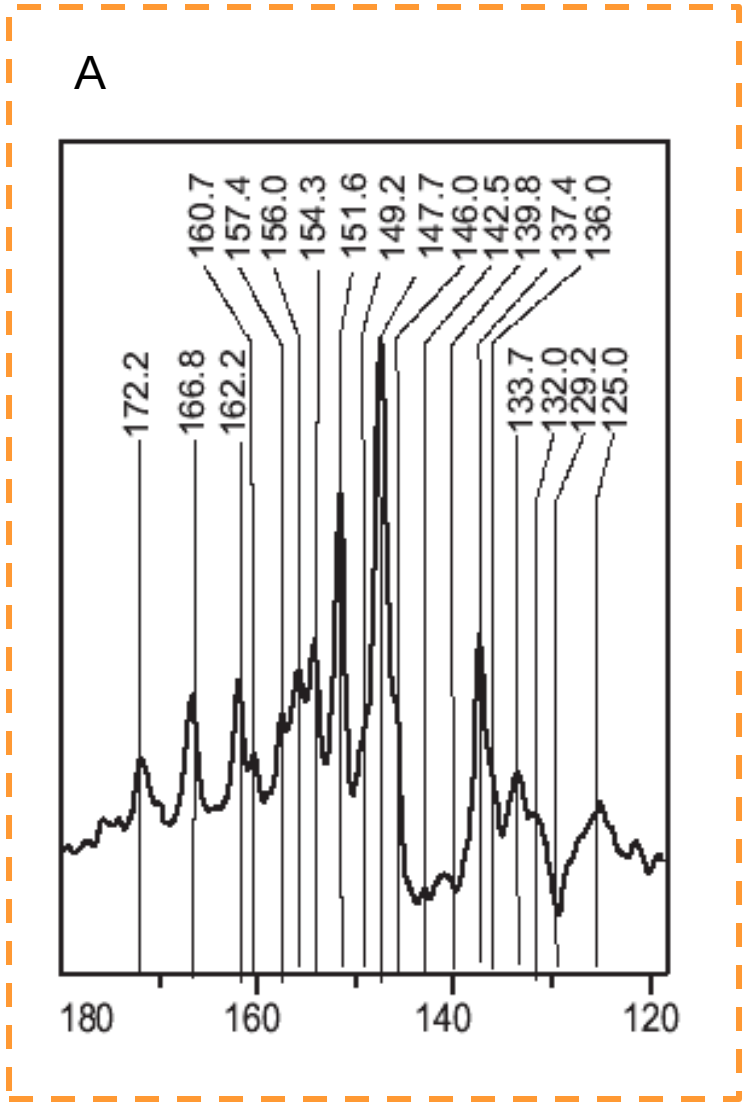


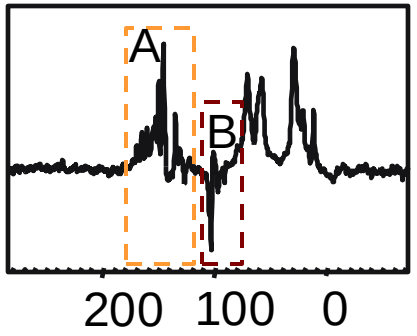


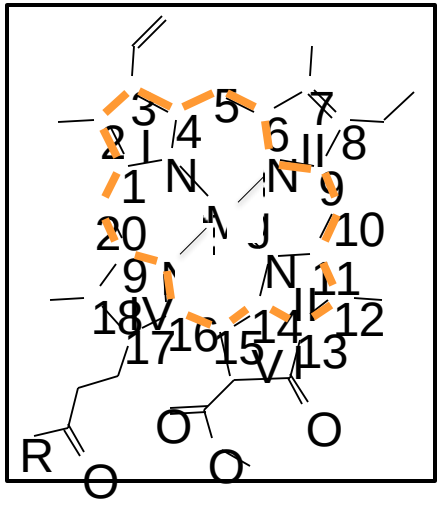


Asymmetry of the electron spin density distribution

^{13}C Photo-CIDNP MAS NMR on D1D2

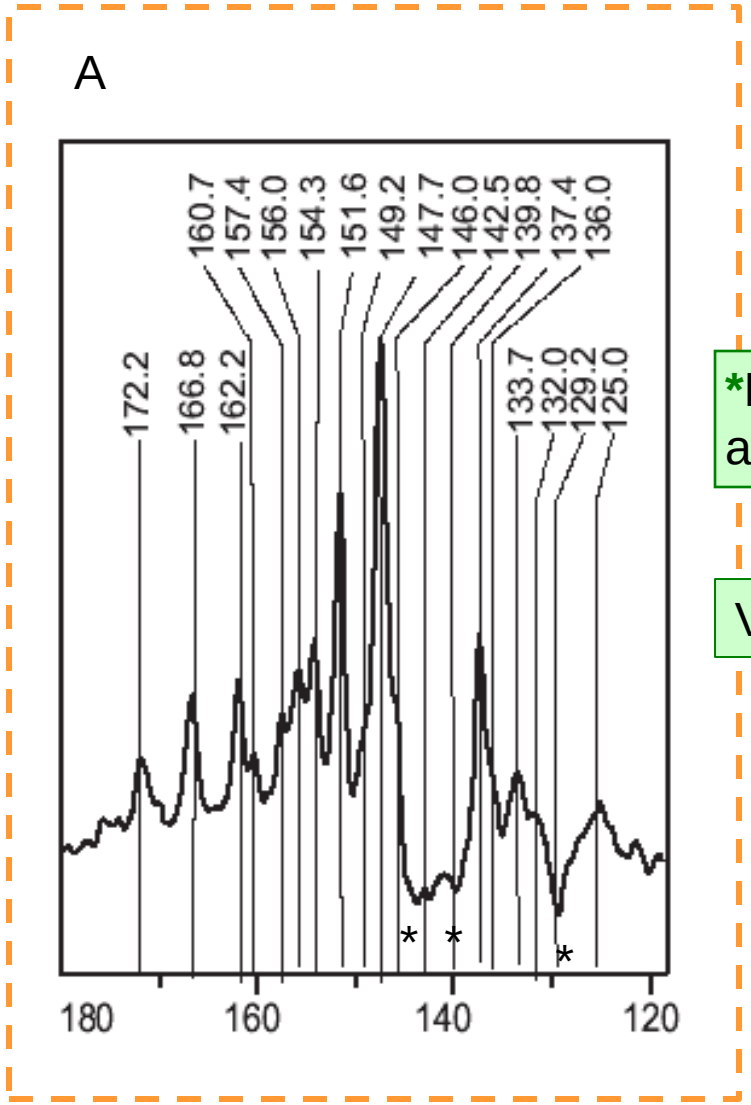


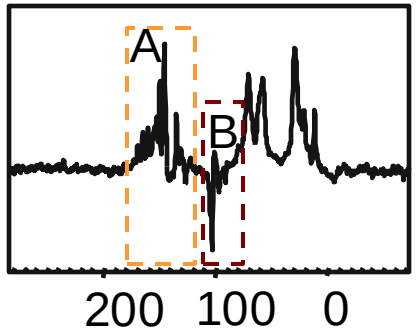




Chemical shifts assigned to a *single* chlorophyll

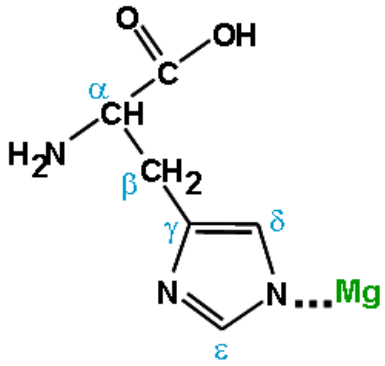
^{13}C Photo-CIDNP MAS NMR on D1D2



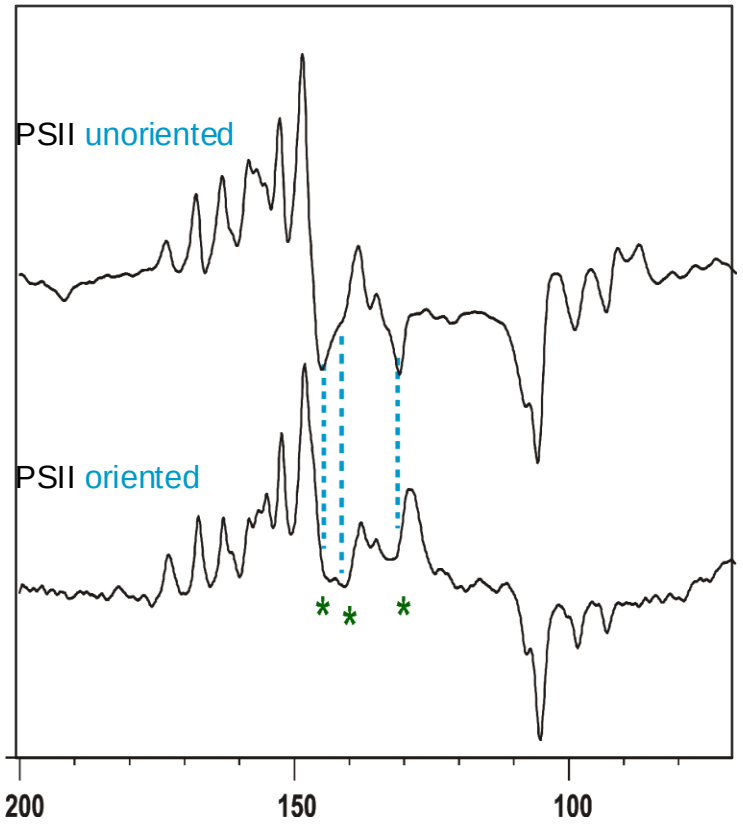


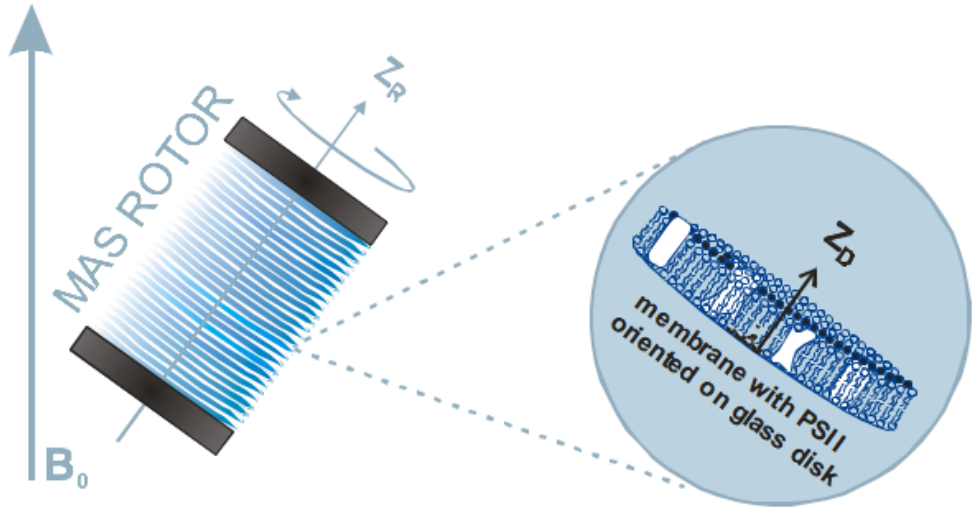
*Emissive ^{13}C signals at 142.5, 139.8 and 129.2 ppm untypical for Chl.

Values match for His, esp. axial His.



^{13}C Photo-CIDNP MAS NMR on D1D2





MAOSS experiments

Difference in orientation backing the model

Diller, Roy, Gast, van Gorkom, de Groot, Glaubitz, Jeschke, Matysik, Alia (2007) PNAS, 104, 12767.

„*Tilt model*“ for P_{D1} donor

Observations

- Inversion
- Deprotanated His →
  [Chl His]$^-$ anion
- Spin density on [Chl His]$^\bullet$ radical

Model

Tilt axial His □ Inversion of spin density

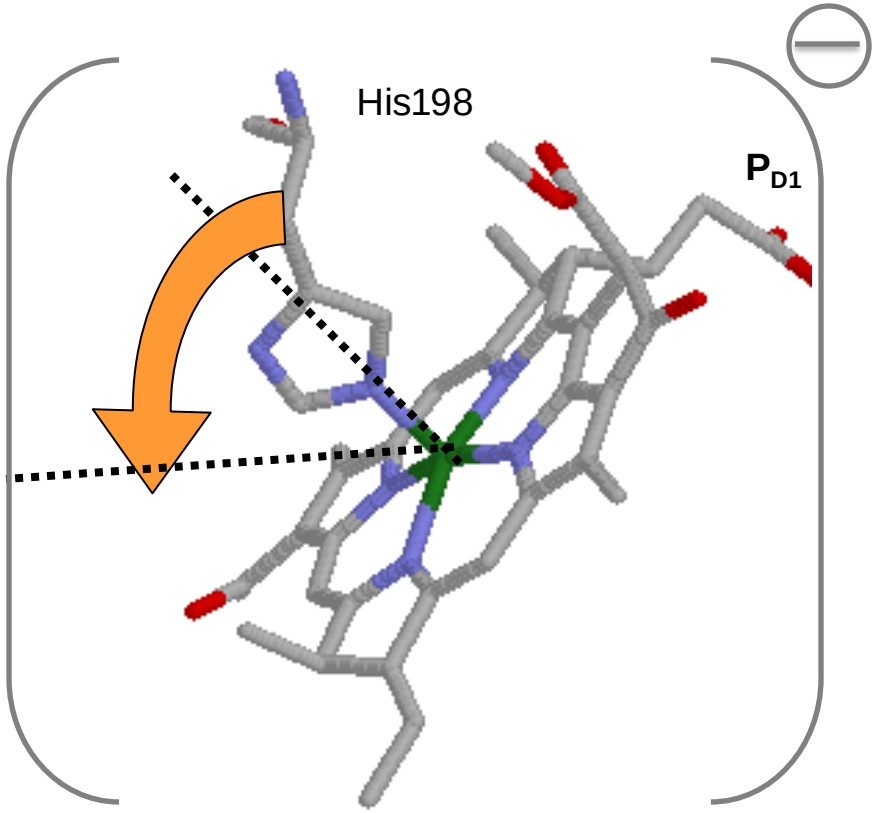
Stabilization of negatively charged ground state

⇩

Lowering of ground state

⇩

Increase of redox potential



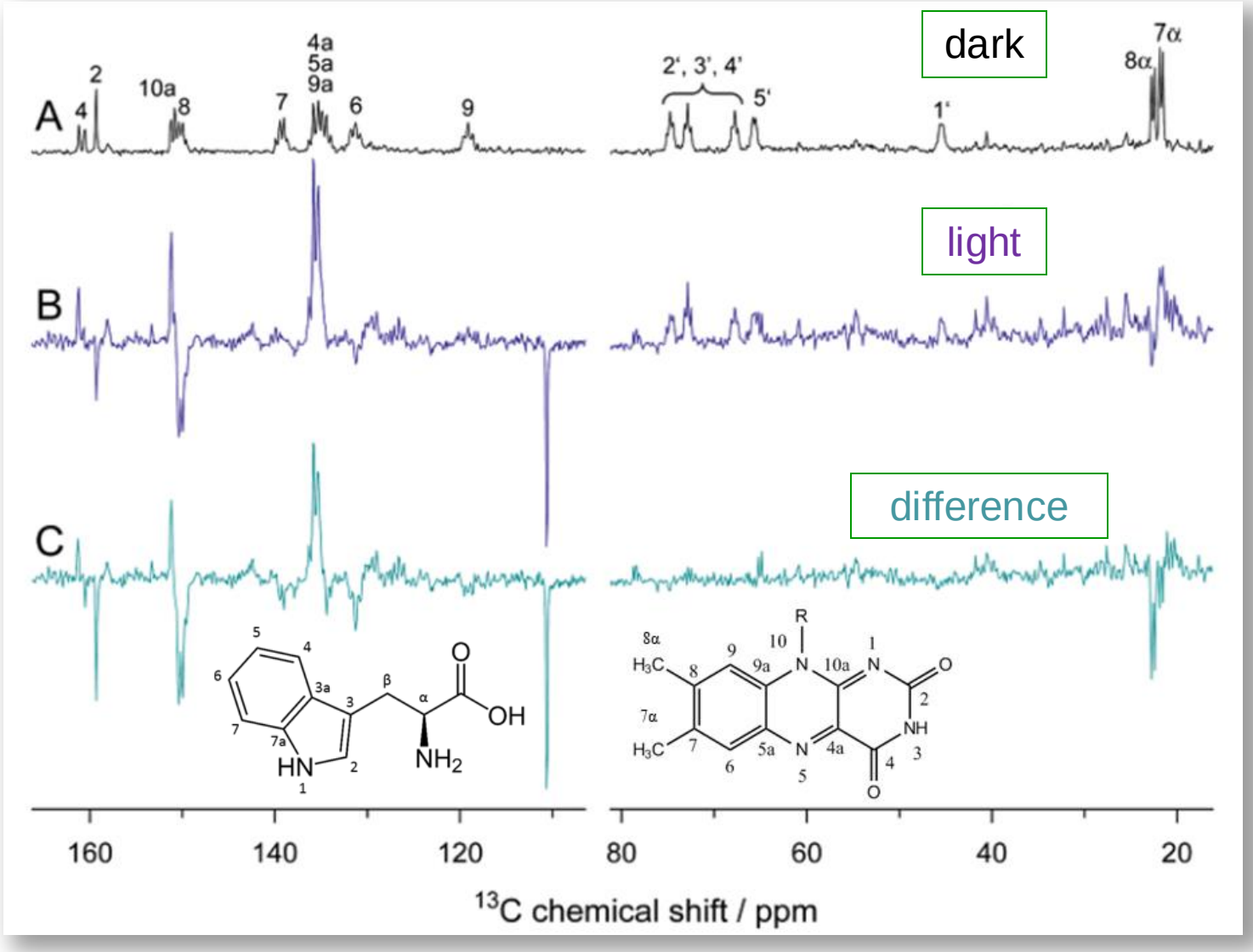
Diller, Roy, Gast, van Gorkom, de Groot, Glaubitz, Jeschke, Matysik, Alia (2007) PNAS, 104, 12767.

Part 1 Photosynthetic Reaction Centers

Part 2 Flavoproteins

Part 3 Artificial electron-transfer diads

Flavin protein: Photo-CIDNP effect observed in phototropin



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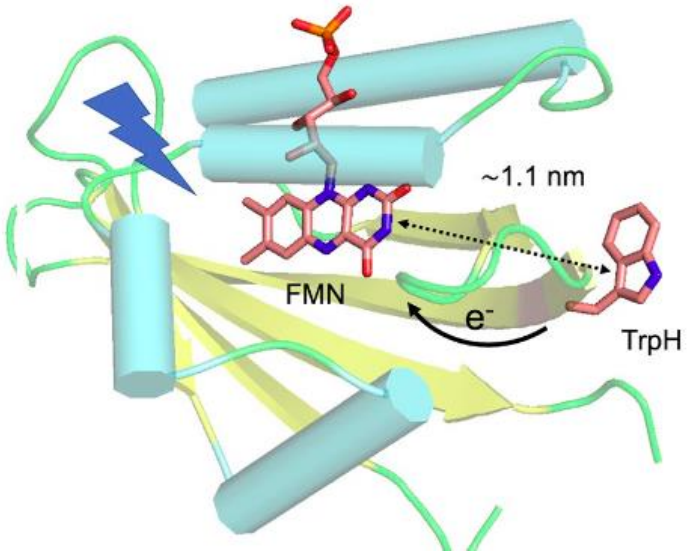
ARTICLES
Published on Web 11/18/2005

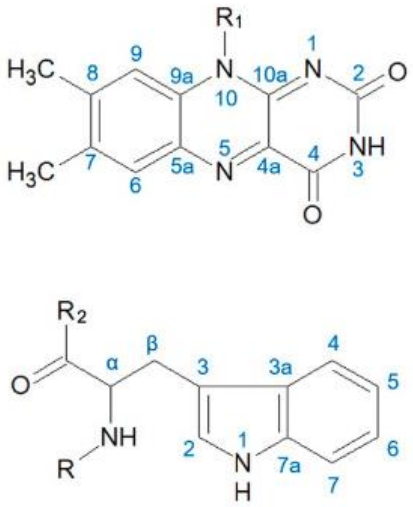
Photochemically Induced Dynamic Nuclear Polarization in a C450A Mutant of the LOV2 Domain of the *Avena sativa* Blue-Light Receptor Phototropin

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

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

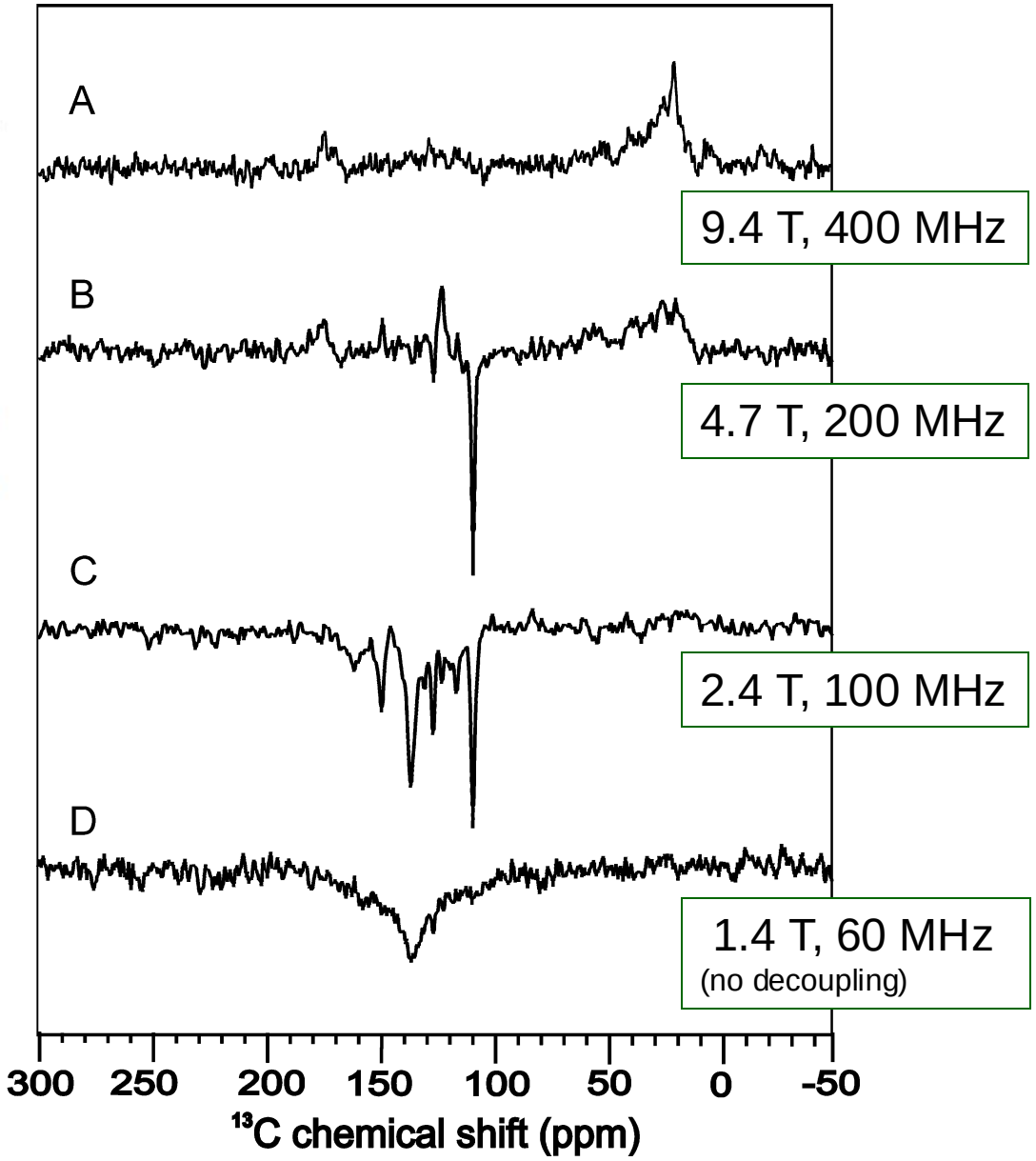
Flavin protein: experimental field-dependence





Phototropin LOV1-C57S

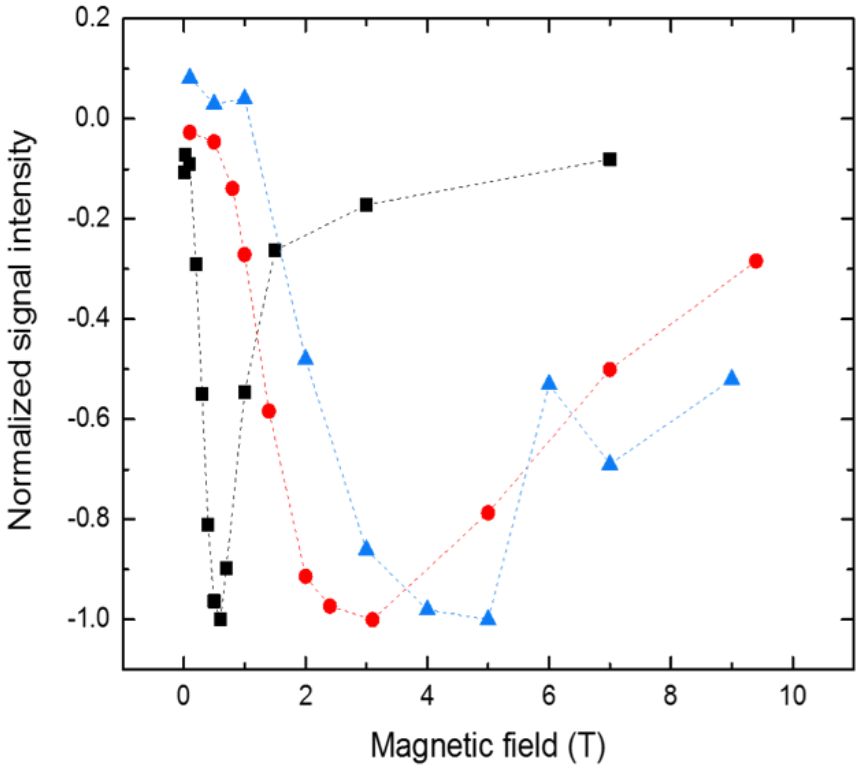
Collaboration T. Kottke



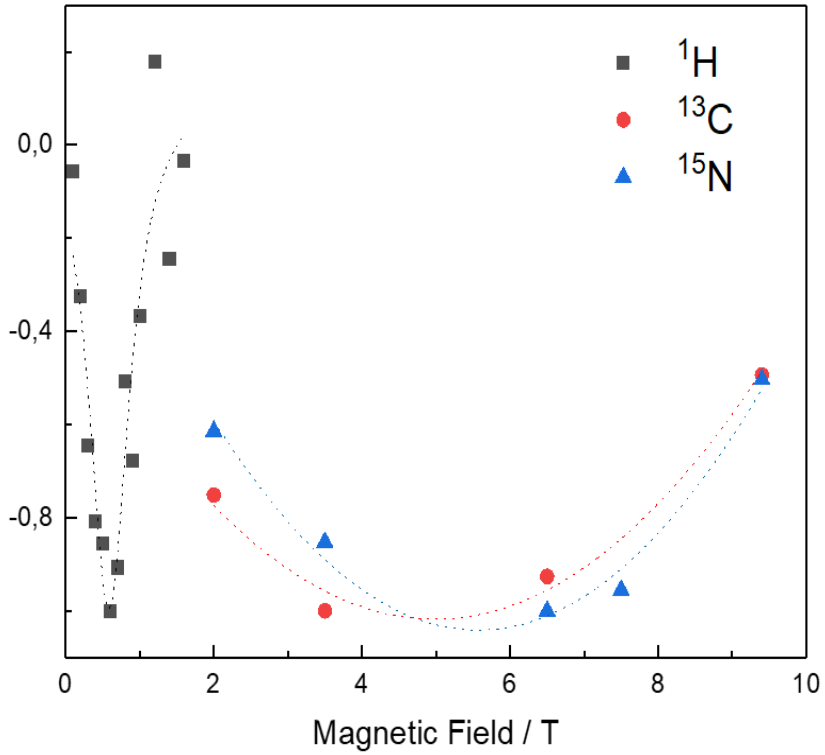
Xiaojie Wang (王孝杰), Smitha Surendran Thamarath, A. Alia, Bela E. Bode, Jörg Matysik (誉宫)
"The solid-state photo-CIDNP effect"
Acta Phys. Chem. Sin. 32, 399-404 (2016).

Flavin proteins: Magnetic-field dependence

Phototropin-LOV1-C57S



Aureochrome-LOV-C287S



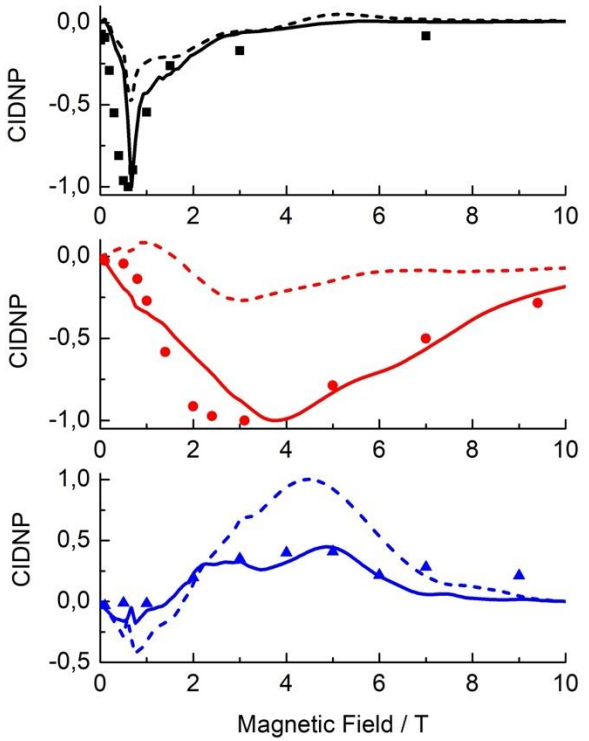
Liquid-state ^{1}H, ^{13}C and ^{15}N NMR

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



^{1}H

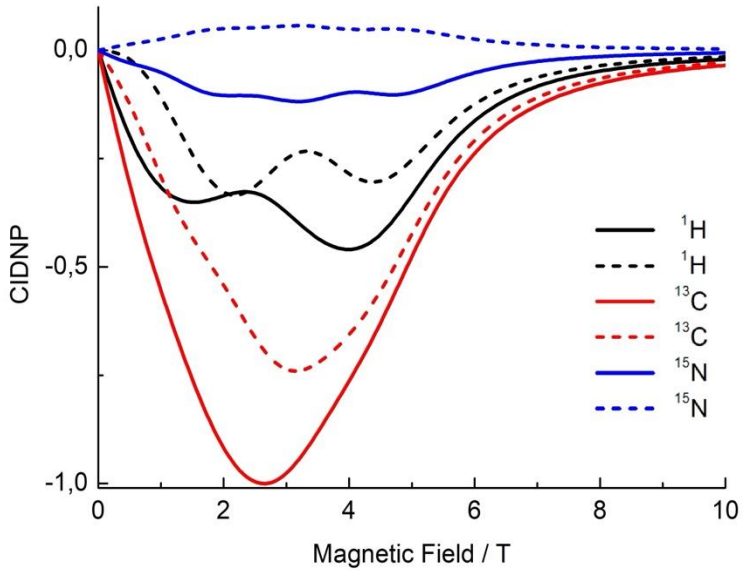
^{13}C

^{15}N

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

Sosnovsky D. et al. (2016)

Isotropic interactions



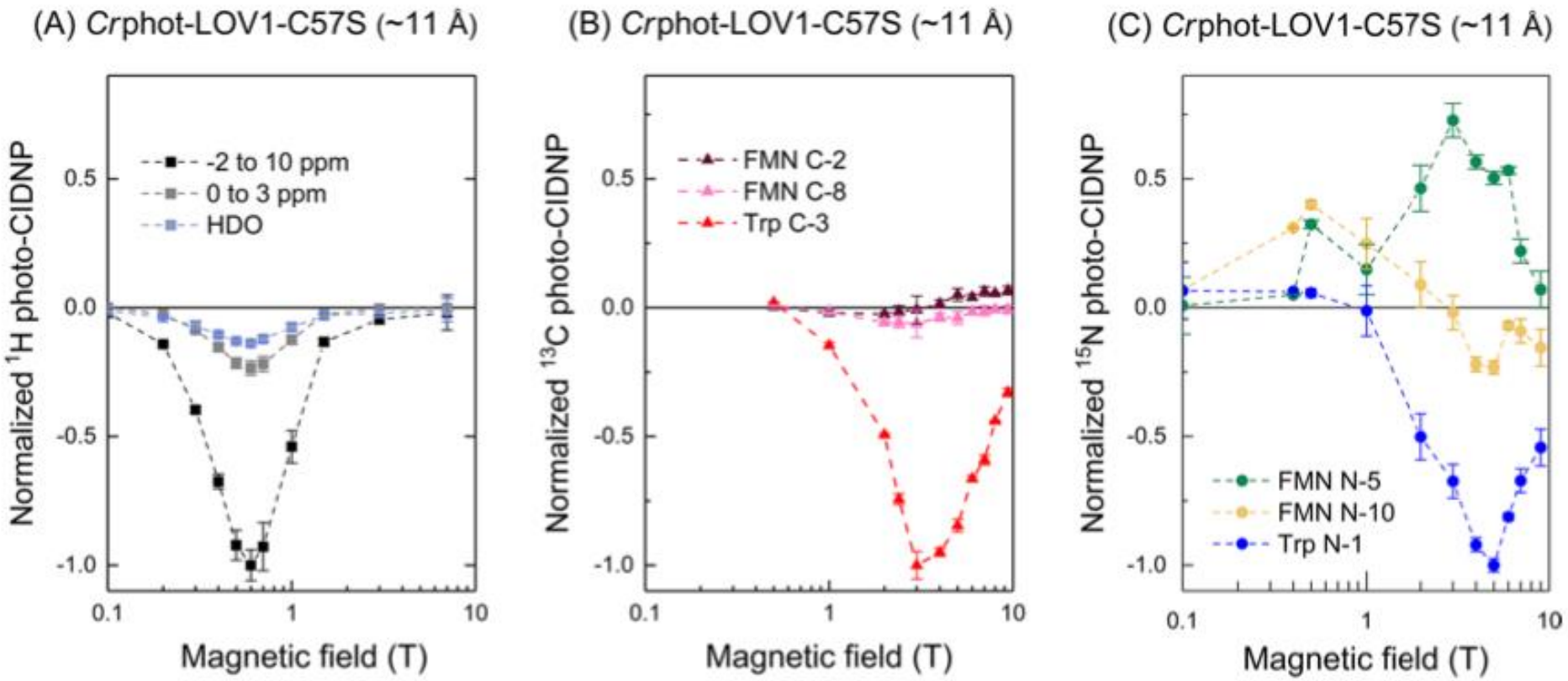
$a_{H_1} = 0.7$ mT
$a_{H_2} = 0.5$ mT
$a_{C_1} = 1.25$ mT
$a_{C_2} = 1$ mT
$a_{N_1} = 0.2$ mT
$a_{N_2} = -0.1$ mT

Liquid-state 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



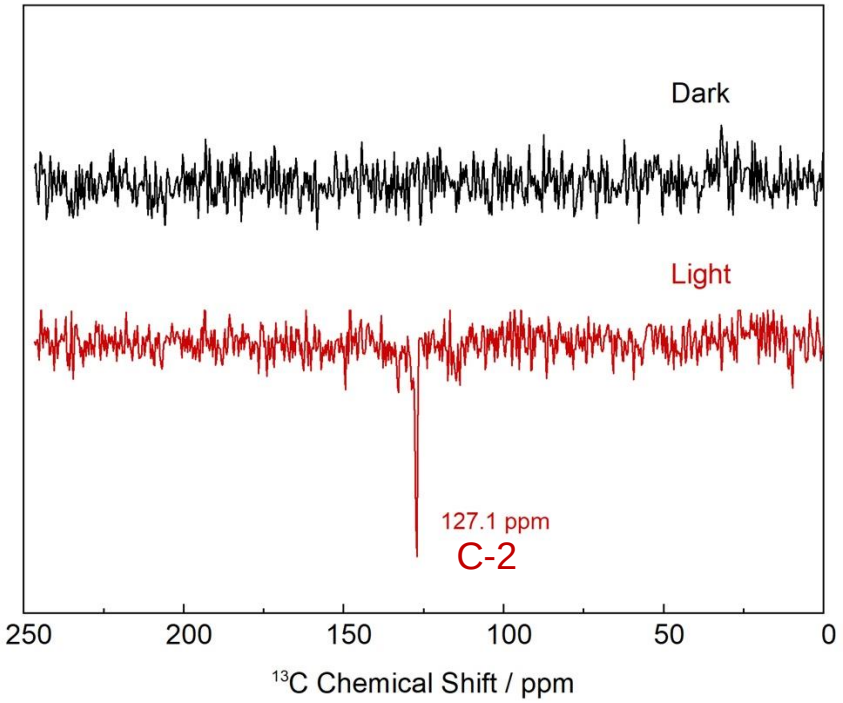
Liquid-state NMR

Collaboration with Alexandra Yurkovskaya and Konstantin Ivanov, Novosibirsk, and Tilman Kottke, Bielefeld.

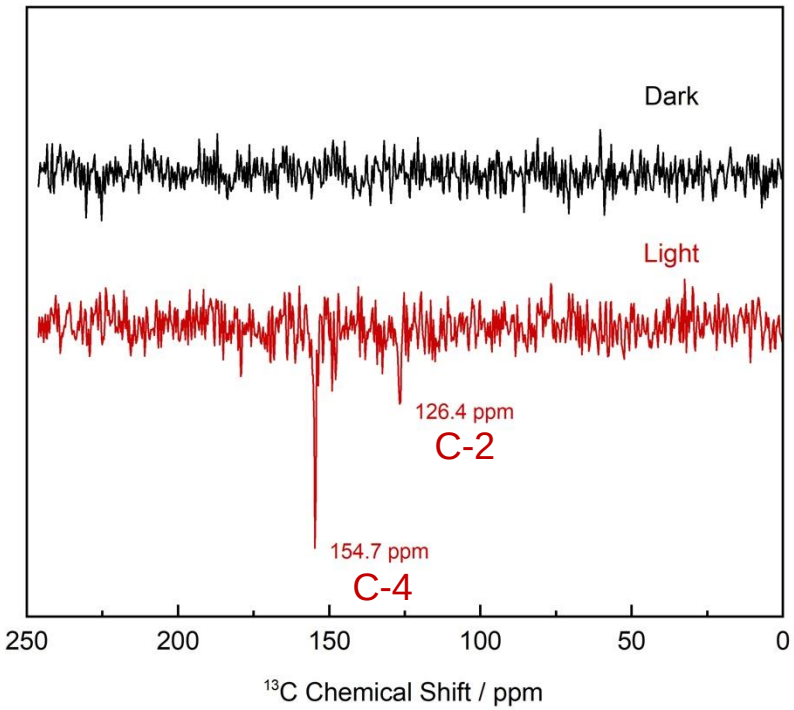
Yonghong Ding et al., Scientific Reports (2020) 10, 18658.

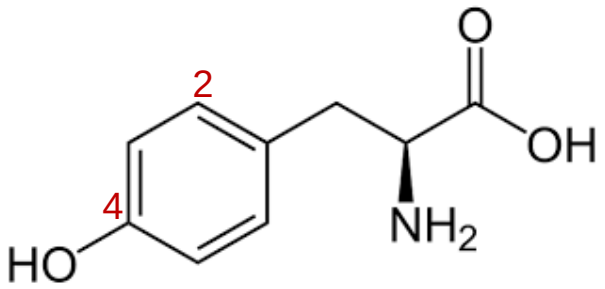
Tyrosine can act as donor!

Natural abundance



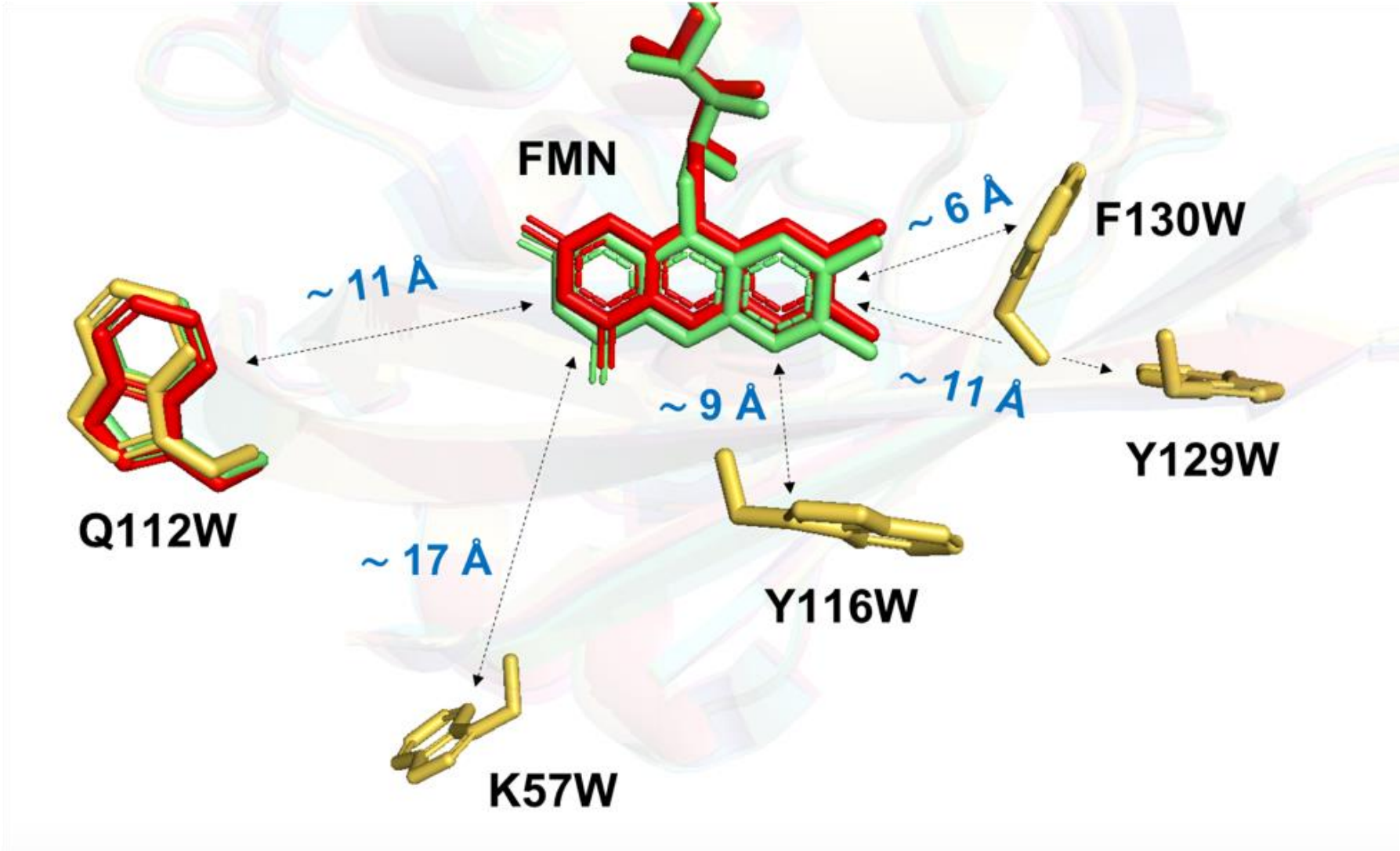
^{13}C-4 Tyr labelled sample





Ruonan Qin et al., to be published

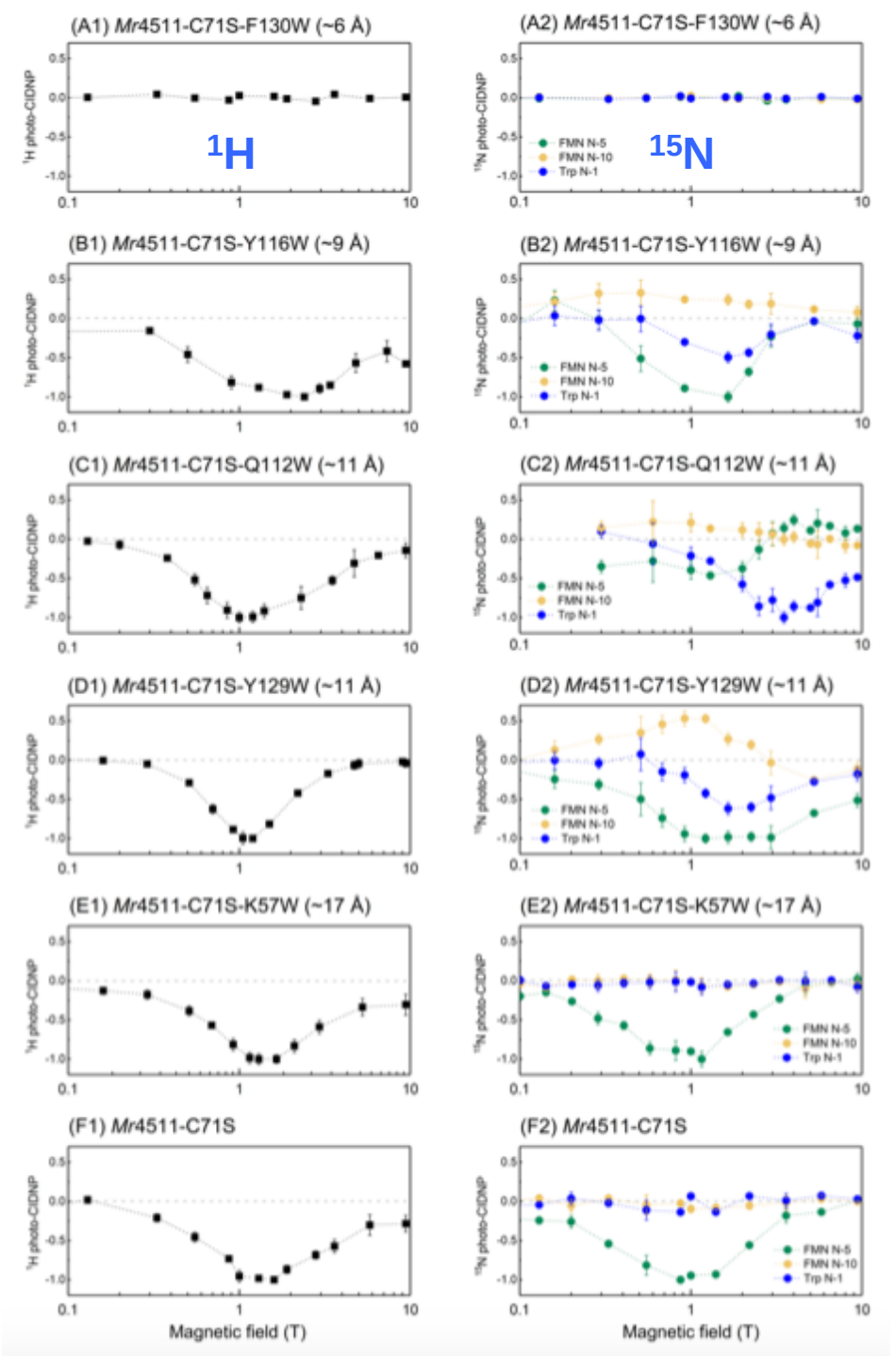
Flavin proteins: Magnetic-field dependence



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

Part 1 Photosynthetic Reaction Centers

Part 2 Flavoproteins

Part 3 Artificial electron-transfer diads

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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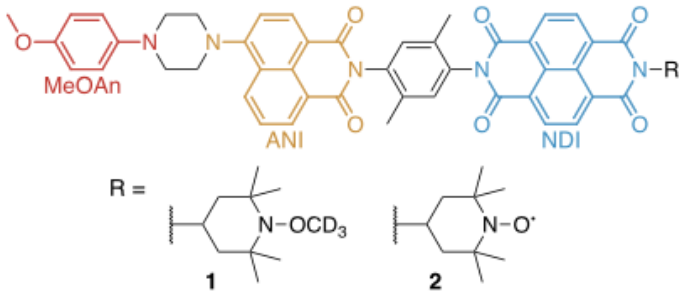


Figure 1. Structures of molecules used in this work. The donor (MeOAn), chromophore (ANI), and acceptor (NDI) moieties in the photoactive part of the structure are shown in red, yellow, and blue, respectively. The linker units are shown in black.

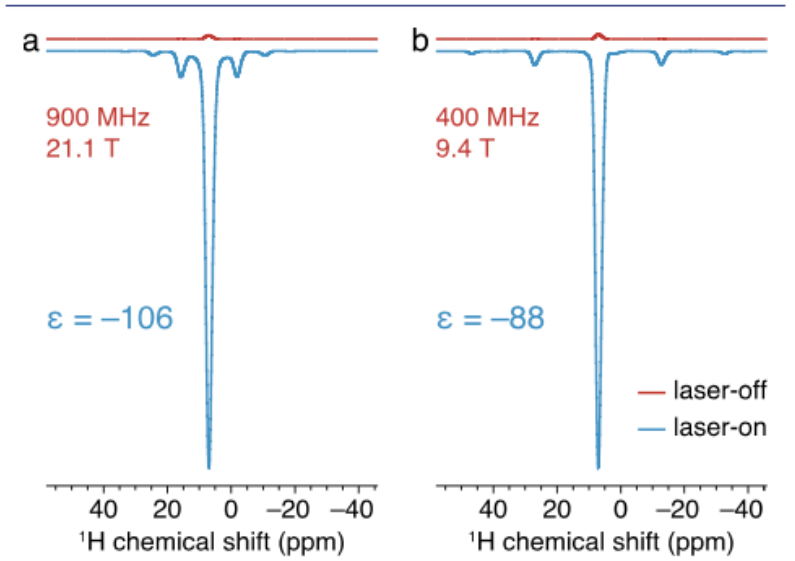
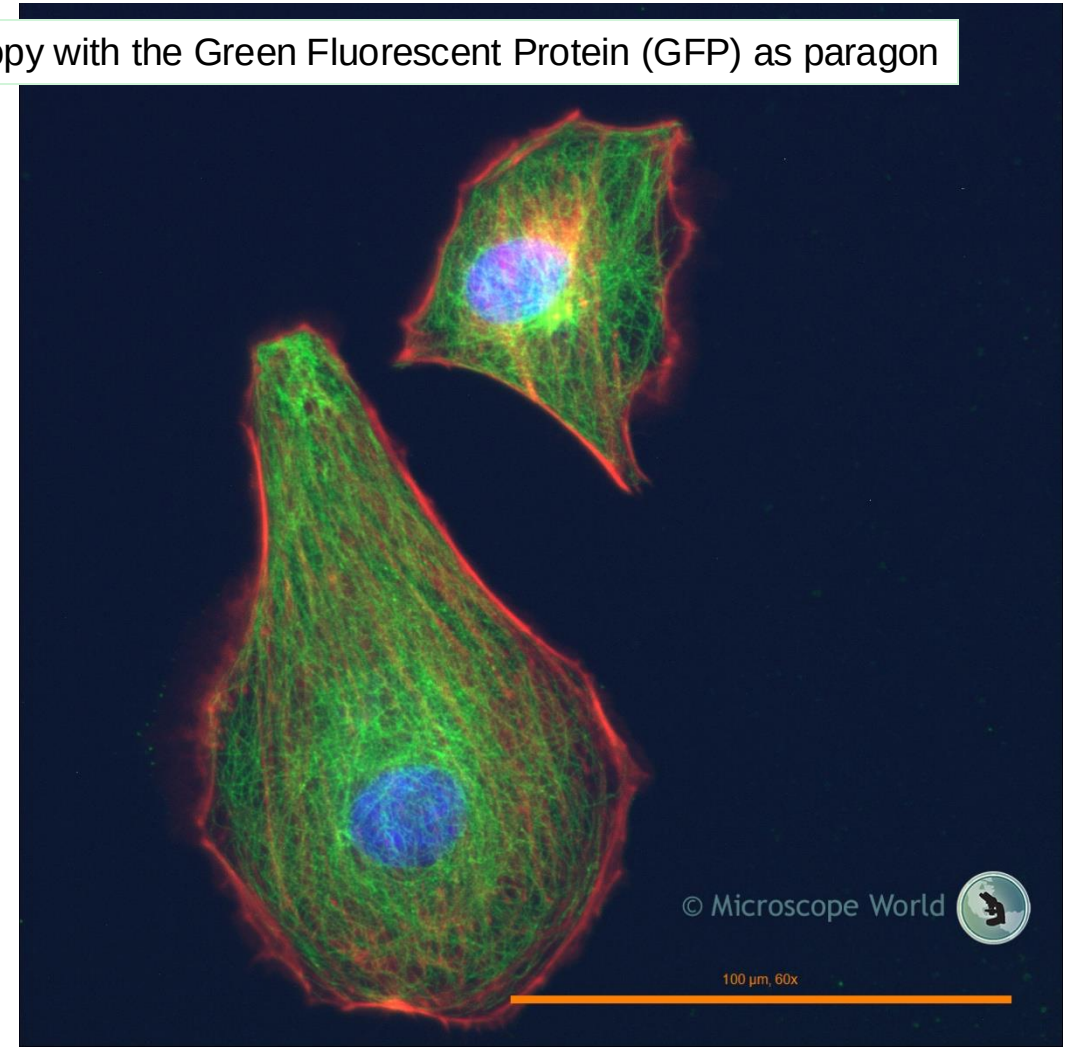


Figure 2. ^{1}H NMR spectra of a frozen solution of 1.5 mM PhotoPol-S in 98.5% OTP-d_{14} recorded at (a) 900 MHz and (b) 400 MHz, with and without continuous 450 nm laser irradiation (blue and red traces, respectively). All spectra were detected with a 70 s recycle delay and 8 kHz MAS using a Hahn echo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

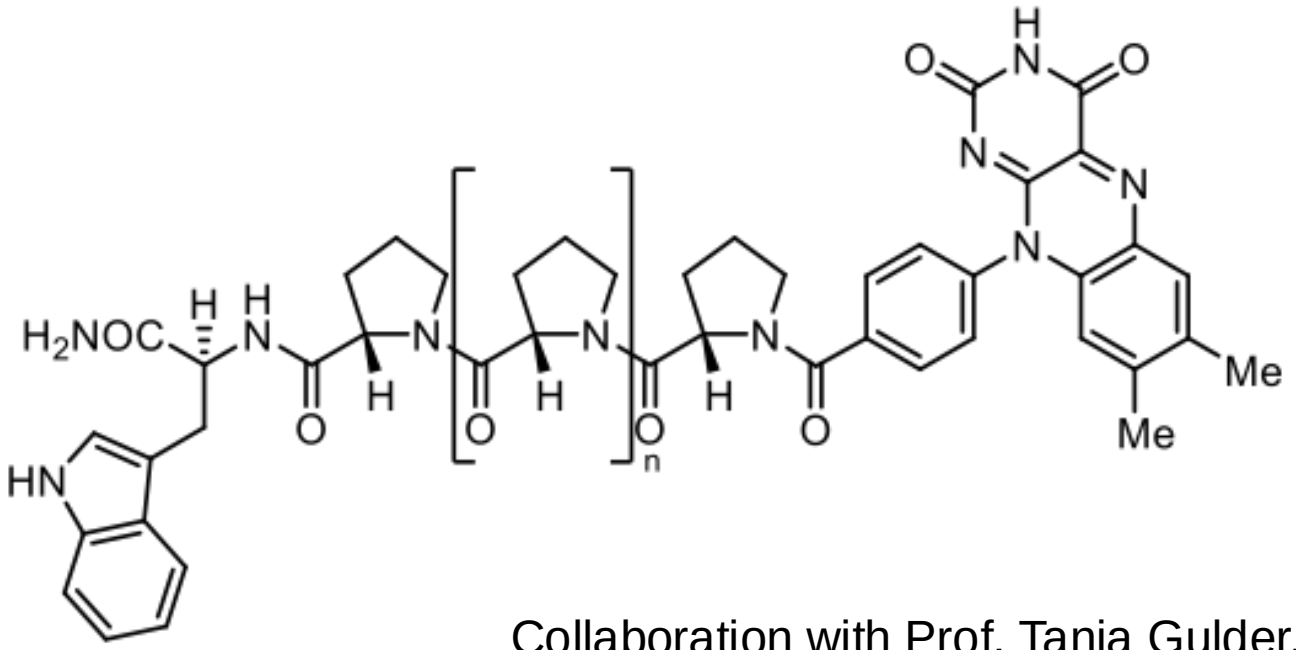
Outlook: Photo-CIDNP MRI flashing up specific surfaces

Fluorescence microscopy with the Green Fluorescent Protein (GFP) as paragon



Osamu Shimomura, Martin Chalfie, and Roger Y. Tsien,
Nobel Prize in Chemistry for 2008
“for the discovery and development of the green fluorescent protein, GFP”.

Bio-compatible diads



Collaboration with Prof. Tanja Gulder, Leipzig & Saarbrücken

and Prof. Ilia Solov'yov, Oldenburg

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

R.W. Fessenden, R. H. Schuler (1963) J. Chem. Phys. 1963, 39, 2147.

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

Bargon J, Fischer H, Johnson U (1967) Kernresonanz-Emissionslinien während rascher Radikalreaktionen.1. Aufnahmeverfahren und Beispiele, Zeitschrift für Naturforschung, A 22, 1551-1555.

Bargon J, Fischer H (1967) Kernresonanz-Emissionslinien während rascher Radikalreaktionen.2. Chemisch Induzierte Dynamische Kernpolarisation, Zeitschrift für Naturforschung, A 22, 1556-1562.

Ward HR, Lawler RG (1967) Nuclear Magnetic Resonance Emission And Enhanced Absorption In Rapid Organometallic Reactions, J Am Chem Soc, 89: 5518.

For personal account: Bargon J (2006) The Discovery of Chemically Induced Dynamic Polarization, Helvetica Chimica Acta, 89, 2082.

Observation of photo-CIDNP

Cocivera M (1968) Optically induced Overhauser effect in solution. Nuclear magnetic resonance emission. J Am Chem Soc 90: 3261 – 3263

The "classical" radical pair mechanism (RPM)

Closs GL and Closs LE (1969) Induced Dynamic Nuclear Spin Polarization In Photoreductions Of Benzophenone By Toluene And Ethylbenzene, J Am Chem Soc 91: 4549-4550.

Kaptein R and Oosterhoff J L (1969) Chemically induced dynamic nuclear polarization II (Relation with anomalous ESR spectra). Chem Phys Lett 4: 195-197.

Further development of method

Pulse NMR methods

Schäublin S, Wokaun A, Ernst RR (1976) The creation of off-diagonal elements in chemically induced dynamic nuclear polarization, Chem. Phys. 14, 285-293.

Schäublin S, Wokaun A, Ernst RR (1977) Pulse techniques applied to chemically induced nuclear polarization, J. Magn. Res. 27, 273-302.

Laser photo-CIDNP as surface probe

Kaptein R, Dijkstra K, Nicolay K (1978) Laser photo-CIDNP as a surface probe for proteins in solution, Nature 274, 293-294.

Polarization transfer

Closs GL, Czeropski MS (1977) Observation of a CIDNP pumped nuclear Overhauser effect, Chem. Phys. Lett. 45, 115-116.

Closs GL, Czeropski MS (1978) Polarization transfer in CIDNP experiments via scalar paramagnetic exchange mechanisms, Chem. Phys. Lett. 53, 321-324.

De Kanter FJJ, Kaptein R (1979) CIDNP trandfer via nuclear dipolar relaxation and spin-spin coupling, Chem. Phys. Lett. 62, 421-426.

Combination with flash photolysis

Hore PJ, Volbeda A, Dijkstra K, Kaptein R (1982) Photoreduction of flavin by NADH, J. Am. Chem. Soc. 104, 6262-6267.

Analysis of organic reaction mechainms

Roth HD (1987) Organic radical cations in fluid solutions: Unusual structures and rearrangements, Acc. Chem. Res. 20, 343-350.

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

Further development of liquid-state mechanims

High-field CIDNP

Chapters by Kaptein and Adrian in: Chemically Induced Magnetic Polarization, L. T. Muus, P. W. Atkins, K. A. McLauchlan & J. B. Pedersen, D. Reidel, Dordrecht, 1977.

Adrian FJ (1977(In: LT Muus et al. (eds) Chemically induced magnetic polarization), pp. 369-381.

Closs GL (1975) On the Overhauser mechanism of chemically induced nuclear polarization as suggested by Adrian, Chem. Phys. Lett. 32, 277-278.

Low-field CIDNP (for example ST□ ±1 RPM)

Closs G L and Doubleday C E (1972) Chemically induced dynamic nuclear spin polarization derived from biradicals generated by photochemical cleavage of cyclic ketones, and the observation of a solvent effect on signal intensities. J Am Chem. Soc 94: 9248 – 9249

de Kanter FJJ, den Hollander JA, Huizer AH et al (1977) Biradical CIDNP and the dynamics of polymethylene chains. Mol Phys 34: 857-874

Kaptein R & den Hollander JA (1972) Chemically induced dynamic nuclear polarization. X. Magnetic field dependence, JACS 94, 6269

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iv) Action spectroscopy

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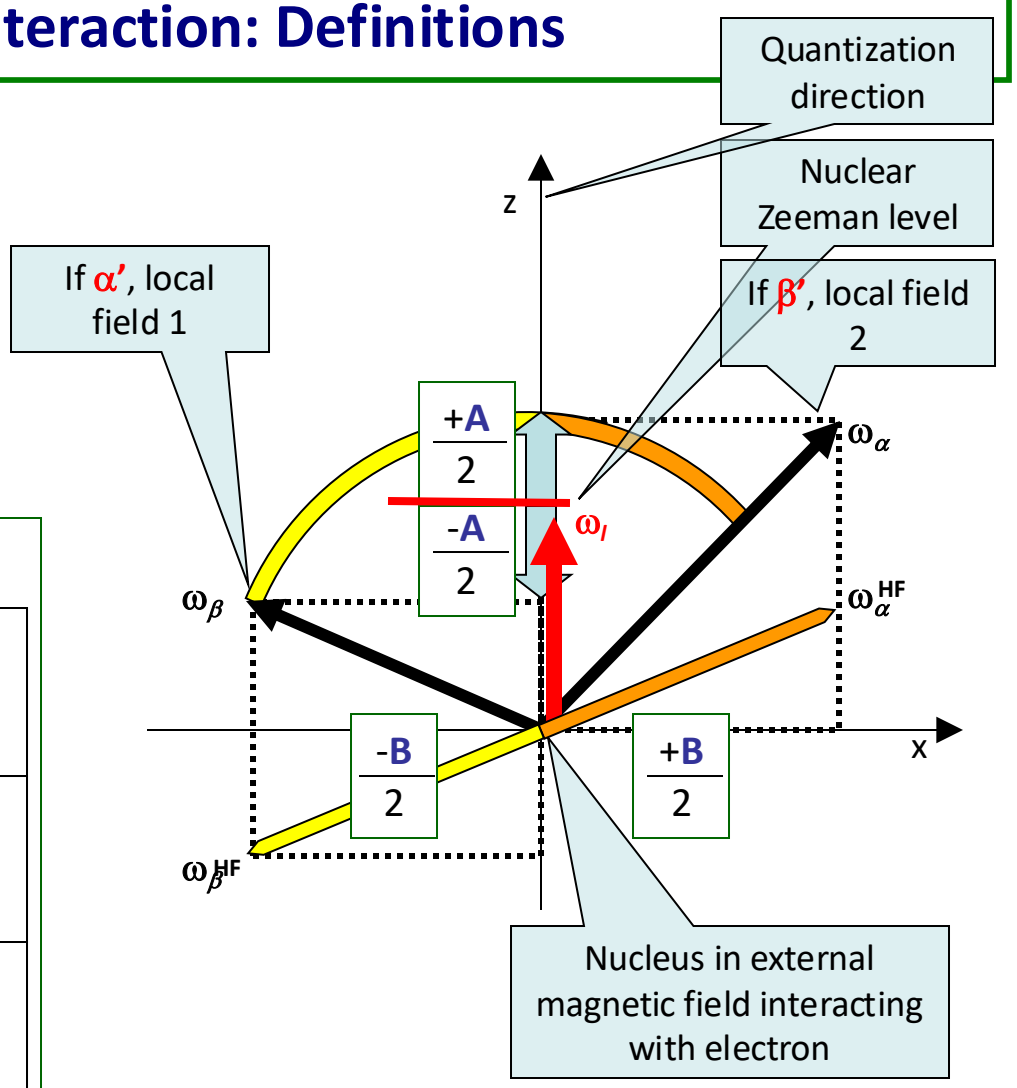
Hyperfine interaction: Definitions

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

$\mathbf{A} = (3\cos^2\theta - 1)\mathbf{T} + \boldsymbol{a}_{iso}$
$\mathbf{B} = 3\sin\theta\cos\theta\ \mathbf{T}$
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

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

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