Transient EPR

Gambarelli Serge

8th BRNO EFEPR SCHOOL
CEITEC
www.eprschool.ceitec.cz
EFEPR

Summary

- General considerations
- Instrumentation
- Major difference compared to standard EPR: non equilibrium polarisation
  - triplet states
  - radical pairs
  - CIDEP of free radicals
- Advanced EPR

General considerations, a little history

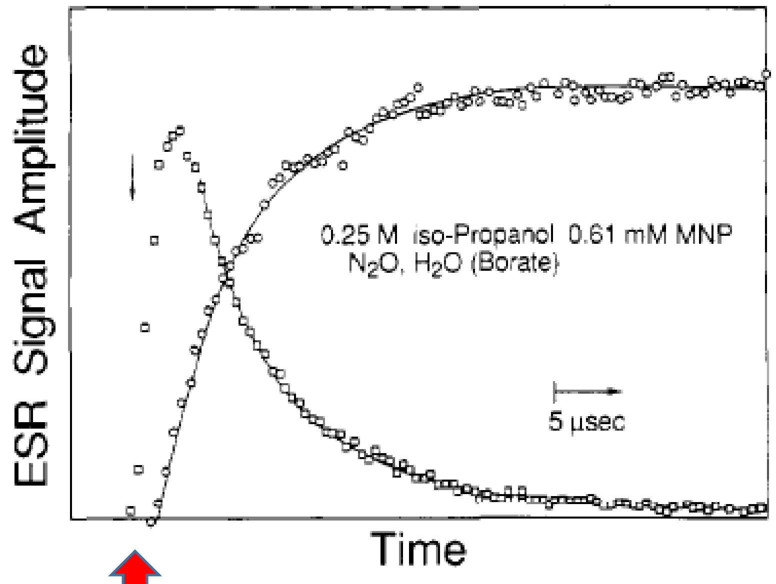
In the beginning… EPR study of photogenerated systems!
Species generated are generally paramagnetic, for instance photosynthesis = "garden of Eden of EPR". Life time tends to be short compared to EPR coupling: consequently need in situ generation.

Simplest method: EPR under illumination, study of steady states.
Possible to observe "very slow" kinetics evolution.

Major observation: if we try to observe **photogenerated** species with a good time resolution (less than 10-100 µs), completely new phenomena observable =>non-Boltzman polarisation

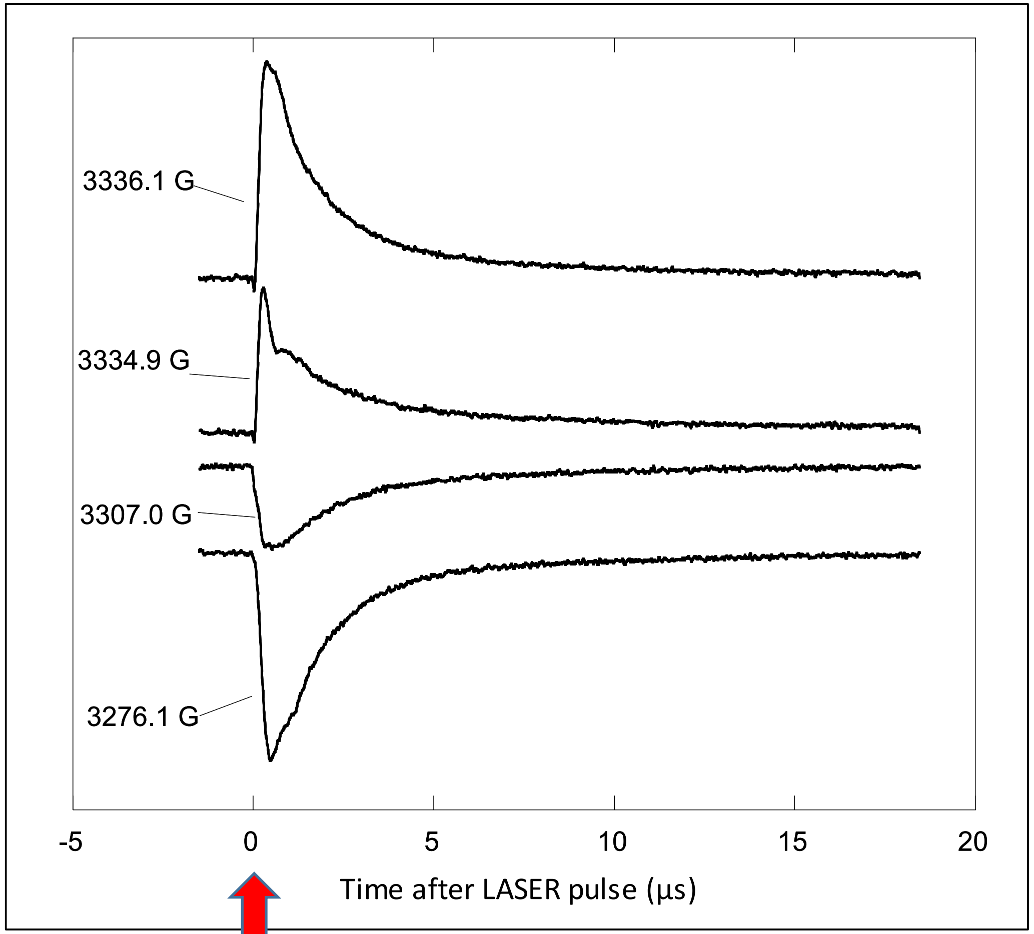
Photolysis vs Radiolysis

Normal situation

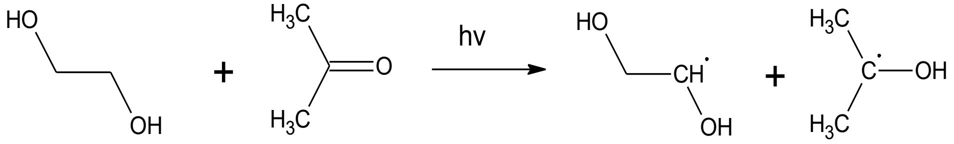


0.5-μs pulse of 2.8 MeV electrons

Unusual line phase

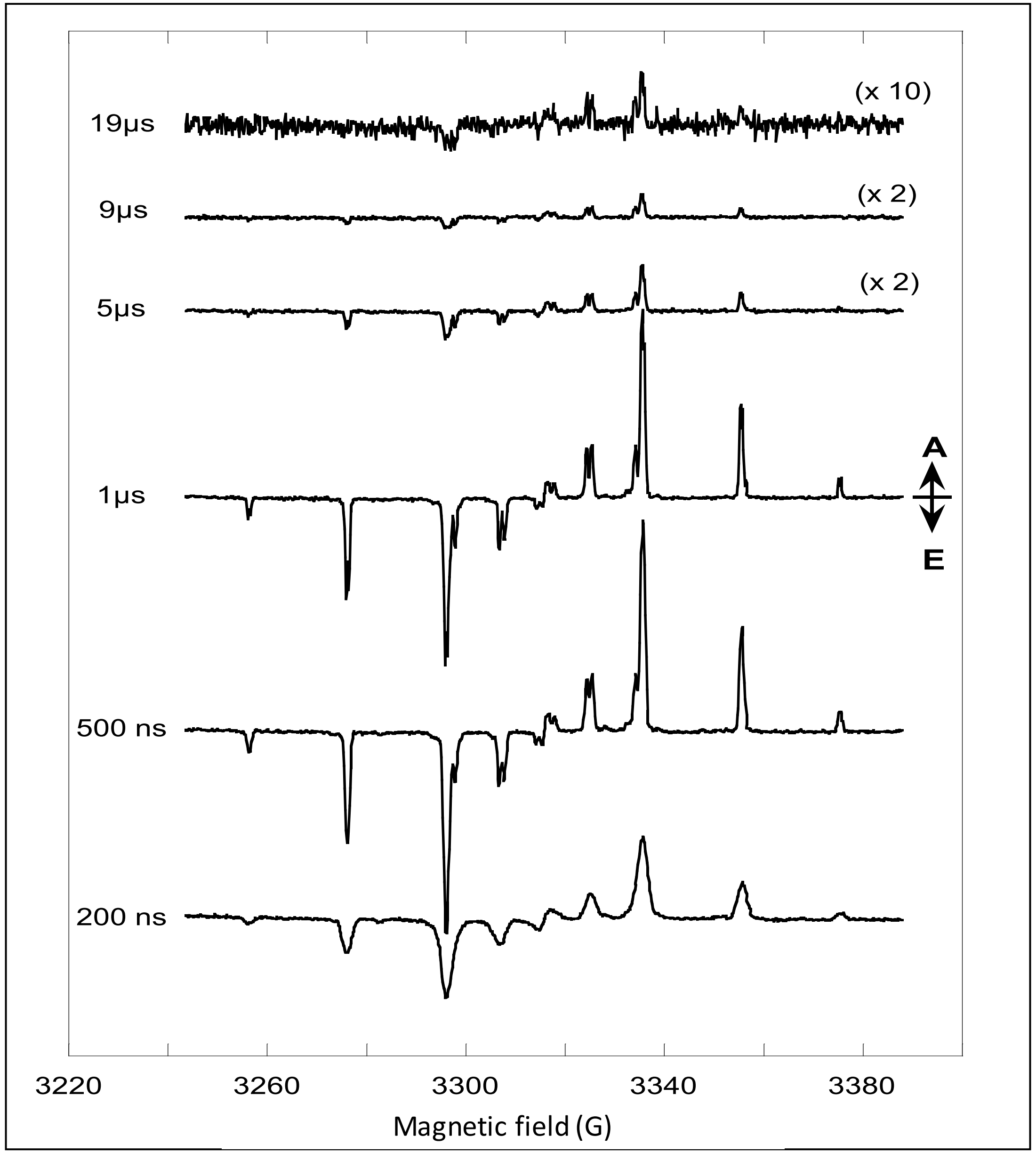


LASER

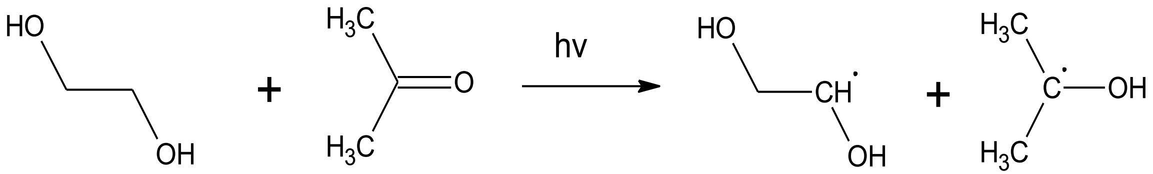


Madden, Taniguchi, JACS, 1991, 113, 5541

Simple example



Photochemical reaction in solution

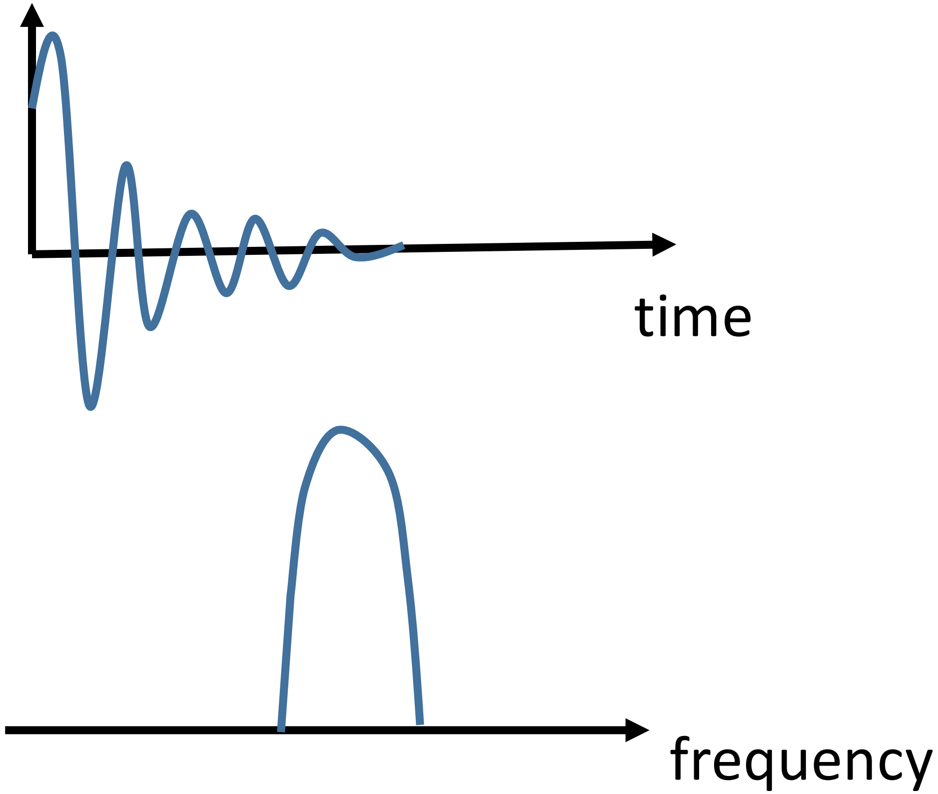


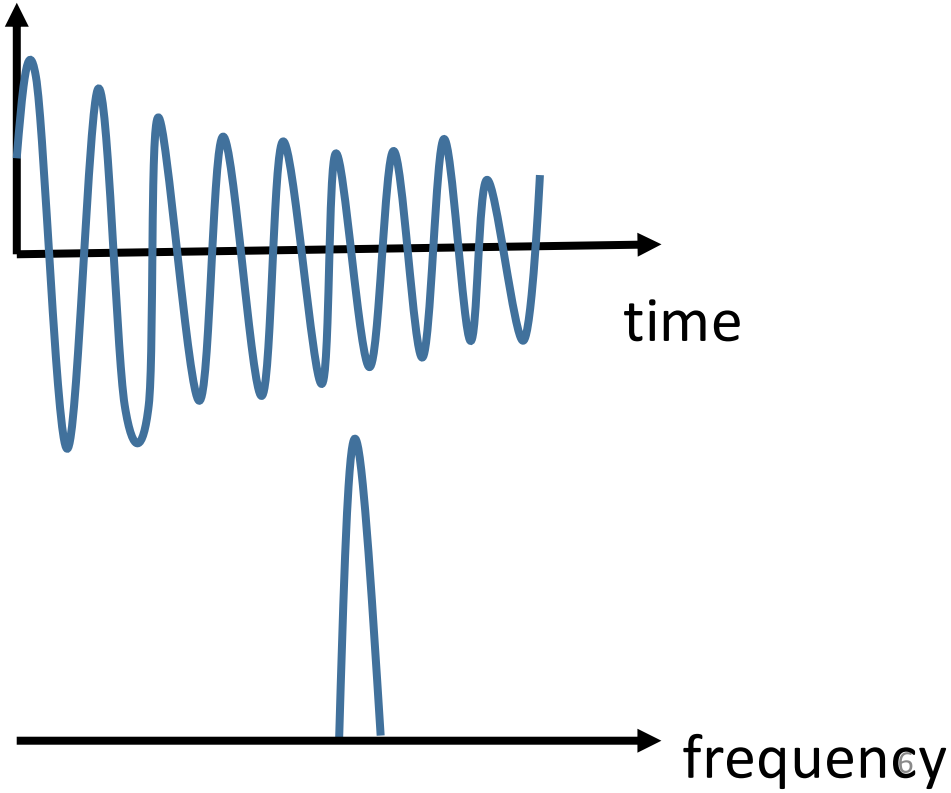
Main points :
- line narrowing
- unusual emission/absorption pattern
- centrosymetric spectrum
- rapid intensity decrease

Time resolution of any spectroscopy

Basic principle: in spectroscopy, lifetime limits the resolution of observation

General idea: to measure energy (frequency) with high precision, we must measure the system for a long time (most evident with an FID measurement).





Time resolution of EPR spectroscopy

Application to EPR:
For g=2 species, 2.8 MHz correspond to 1 G

Difficult to detect small hyperfine species (1 – 10 G) with rapidly decaying species
Quite easy to detect ZFS of triplet with D around 100 G

N.B. these numbers correspond to the theoretical maximum time resolution.
In practise, time resolution can be much worse due to instrumental/practical constraints.

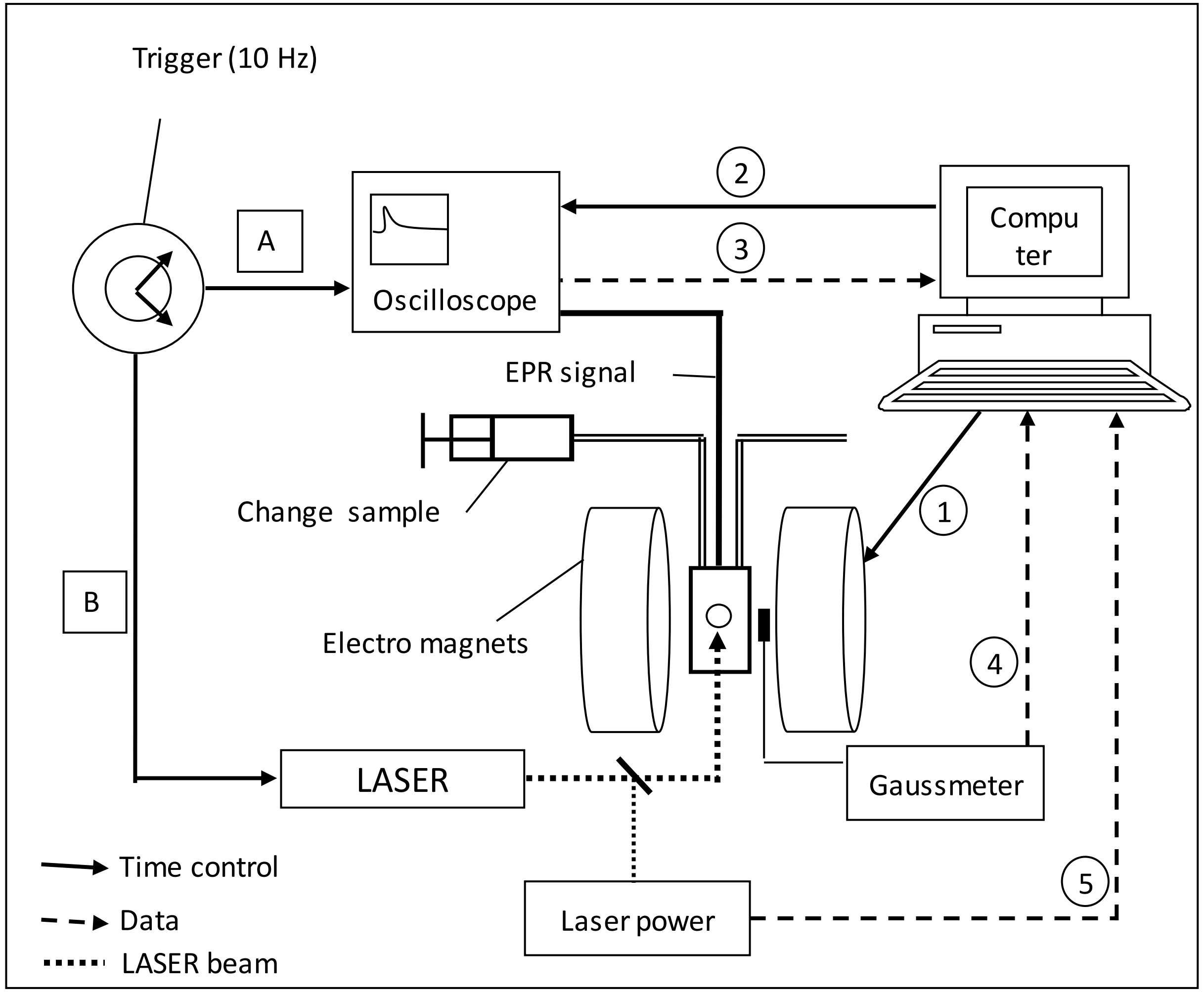
Advanced EPR sequences (e.g. HYSCORE, pENDOR) last at least several µs.

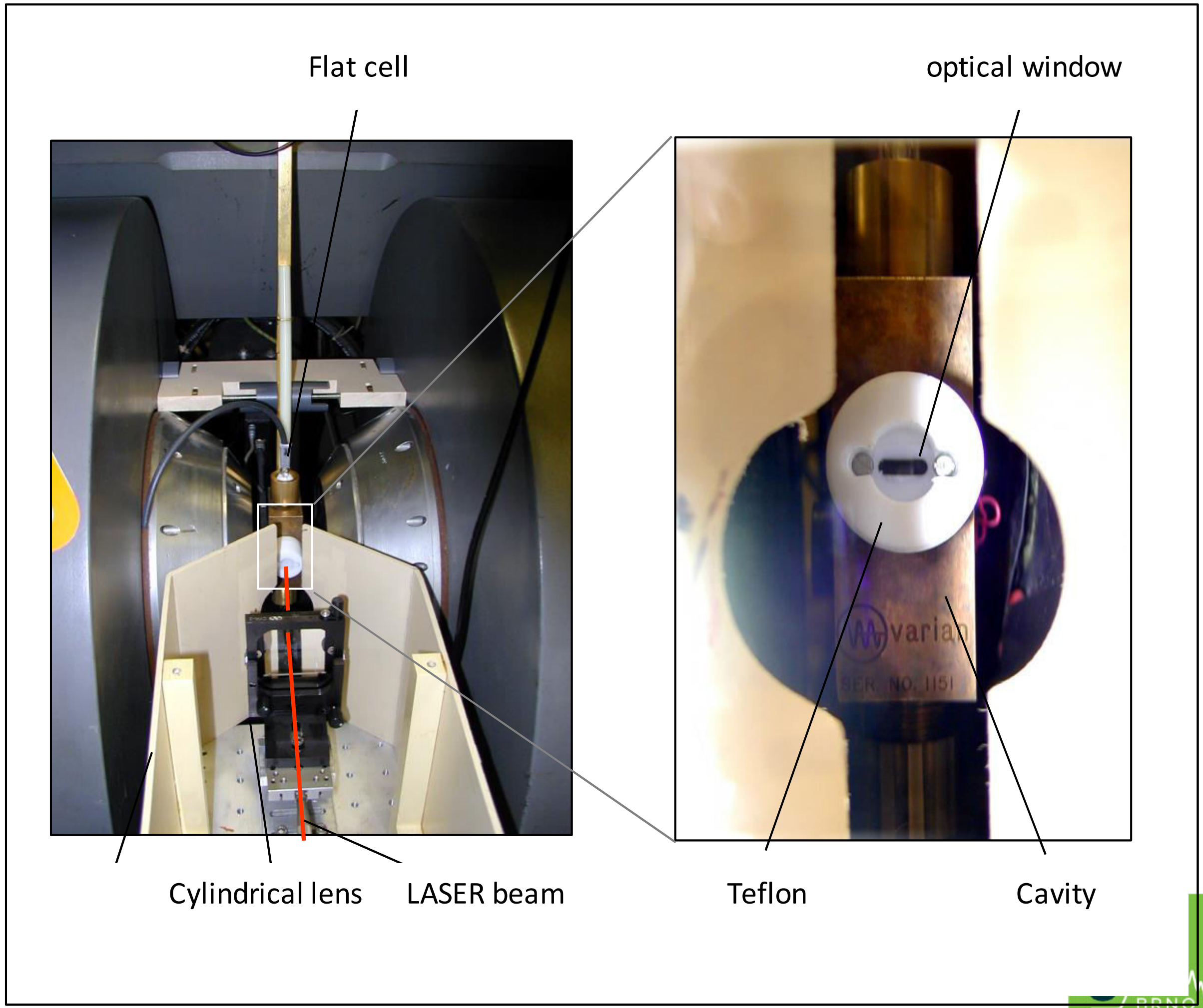
Practical issues

- Sample degradation (bleaching) → altered sample
- No field modulation (too slow) → sensitivity loss for CW
- Laser repetition frequency → sensitivity loss for pulsed EPR

Basic setup

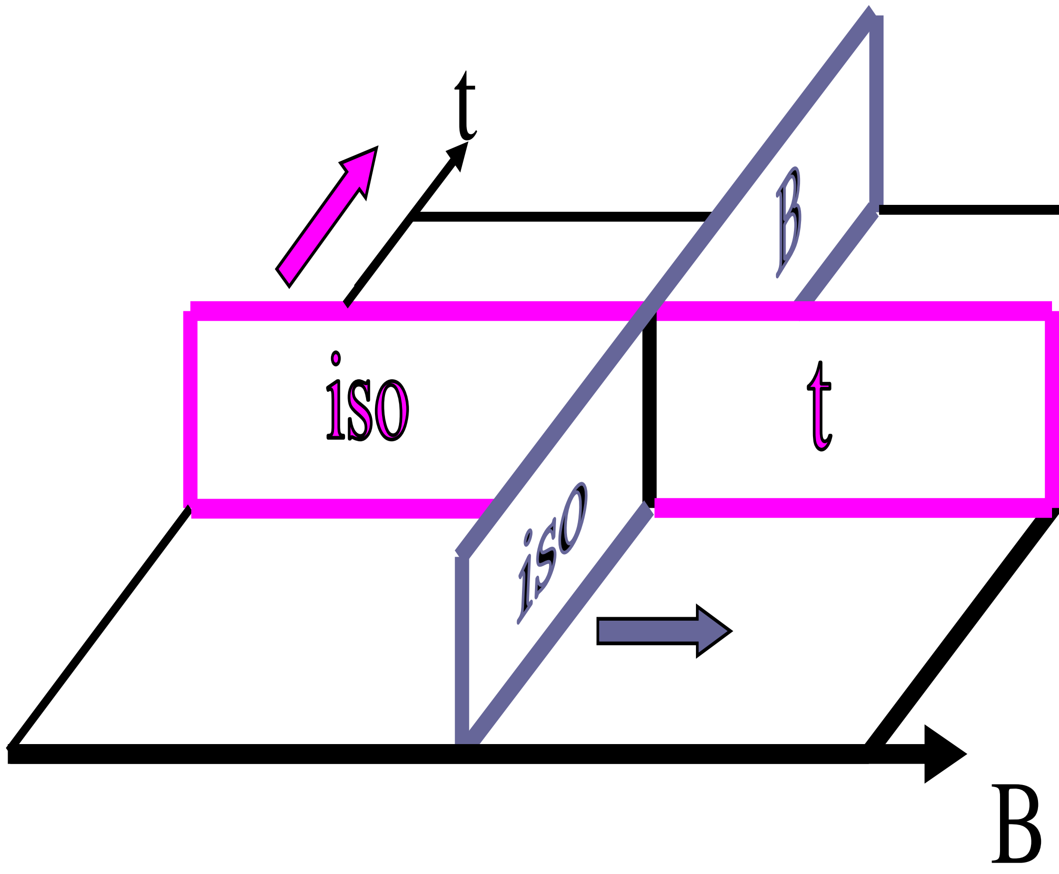
UV light (266 nm), liquid sample, CW EPR





For visible wavelengths, easier to use optical fiber

How to acquire a 2D (time, B) spectrum



Major limitation: impossible to rapidly change magnetic field. Even rapid scan methods are too slow.

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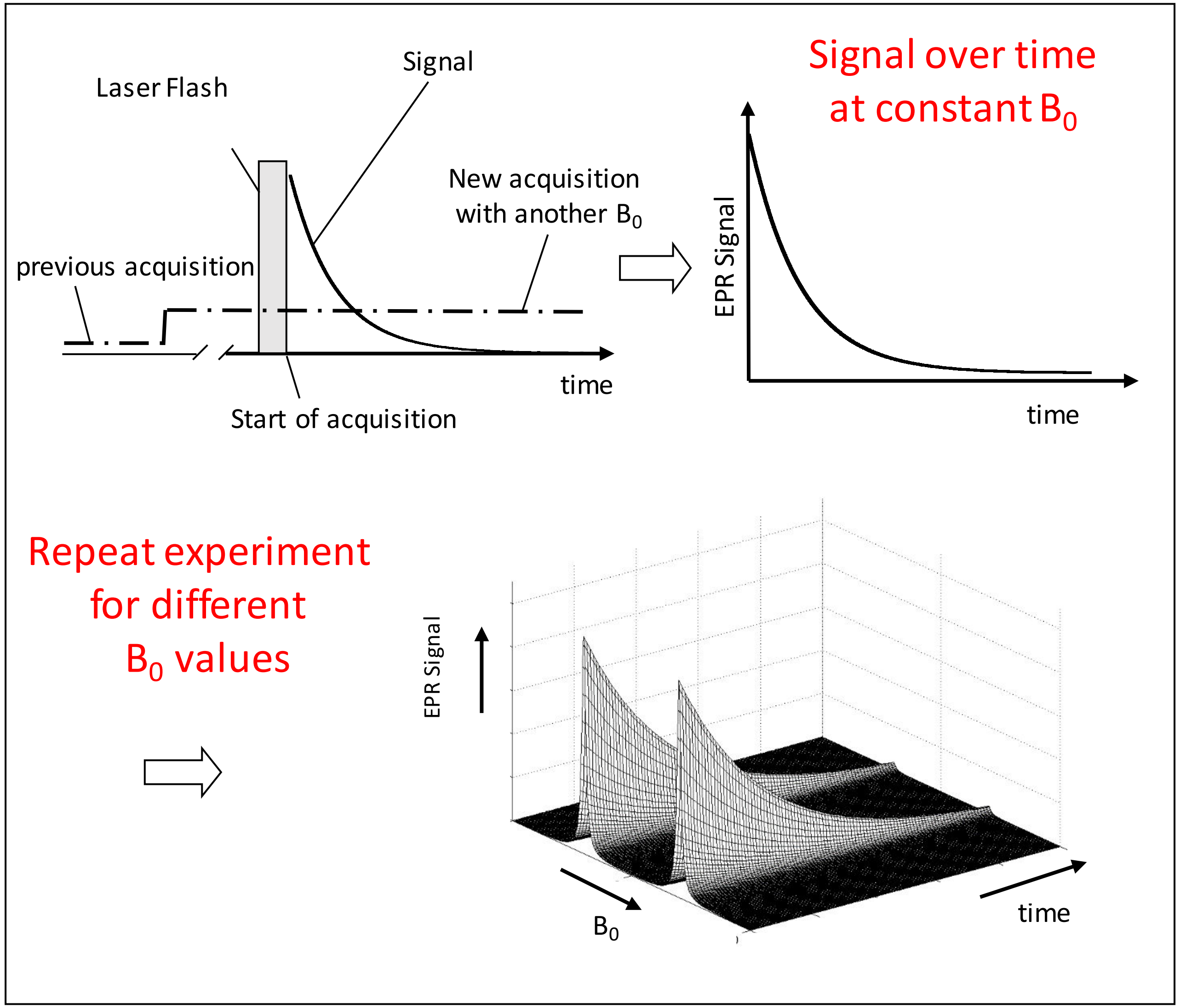
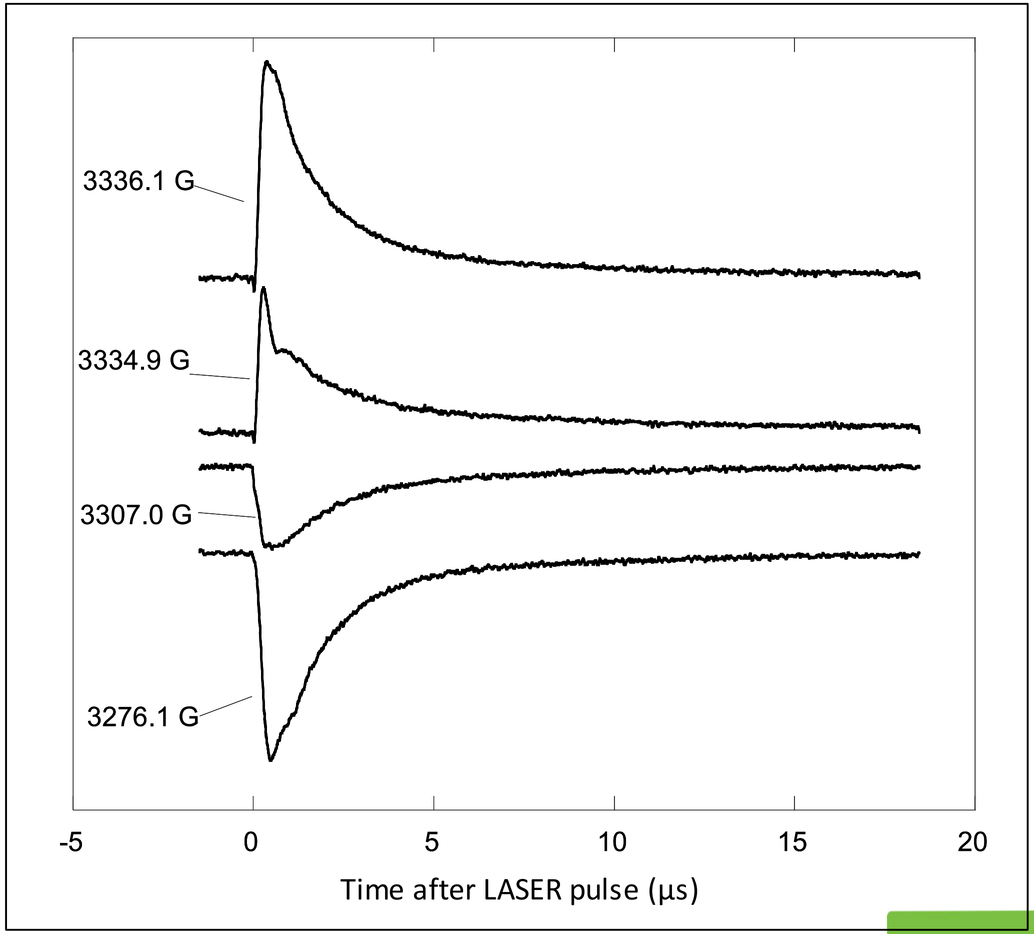
First acquisition mode: constant B





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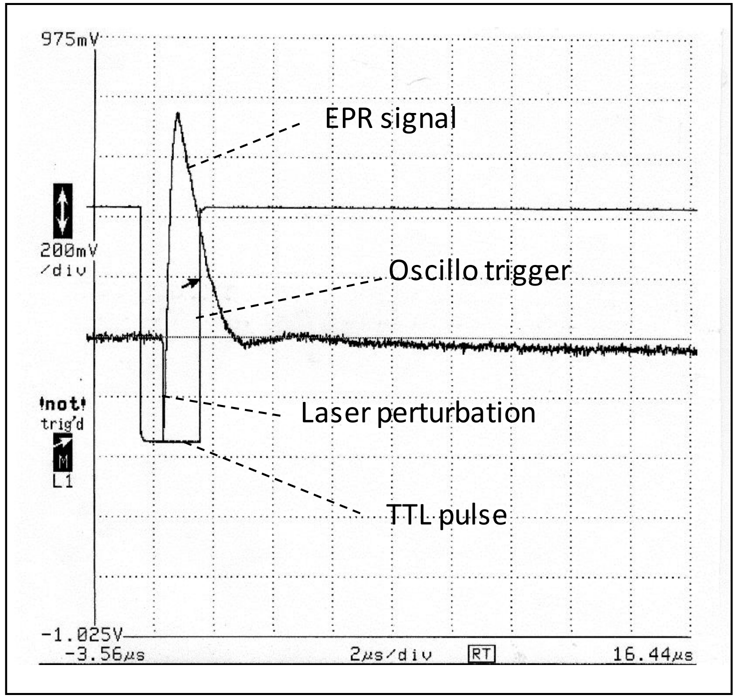
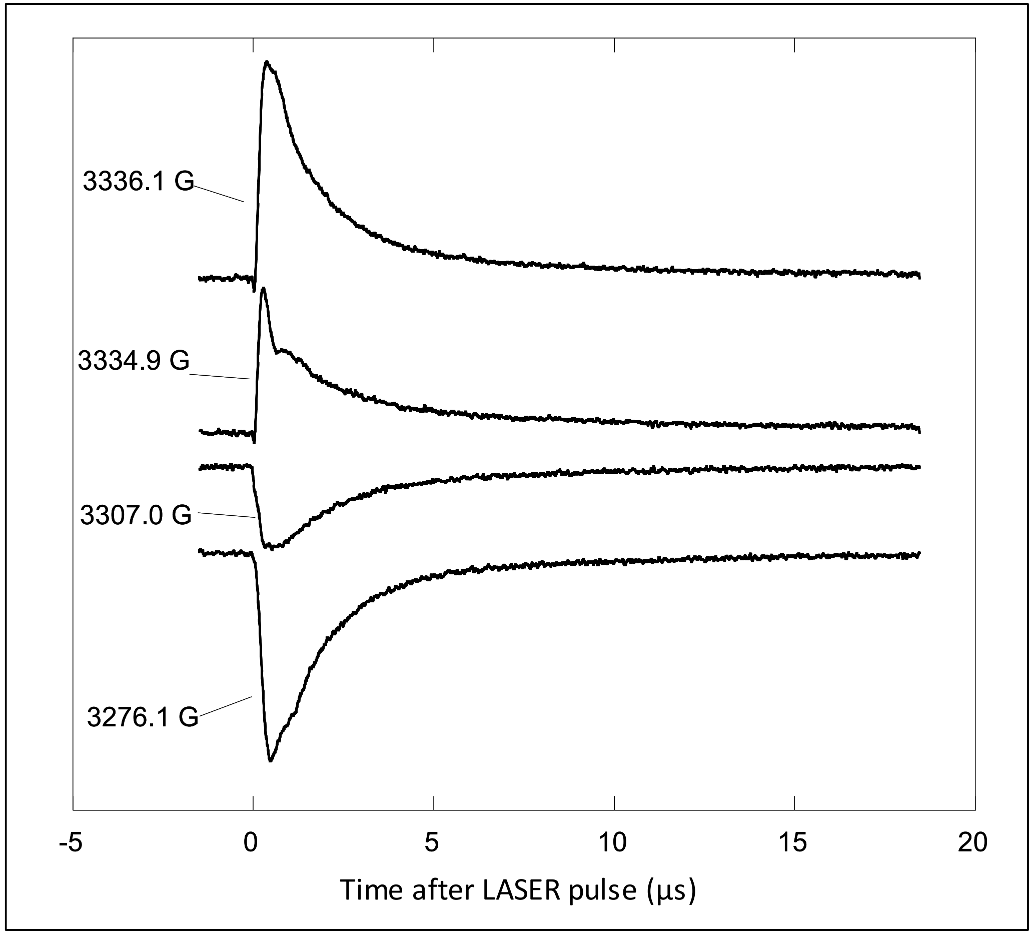
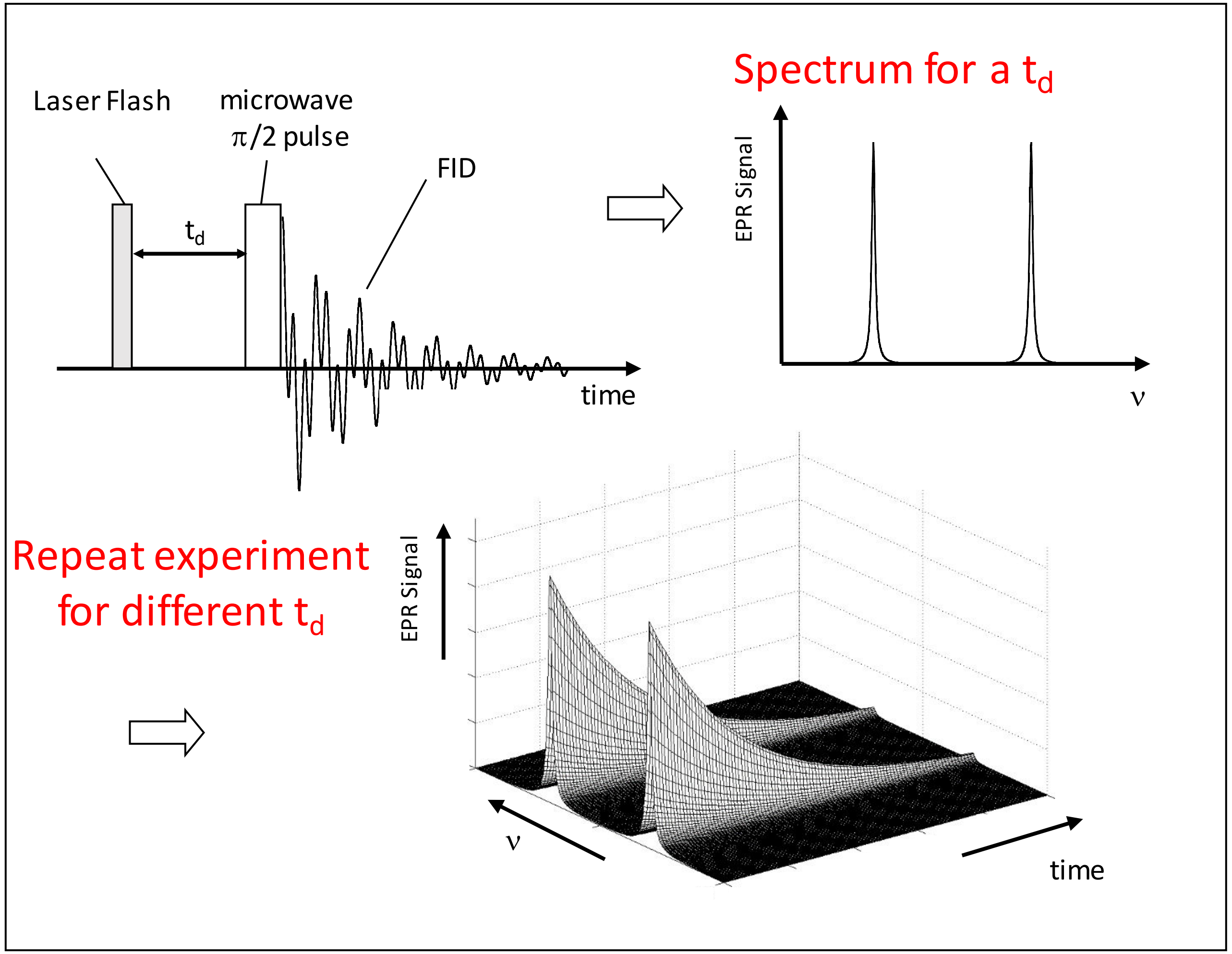
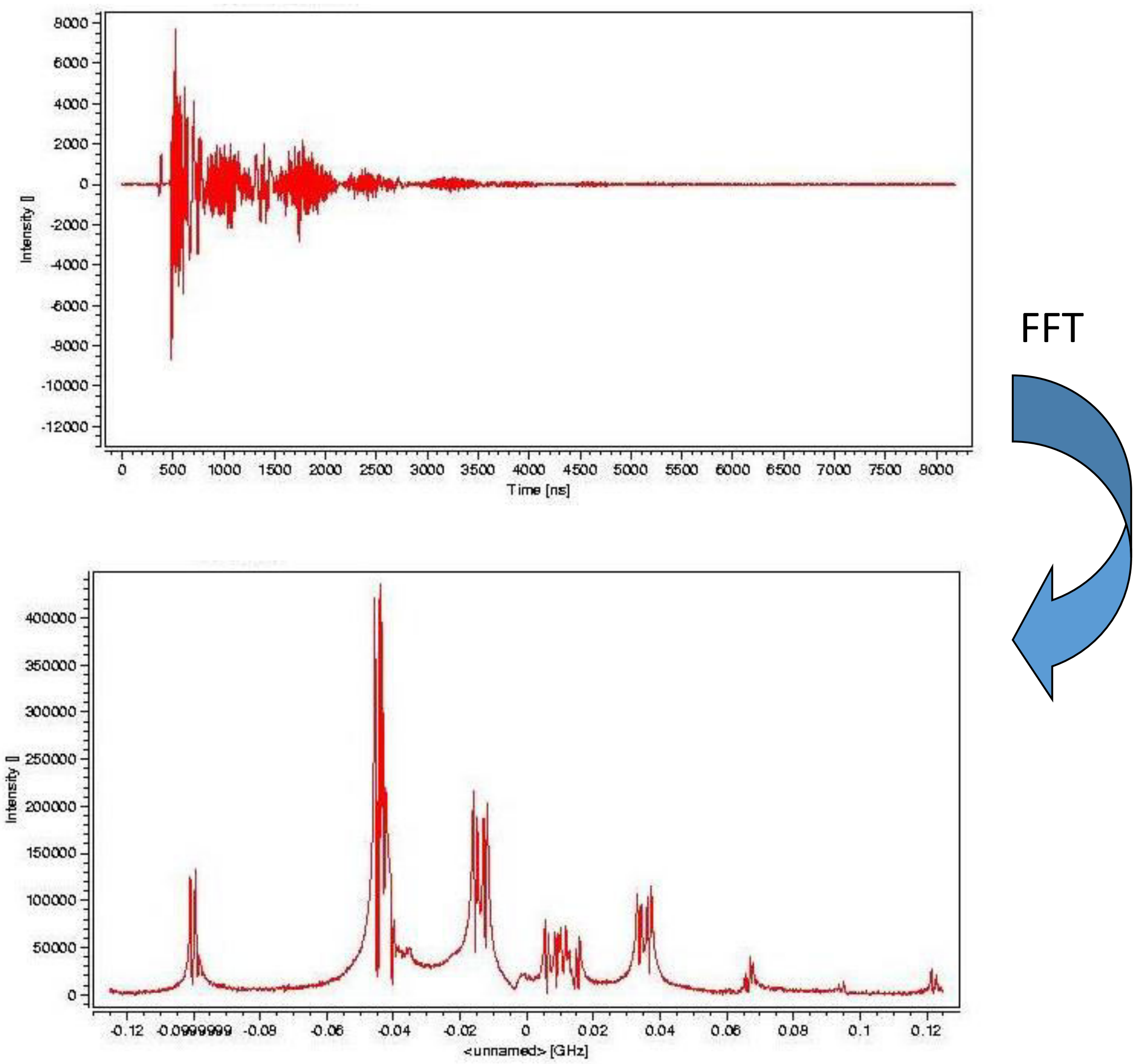




Second acquisition mode



Second acquisition mode



- Only possible with pulsed measurement mode.
- Narrow species only.
- Problem if the signal is broad (triplet…): only measures a small part at a time.
- Especially good for systems with numerous narrow lines (multiplex advantage).

Intensity of an EPR transition

In (EPR) spectroscopy, intensity of a transition between two levels is proportional to:

- transition probability (quantum mechanics)
- population difference between these two levels (cf. Curie's Law)

In absence of saturation, polarisation rather low.
Line always in emission (without lock-in)

$$r = \frac{P_h}{P_l} = e^{-\Delta E/kT} = e^{-g\mu B/kT}$$

Classical methods to increase population difference:

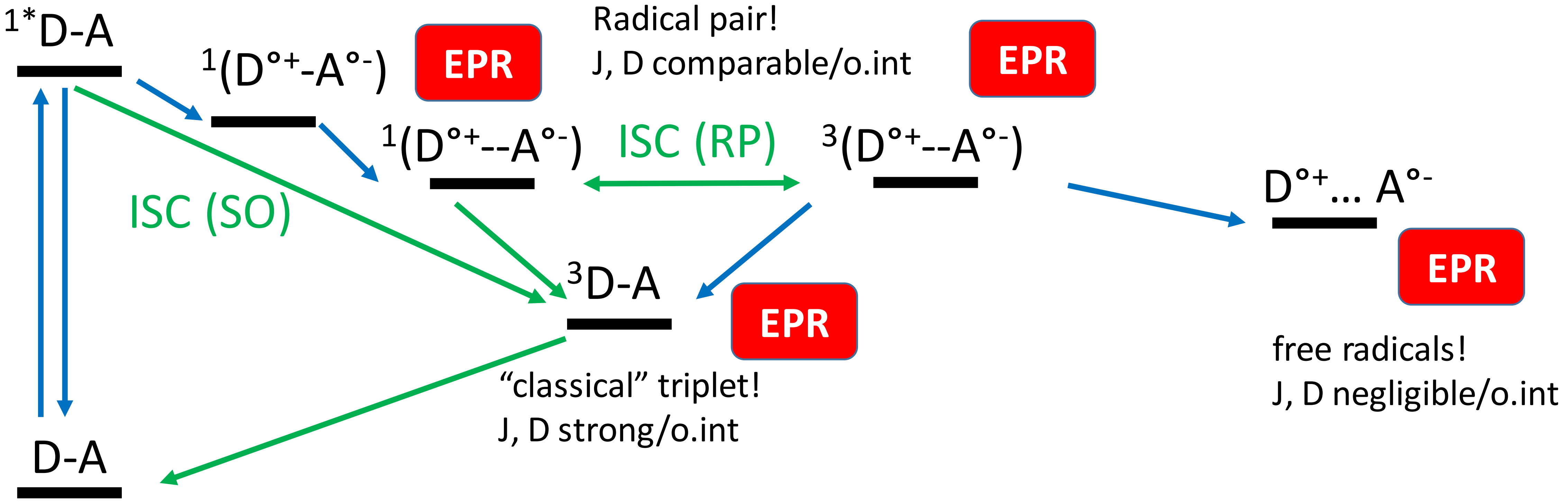
- increase static magnetic field
- decrease temperature

Population difference in EPR:
Room temperature, X band, g=2, r = 0.9985
4 K, X band, g=2, r = 0.892
4 K, W band, g=2, r = 0.32

In photogenerated species, non-Boltzmann populations with huge polarisation

If non-Boltzmann population, return to equilibrium with characteristic time T_1 (cf. inversion recovery experiment in pulsed EPR)

General overview (simple case!)



o.int : other interactions (Zeeman, hyperfine…) in the hamiltonian

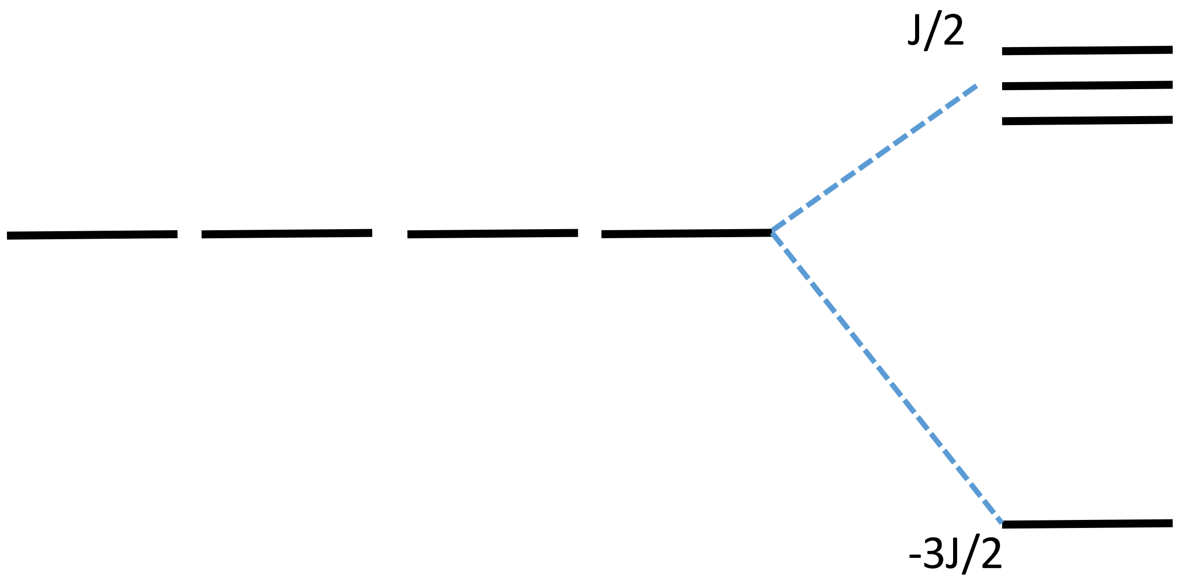
Polarization in transient EPR is the result of all these processes

Spin states have a major impact!

Triplet /Singlet states

$$H = J(S^2 - 3/2) + \mathbf{SDS} + Ze_A + Ze_B$$
$$= J(S^2 - 3/2) + D(S_z^2 - S^2/3) + E(S_x^2 - S_y^2) + Ze_A + Ze_B$$

$T_1 = \alpha_A\alpha_B$
$T_0 = (\alpha_A\beta_B + \beta_A\alpha_B)/2^{0.5}$
$T_{-1} = \beta_A\beta_B$
$S_0 = (\alpha_A\beta_B - \beta_A\alpha_B)/2^{0.5}$



Singlet and triplet states well isolated from each other

Triplet /Singlet states

If J and D strong enough, we can work only in the triplet state

$$H = D(S_z^2 - S^2/3) + E(S_x^2 - S_y^2) + g\beta B S_z$$
$$= D(S_z^2 - S^2/3) + E(S_x^2 - S_y^2) + \omega S_z$$

$$H = \begin{pmatrix} D & 0 & E \\ 0 & 0 & 0 \\ E & 0 & D \end{pmatrix} - 2D/3$$

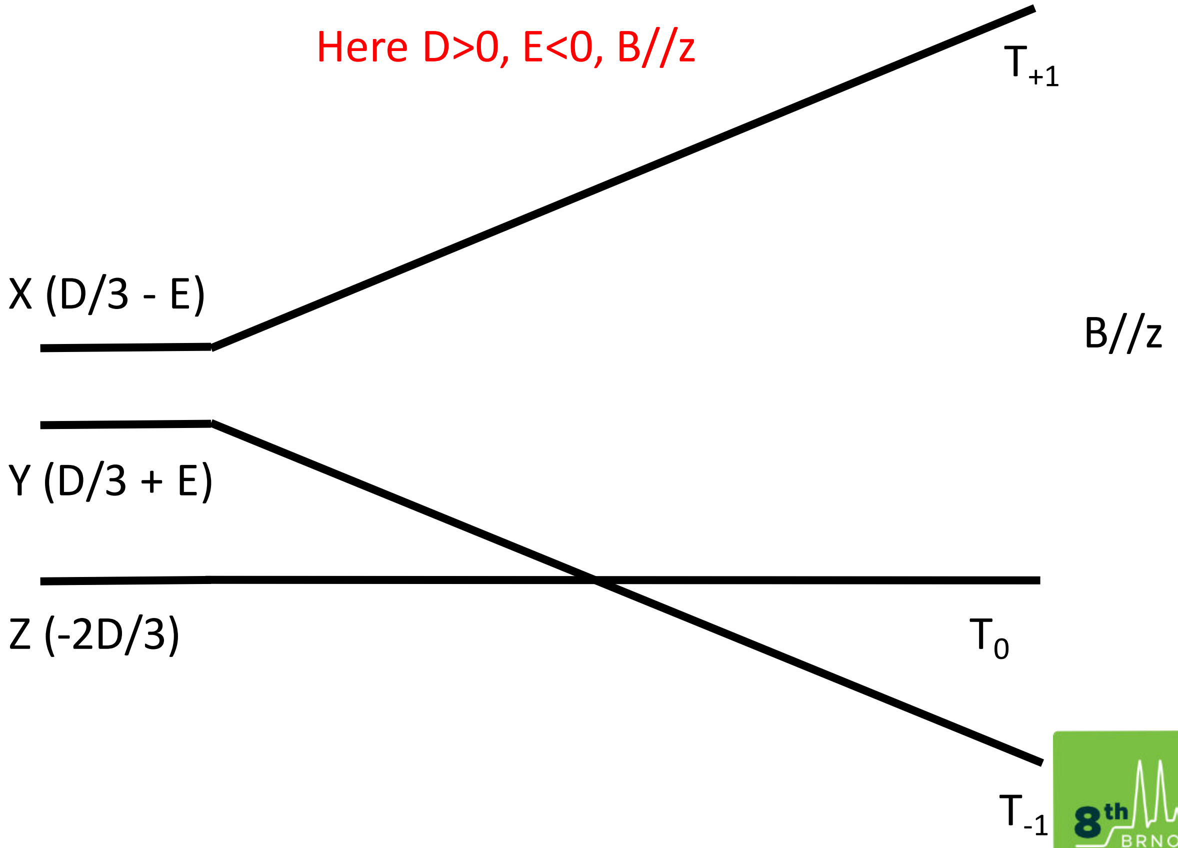
$Z = T_0$ $\quad E_n = -2D/3$

$X = (T_{+1} - T_{-1})/2^{0.5}$ $\quad E_n = D/3 - E$

$Y = (T_{+1} + T_{-1})/2^{0.5}$ $\quad E_n = D/3 + E$

Zero field eigenfunctions and eigenvalues
(**T_0 , T_{+1} , T_{-1} are the high-field eigenfunctions**)

Here D>0, E<0, B//z



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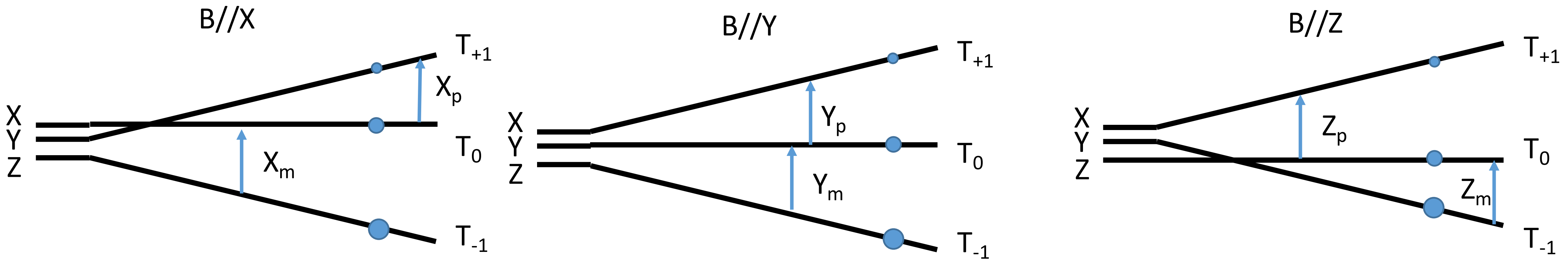
Powder spectrum with Boltzman population

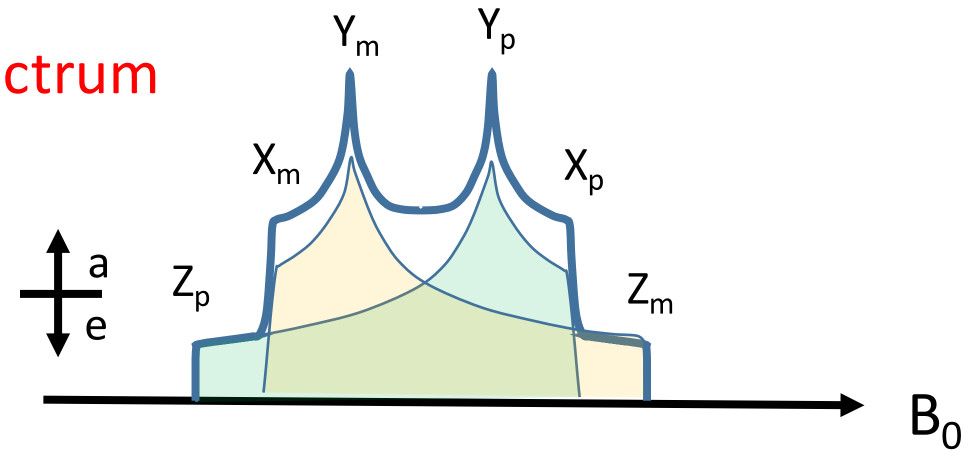
ZFS << Zeeman << J

Classical case

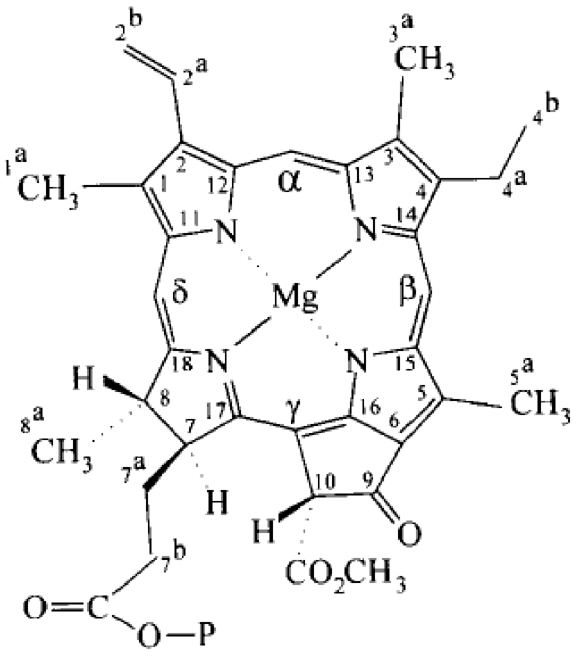


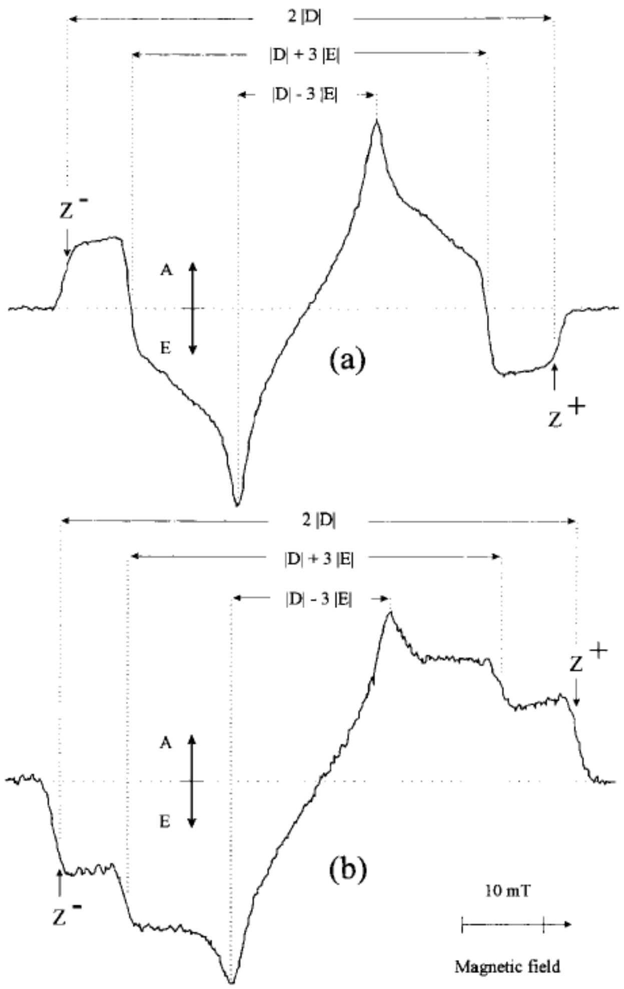
No field modulation:

In CW classical EPR, we obtain derivative of this spectrum



TR–EPR: Prototypical example





Without modulation, and after light excitation

- unusual sign patterns
- patterns differ from each other

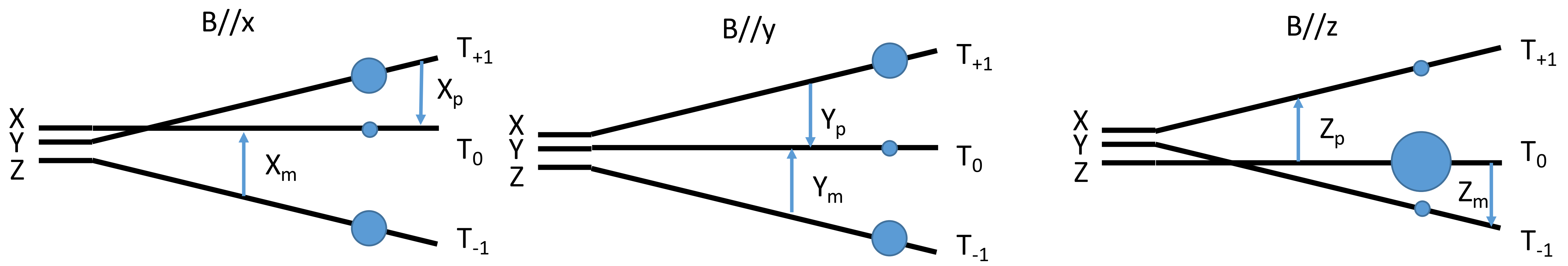
But basically the same compounds (complex vs isolated)
Note that D and E are **(nearly)** the same!

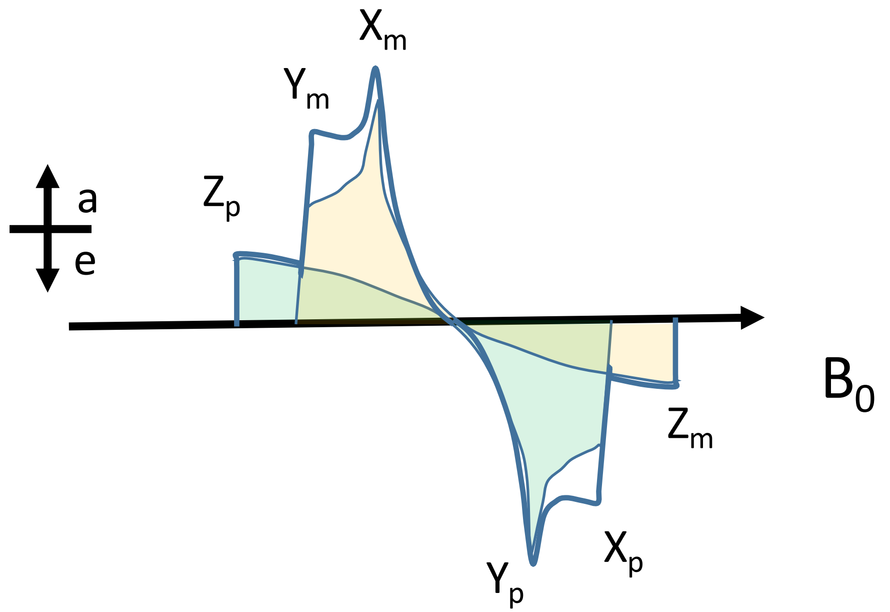
Why is polarisation so different?

Di Valentin, …, Möbius, Chem Phys Lett, 1996, 248, 434

Polarisation from spin orbit ISC

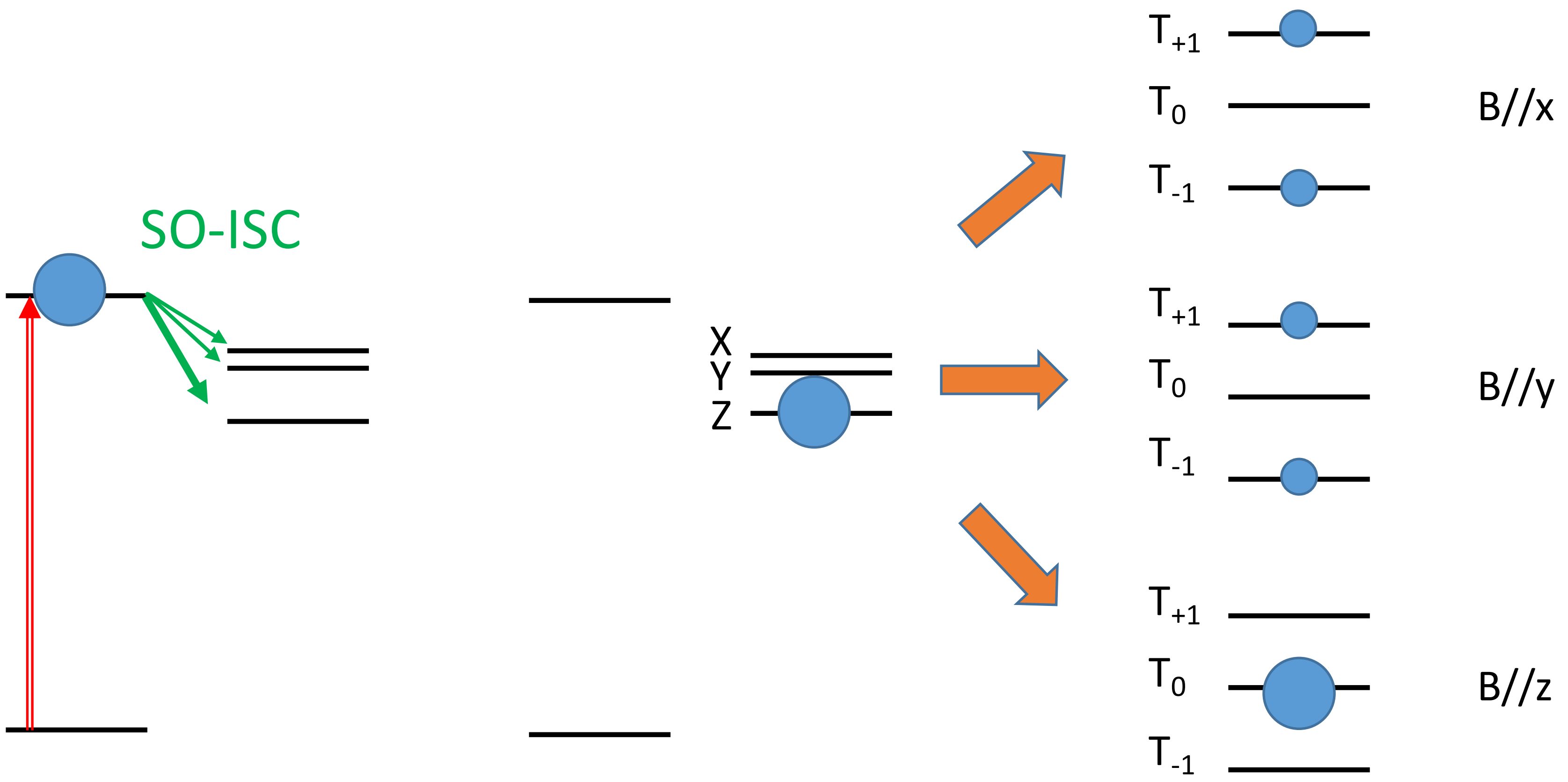
ZFS << Zeeman << J





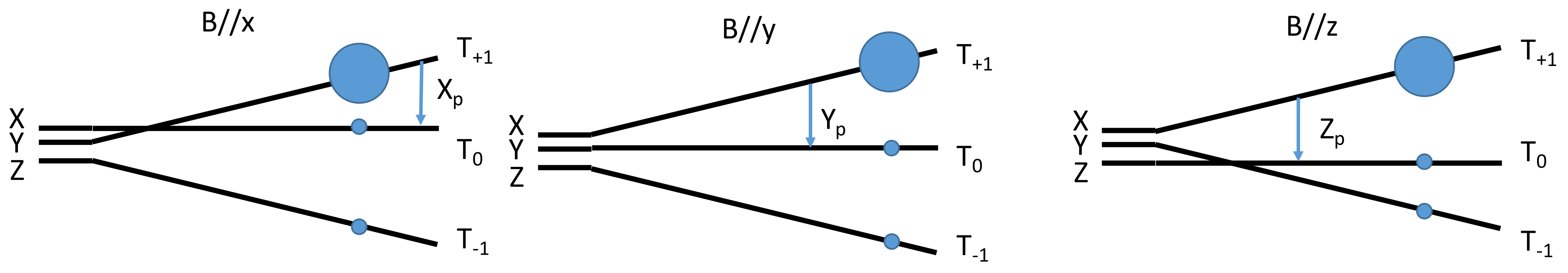
Spin orbit ISC rules

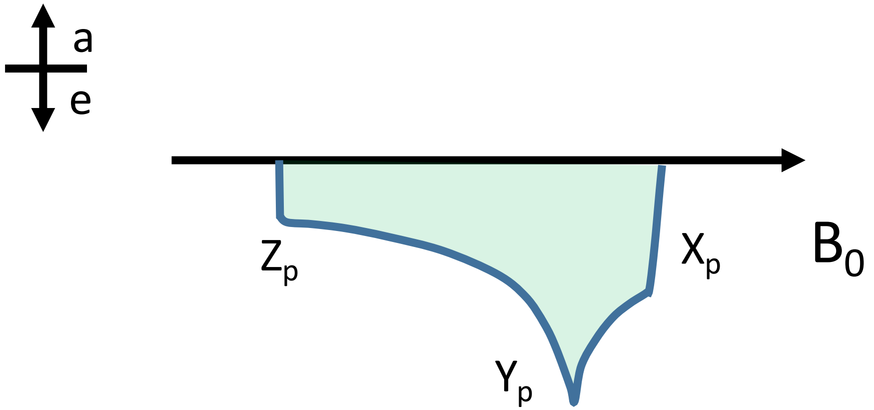
Spin orbit ISC efficiency is not the same with X Y Z states (0 field)
We observe the "projection" of these populations on high field functions T_{+1} T_0 T_{+1}
(see Budil and Thurnauer, BBA, 1991, 1057, 1)



Polarisation from RP ISC

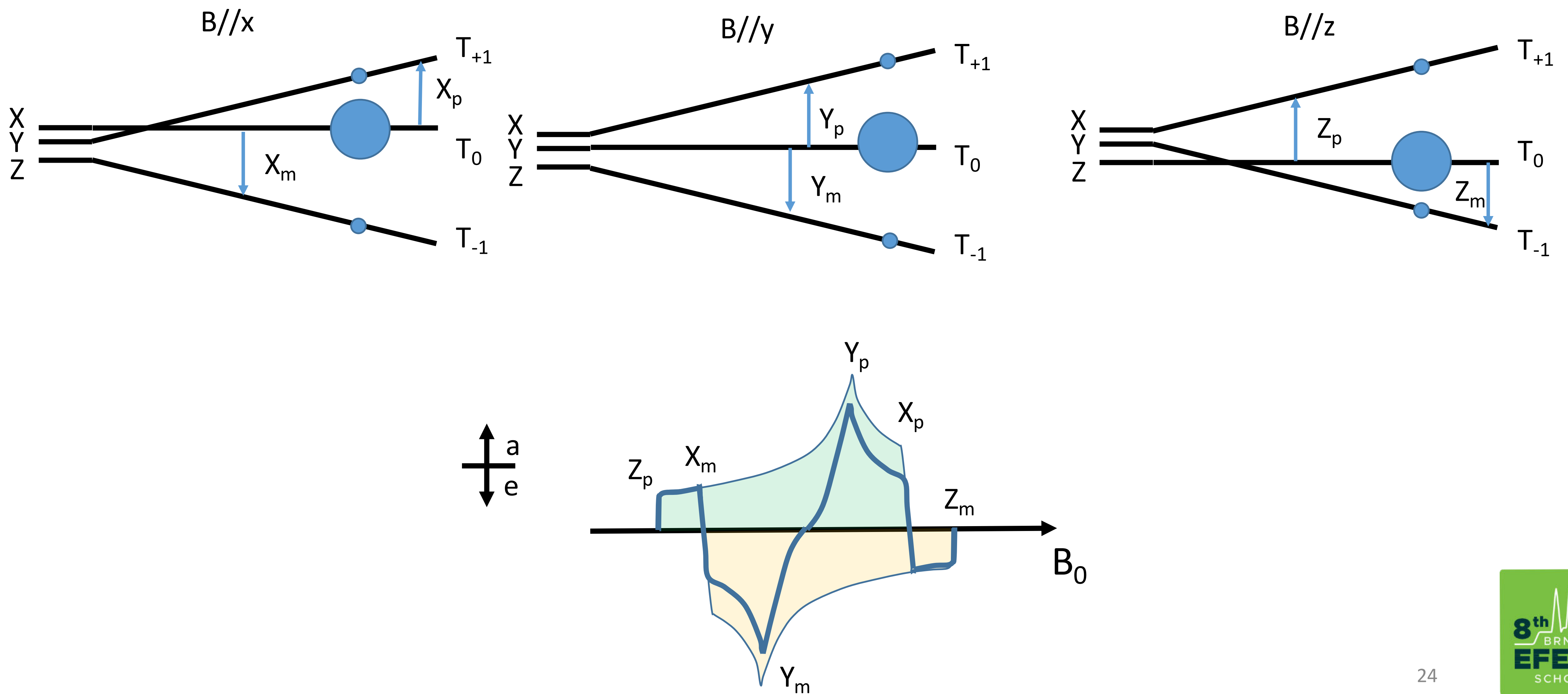
ZFS << Zeeman << J



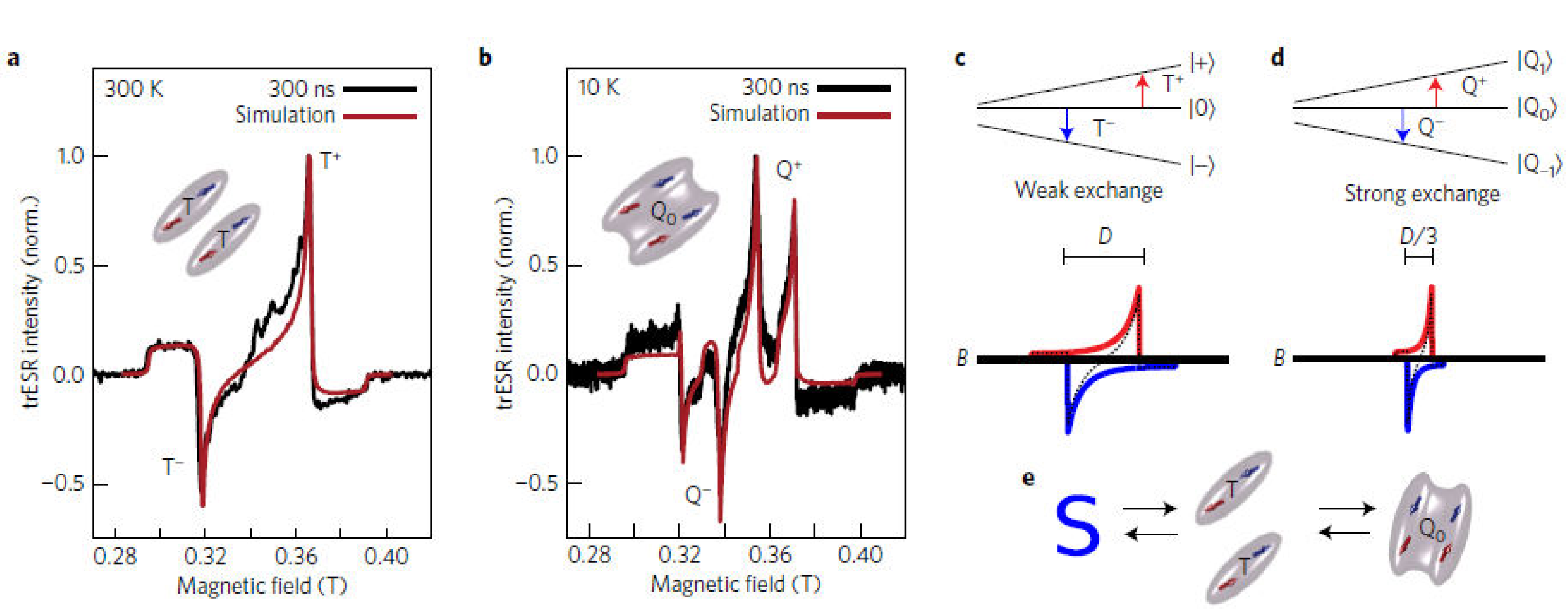


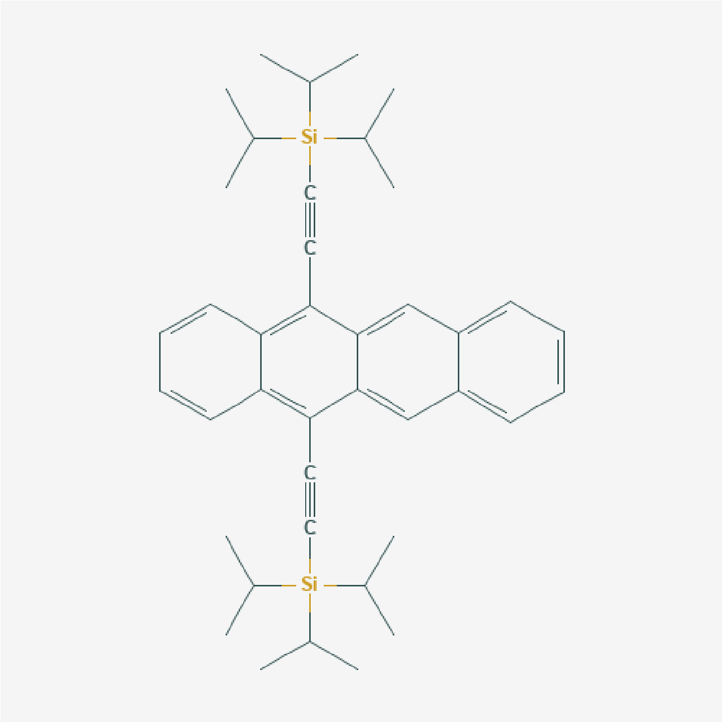
From (RP) ISC

ZFS << Zeeman << J



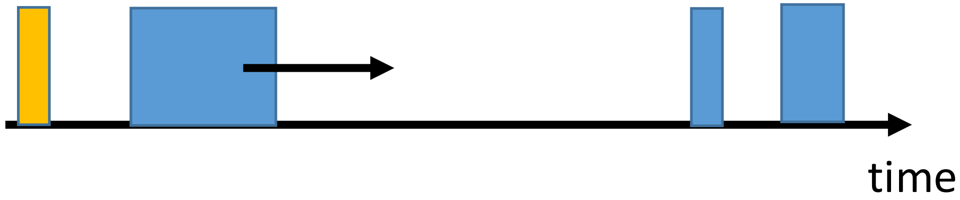
Same phenomena with more complex systems: Singlet Fission



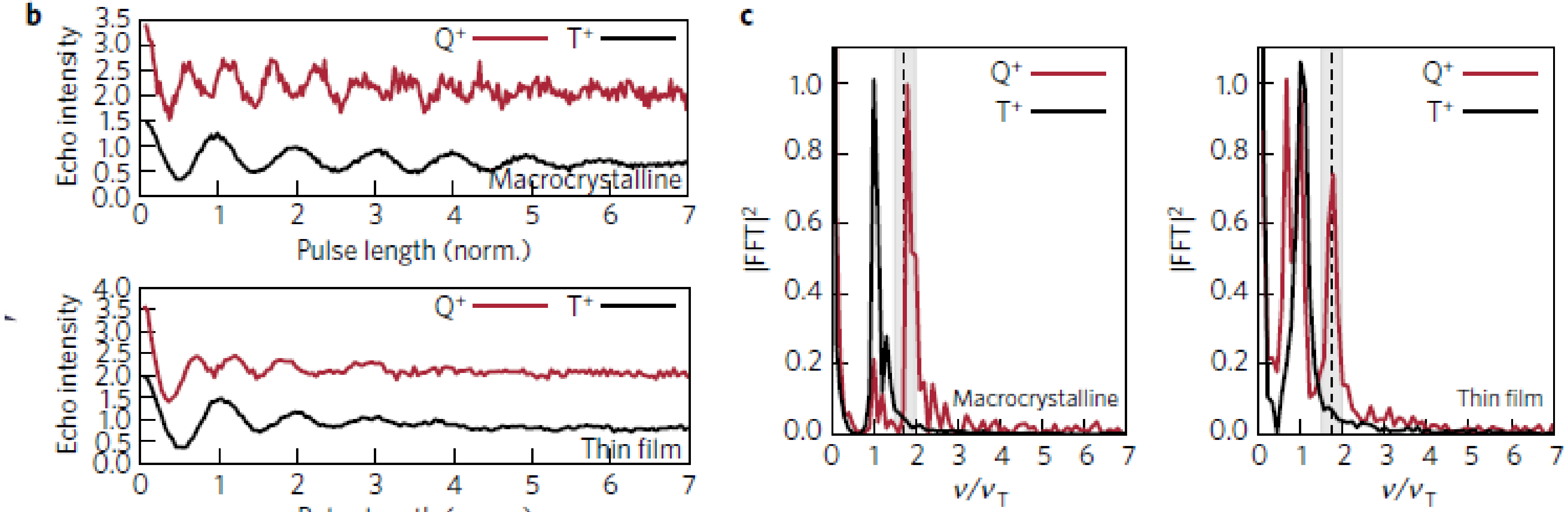


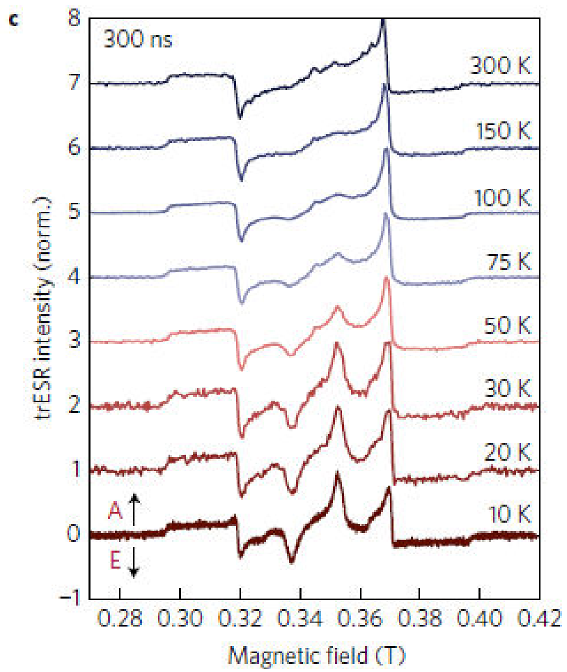
Weiss, ..., Behrends, Nature Physics, 2017, 13, 176

Singlet fission

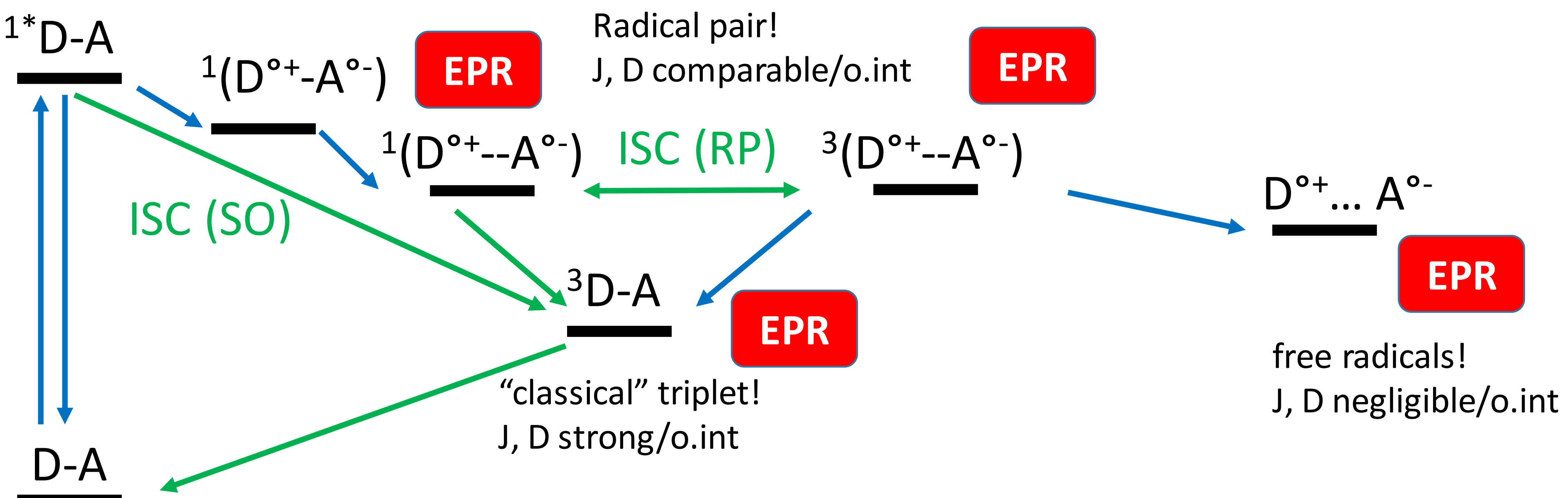


Nutation experiment : Quintet proof





General overview (simple case!)



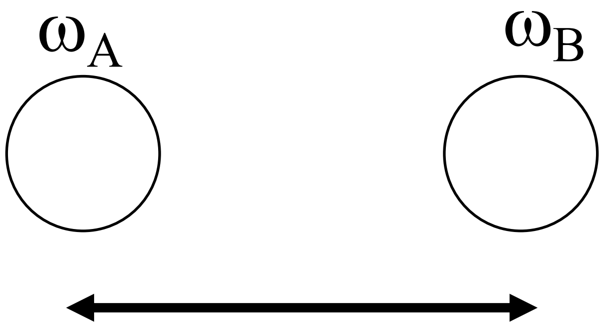
o.int : other interactions (Zeeman, hyperfine…) in the hamiltonian

Polarization in transient EPR is the result of all these processes

Spin states have a major impact!

A key intermediate

Photogenerated Radical pair (RP)



A radical pair can be "created"
- in a singlet state
- in one of the triplet states

$$H = J(S^2 - 3/2) + \mathbf{SDS} + Ze_A + Ze_B$$
$$= J(S^2 - 3/2) + D(S_z^2 - S^2/3) + E(S_x^2 - S_y^2) + Ze_A + Ze_B$$

- Exchange interaction J (exponential decay with r)
- Dipolar interaction ($1/r^3$ decay)
- Different resonance frequencies (g and hyperfine included)

RP Hamiltonian

We neglect dipolar interaction (for the moment)

$$\begin{array}{cccc} T_1 & T_0 & S_0 & T_{-1} \end{array}$$

$$\begin{pmatrix} J/2+\Omega & 0 & 0 & 0 \\ 0 & J/2 & \Delta & 0 \\ 0 & \Delta & -3J/2 & 0 \\ 0 & 0 & 0 & J/2-\Omega \end{pmatrix}$$

$$\Delta = 0.5(\omega_A - \omega_B)$$

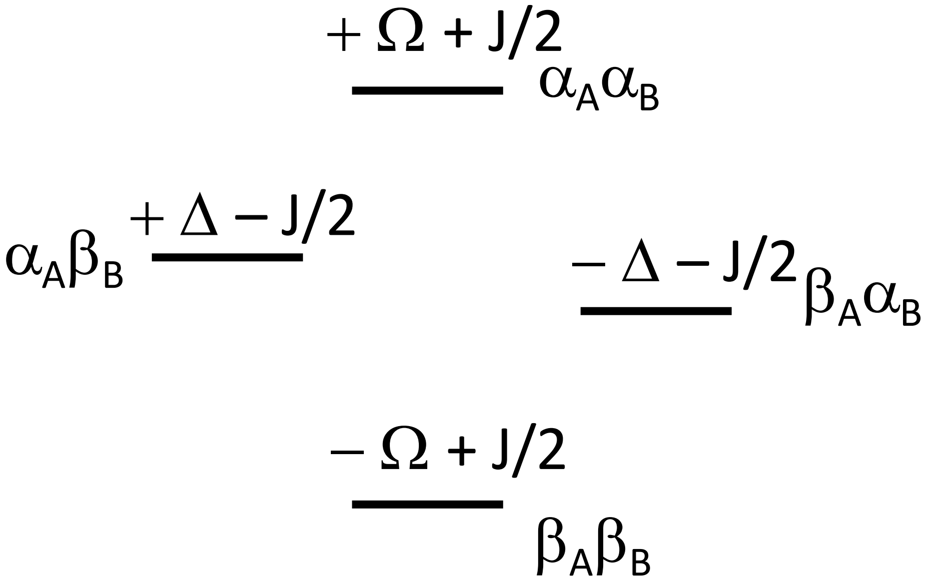
$$\Omega = 0.5(\omega_A + \omega_B)$$

Triplet-singlet functions are eigenfunctions of H (S good quantum number) if $|J| \gg |\Delta|$

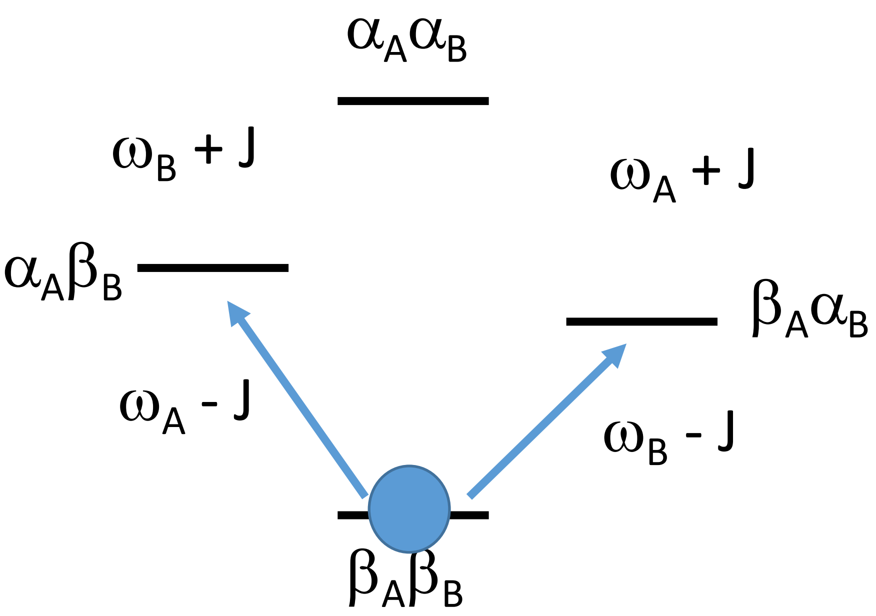
Direct product functions are eigenfunctions of H if $|J| \ll |\Delta|$

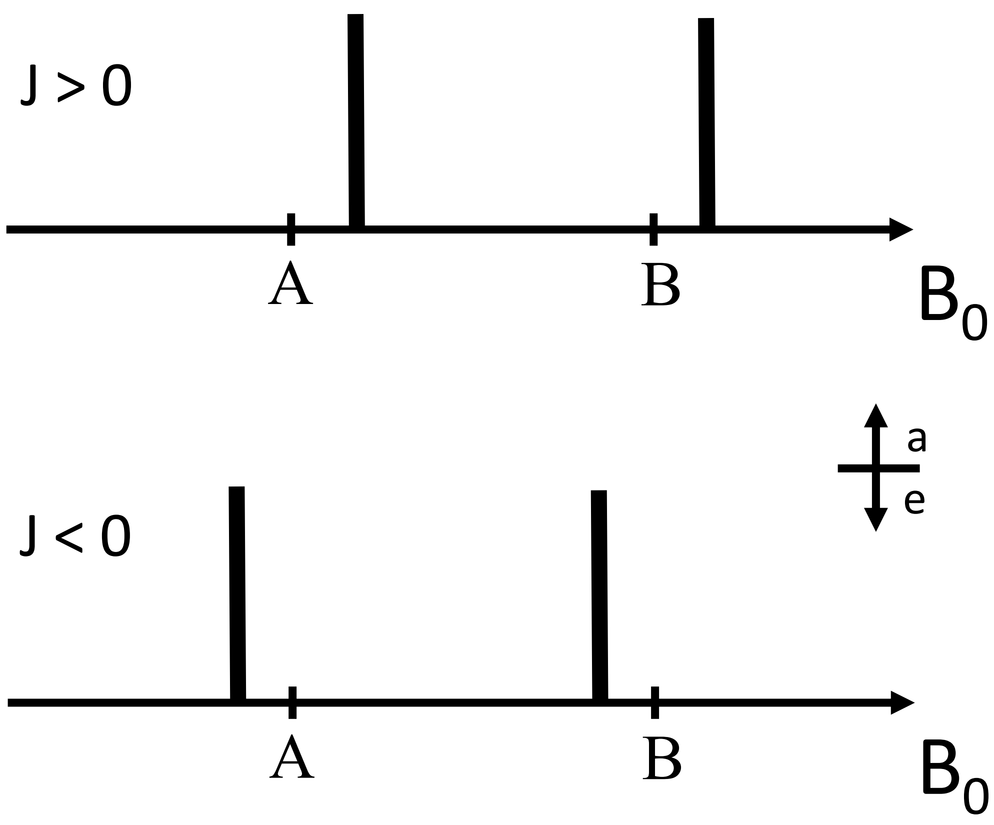
Singlet-triplet functions mixed if $|J| \approx |\Delta|$

T_{-1} systems



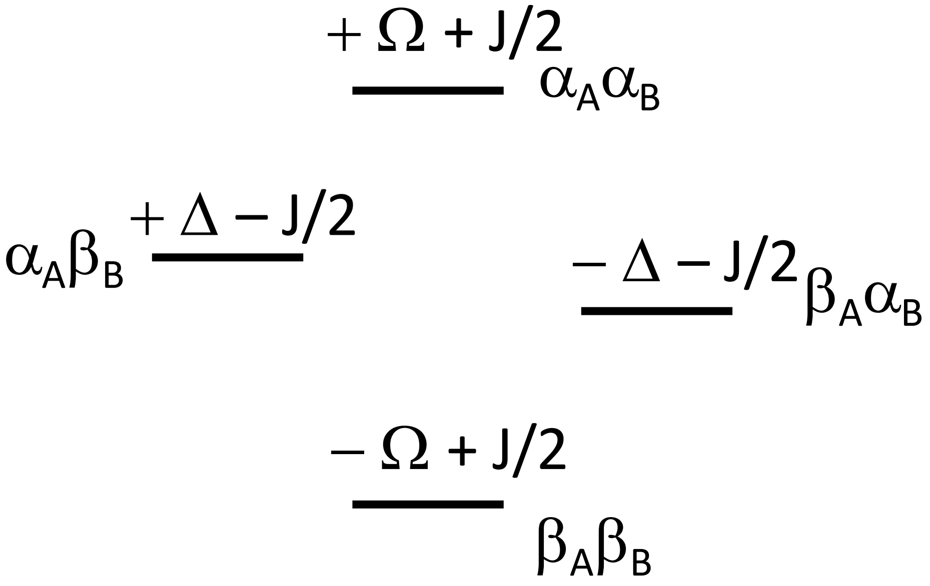
$\Delta > 0$



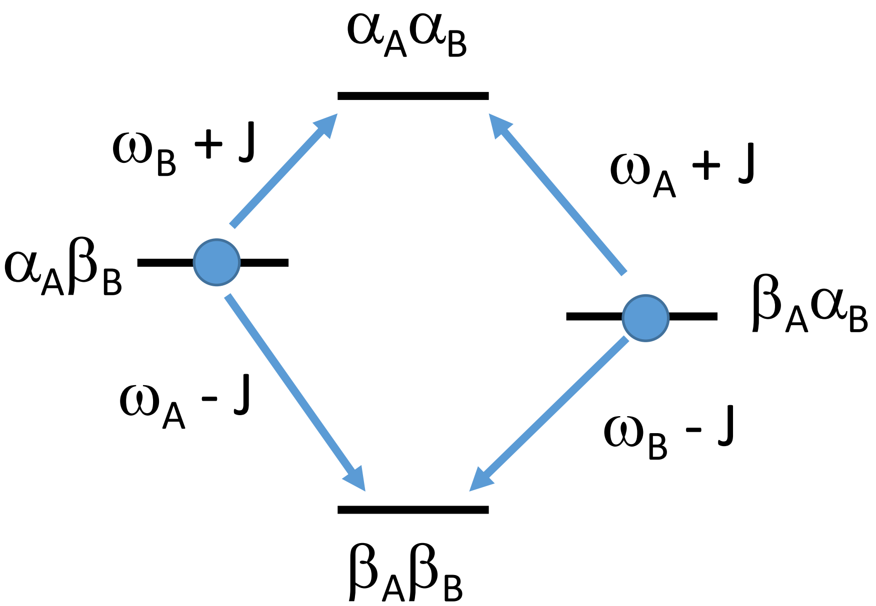


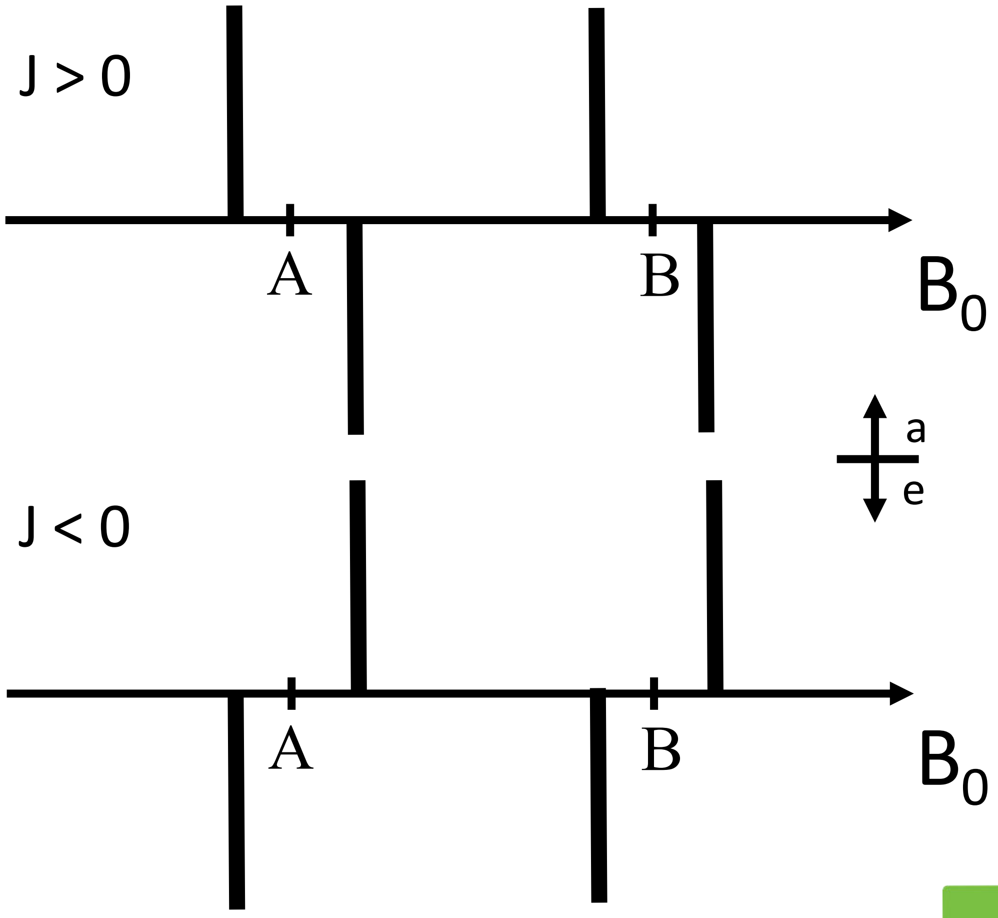
T_1 systems easy to guess!

T_0 / S_0 systems



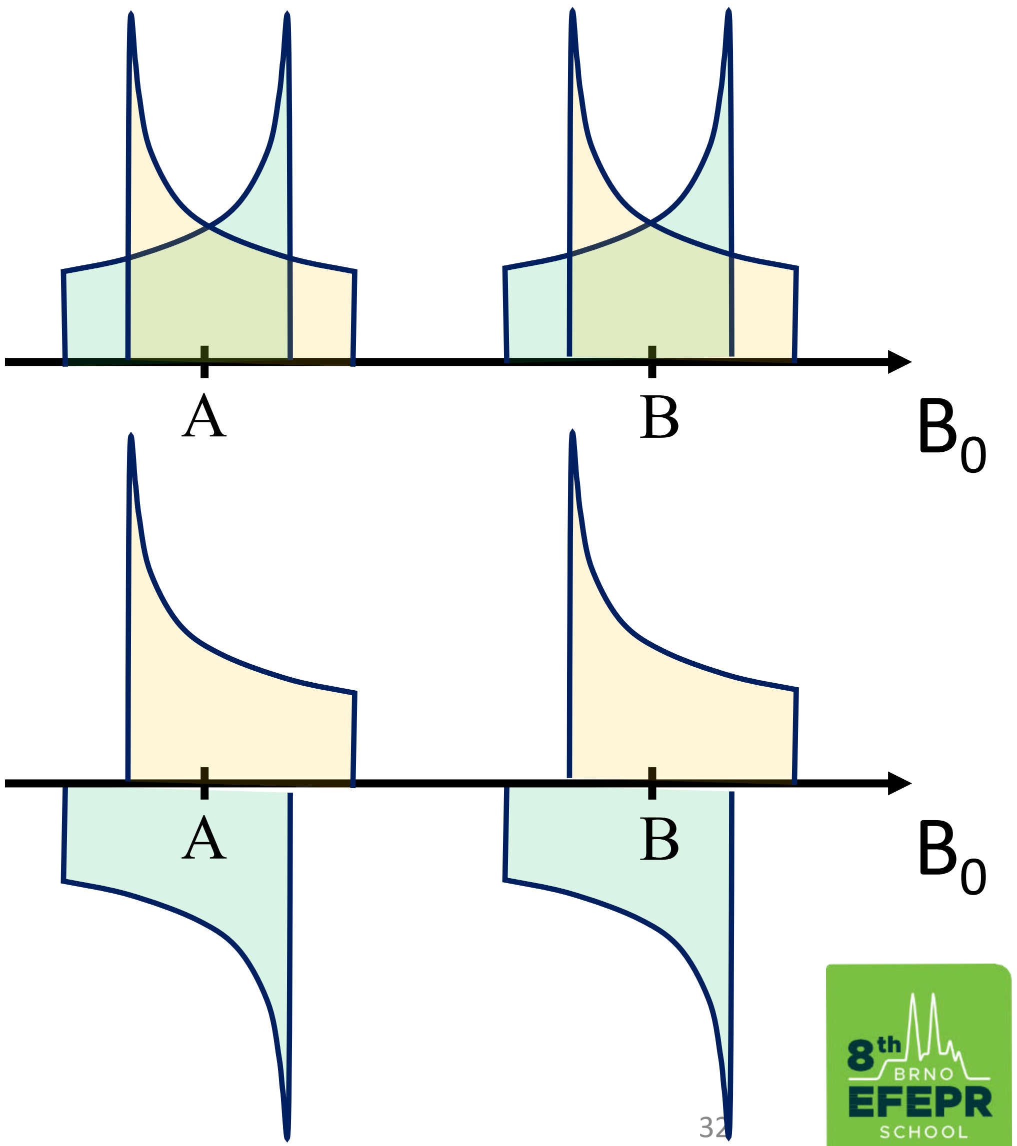
$\Delta > 0$





With dipolar interaction

We can add ZFS as a first order perturbation



RP ISC

$|J| >> |\Delta|$

$\Psi(0) = T_0$ (from a photochemical reaction)

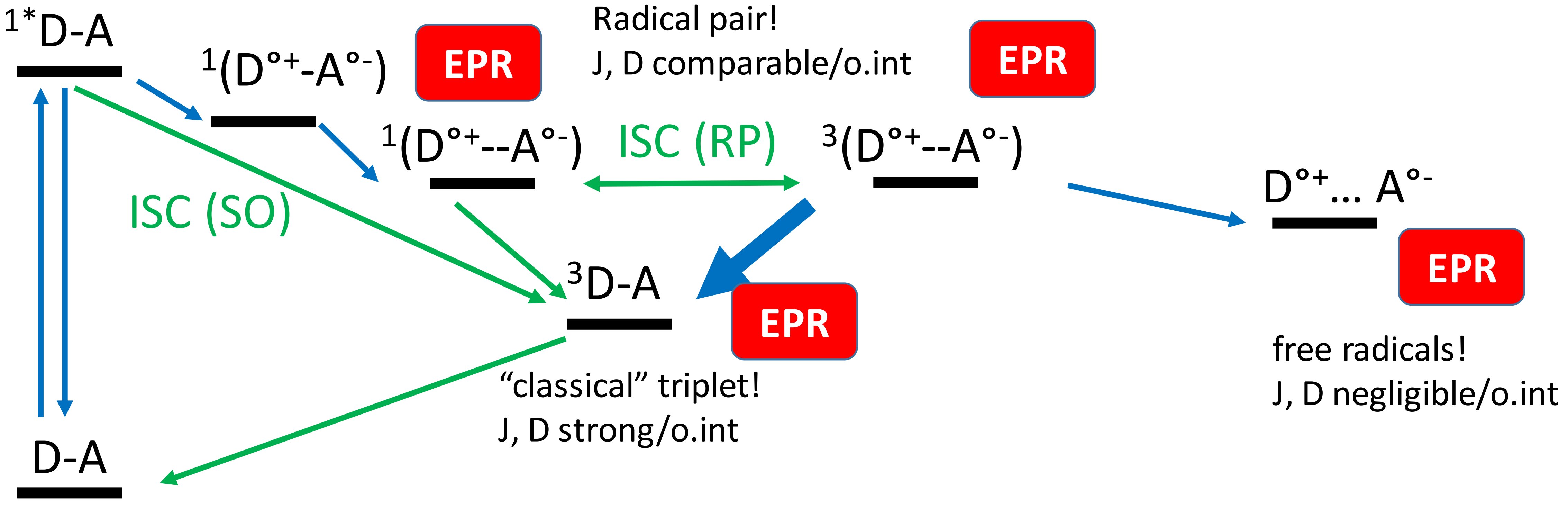
$|J| << |\Delta|$

$\Psi(t) = (\alpha_A\beta_B\, e^{-i\Delta t} + \beta_A\alpha_B\, e^{i\Delta t})/2^{0.5}$ ⟷ $\Psi(t) = \cos(\Delta t)\, T_0 - i\, \sin(\Delta t)\, S_0$

This is the same result, just written in two different bases!!

- Even a pure singlet (triplet) state takes on a triplet (singlet) nature after a period of time (ISC).
- Recombination to a triplet state with lower energy is possible when the “triplet nature” is important.
- Populations in the direct product basis do not change.

General overview (simple case!)



o.int : other interactions (Zeeman, hyperfine...) in the hamiltonian

Polarization in transient EPR is the result of all these processes

Spin states have a major impact!

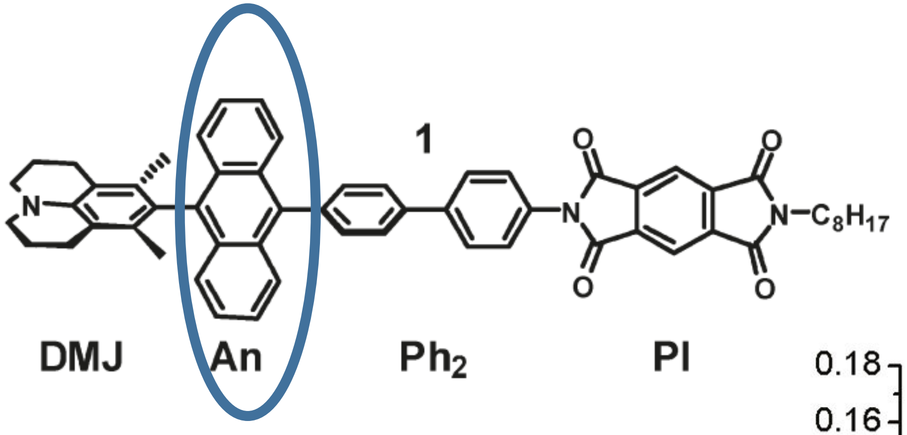
Model systems: J, D... well defined

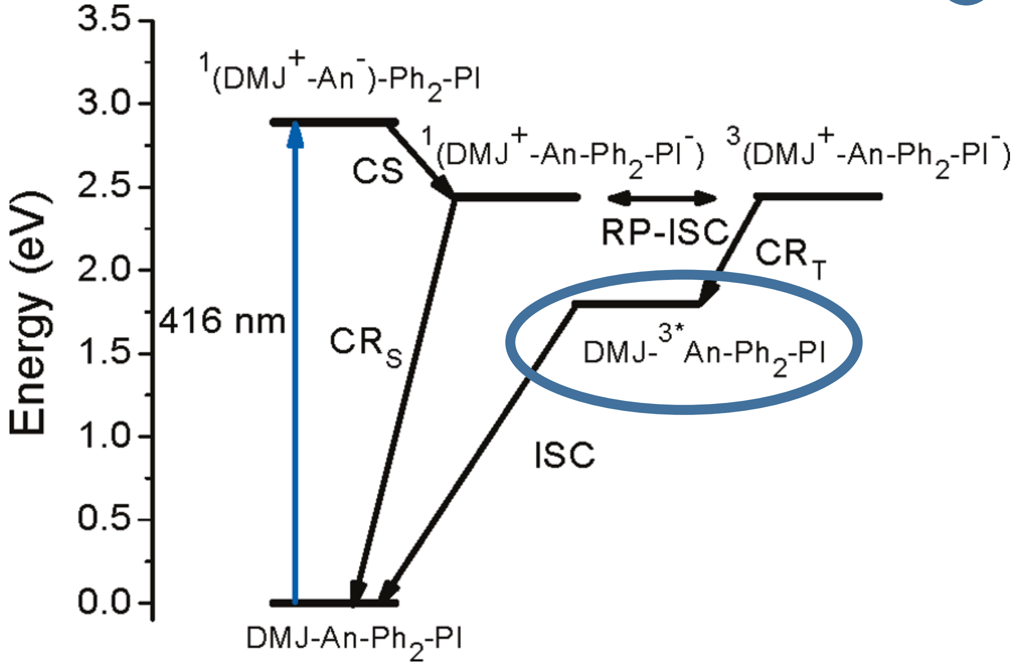
These phenomena are difficult to study for (flexible) systems in liquid state.
J, ZFS change rapidly with the distance (and time): complex simulations needed for quantitative results.

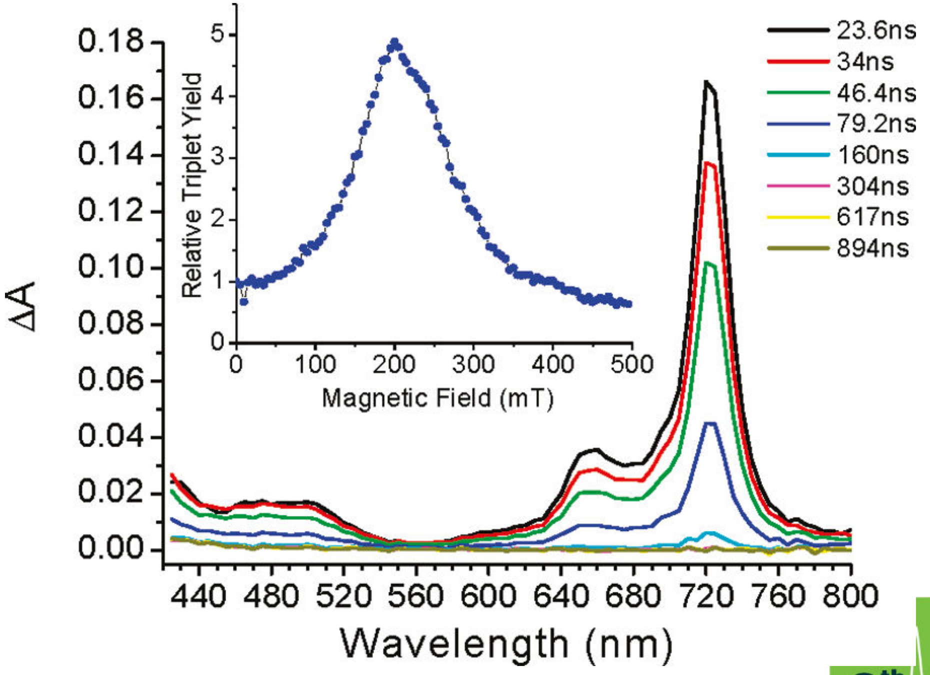
Solution: use a study rigid system!!

Large body of work to develop models for (artificial) photosynthesis processes!

(RP)ISC vs Field (I)







Colvin, , …, Wasielewski, JACS, 2011, 133, 1240

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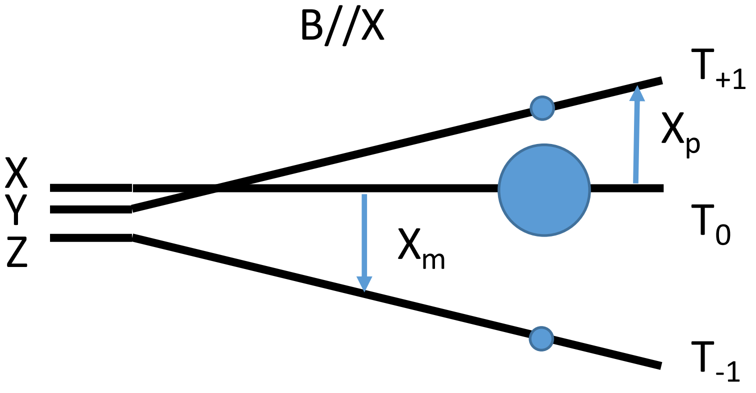
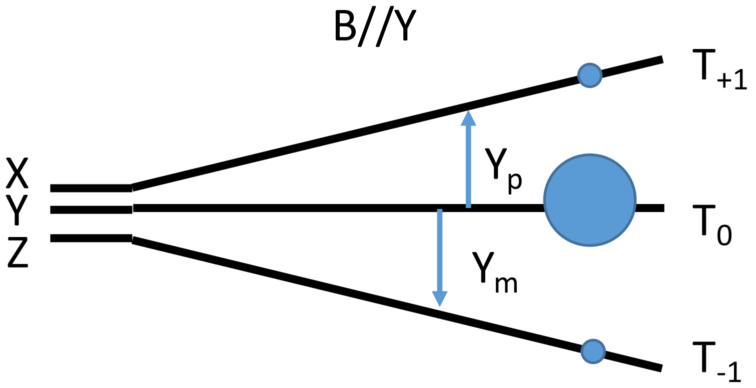
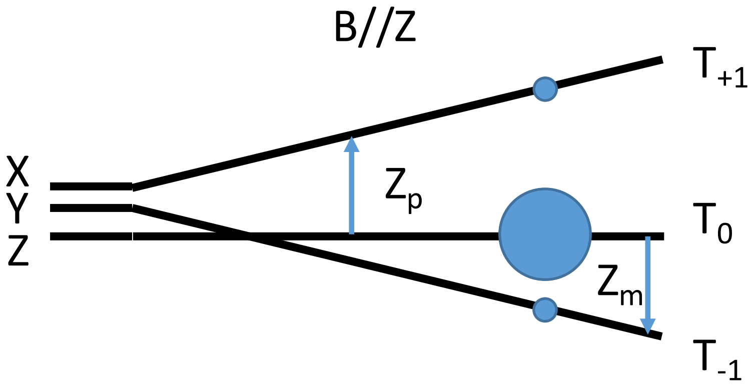
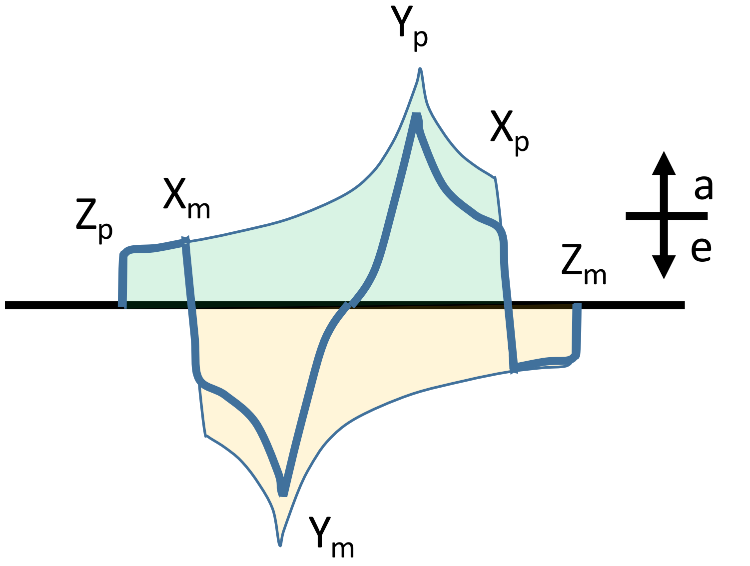
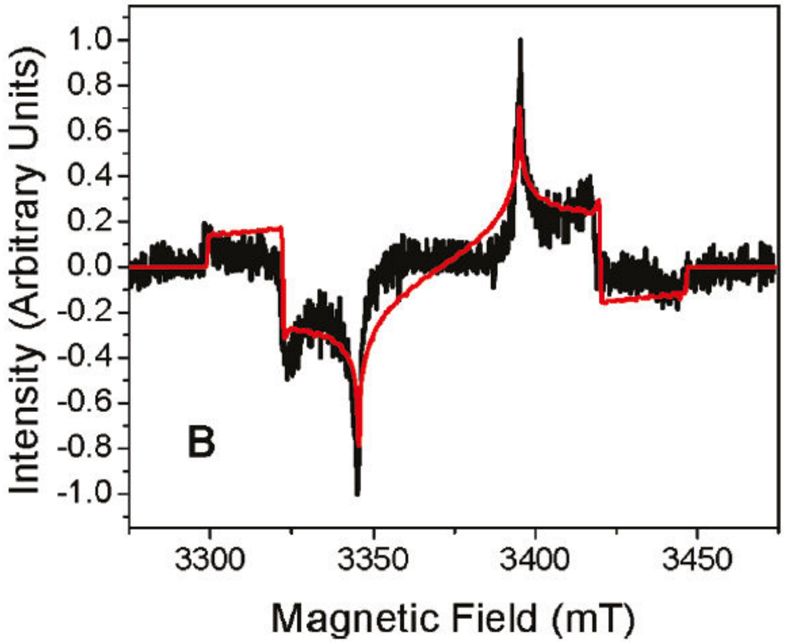
(RP)ISC vs Field (II)

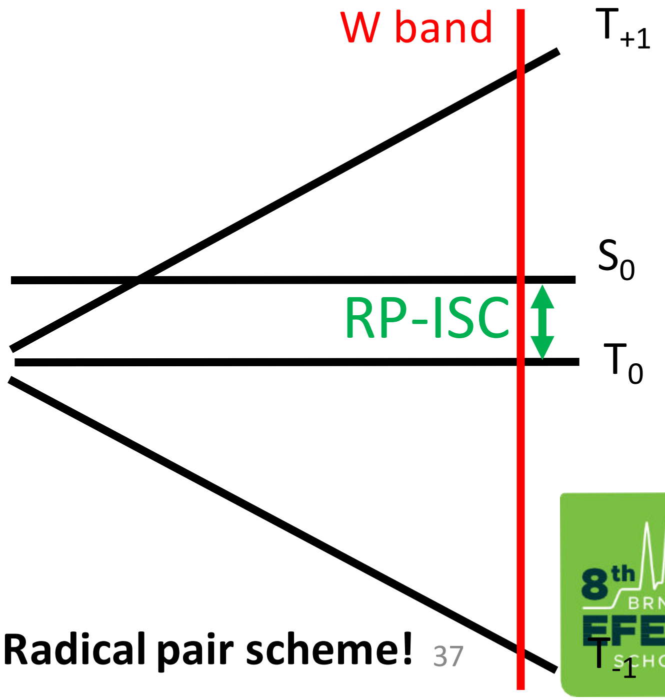






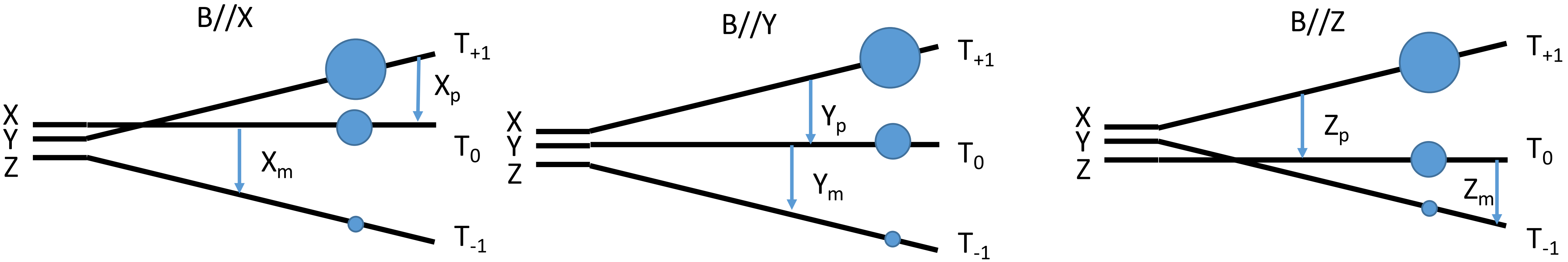


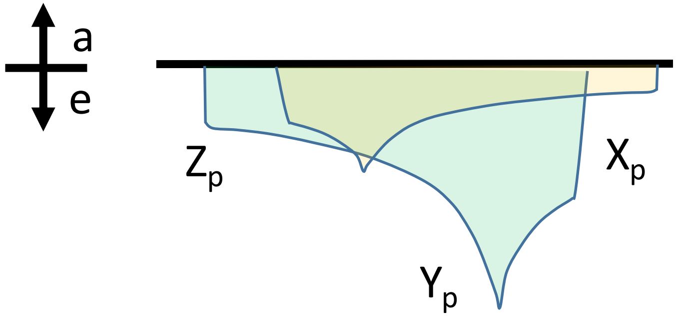


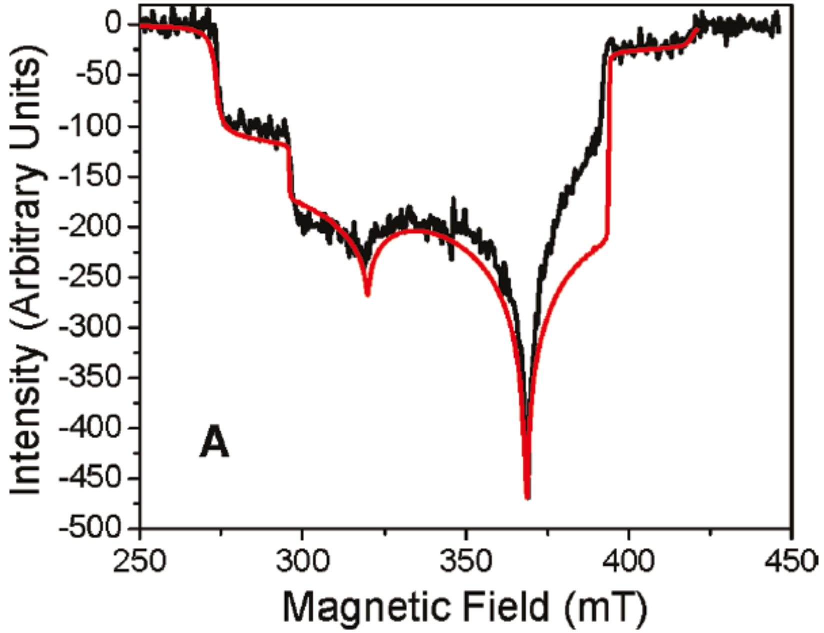


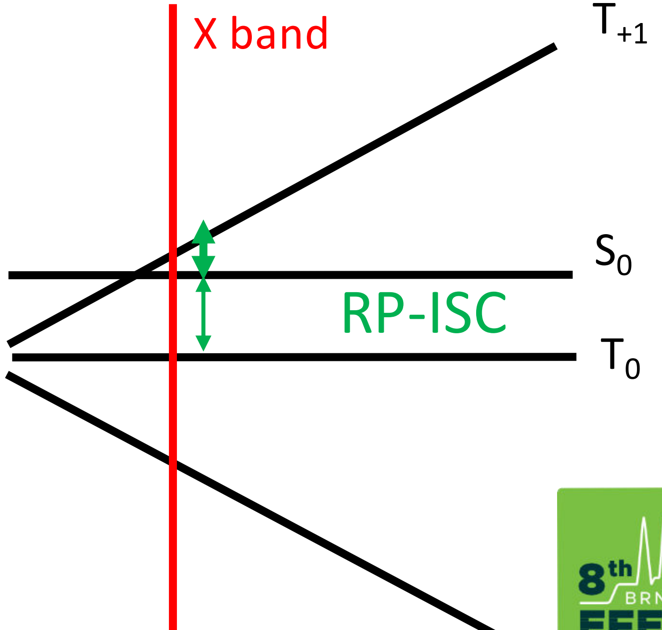
Radical pair scheme!

(RP)ISC vs Field (III)









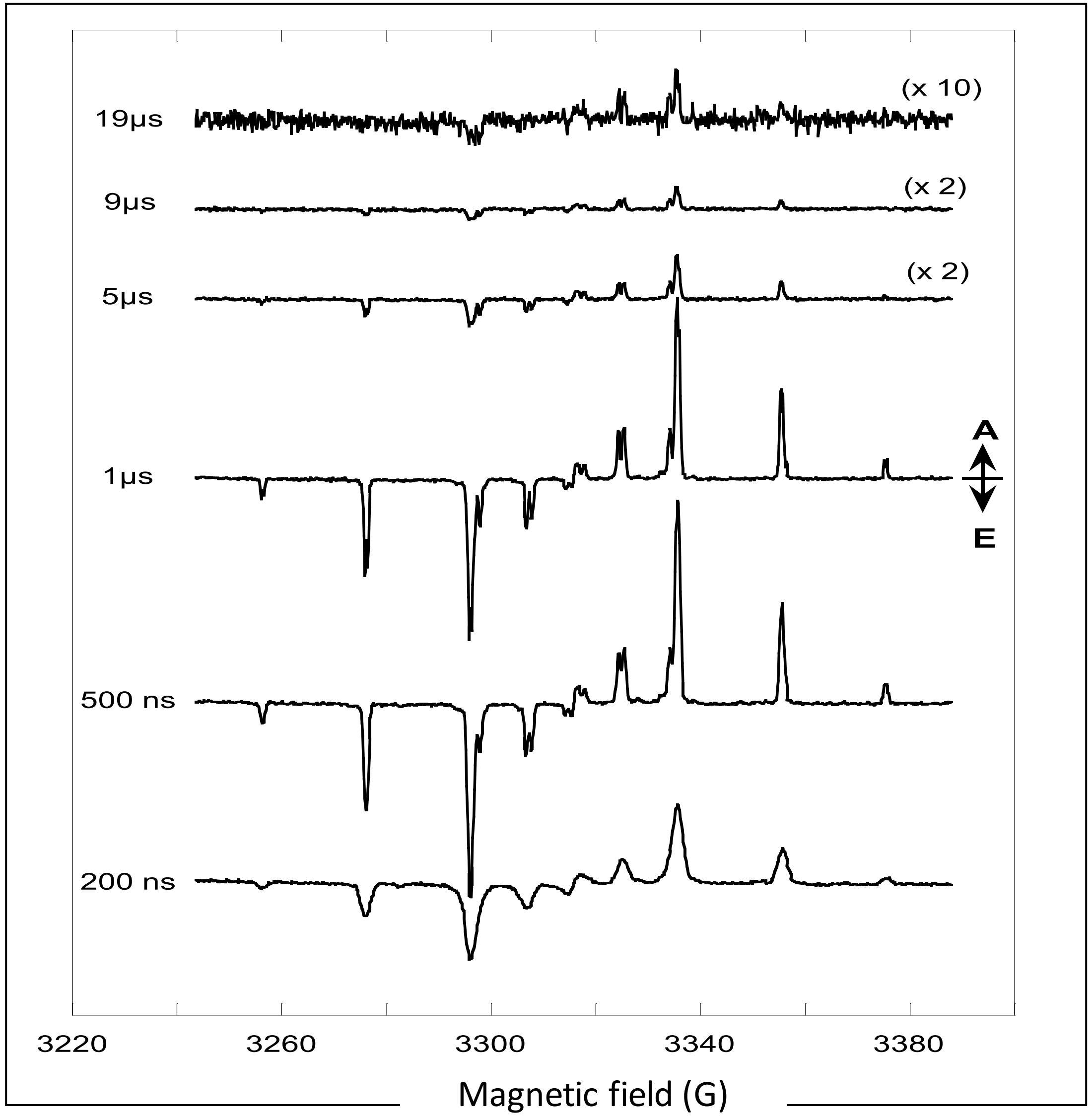
Radical pair scheme!

Chemically Induced Dynamic Electron Polarization (CIDEP)

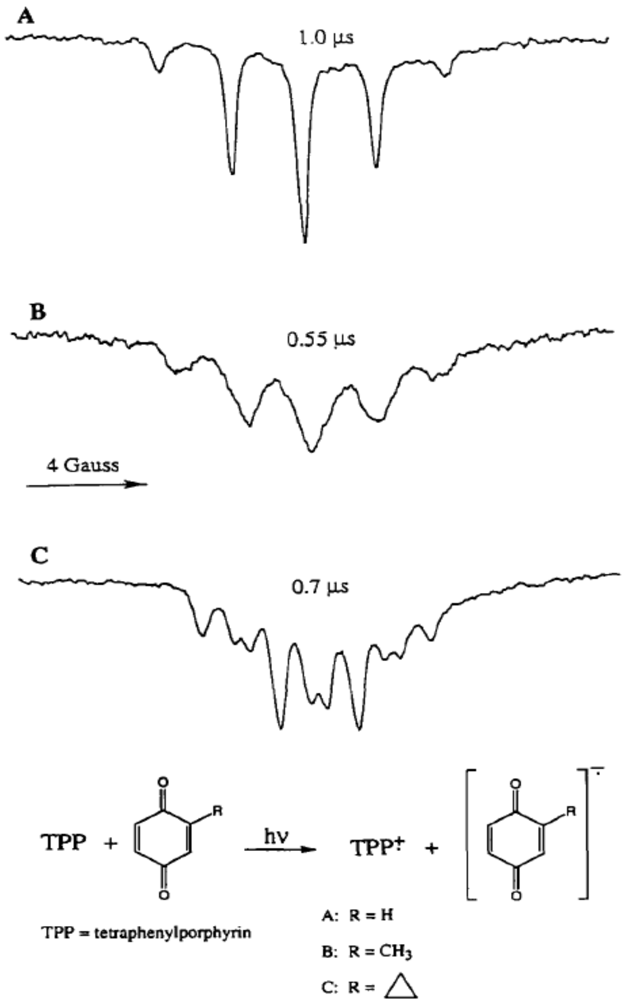
- What is the residual polarization of radicals when they no longer interact with each other in the liquid state?
- Formally, prevent coupling between centres in radical pair (increase distance) and see what happens
- In reality, re-encounters play a significant role, because what happens in the intermediate regime (and the kinetics of it) is very important.
- Detailed quantitative computations are a nightmare.

CIDEP: Triplet versus Radical Pair mechanism

RPM

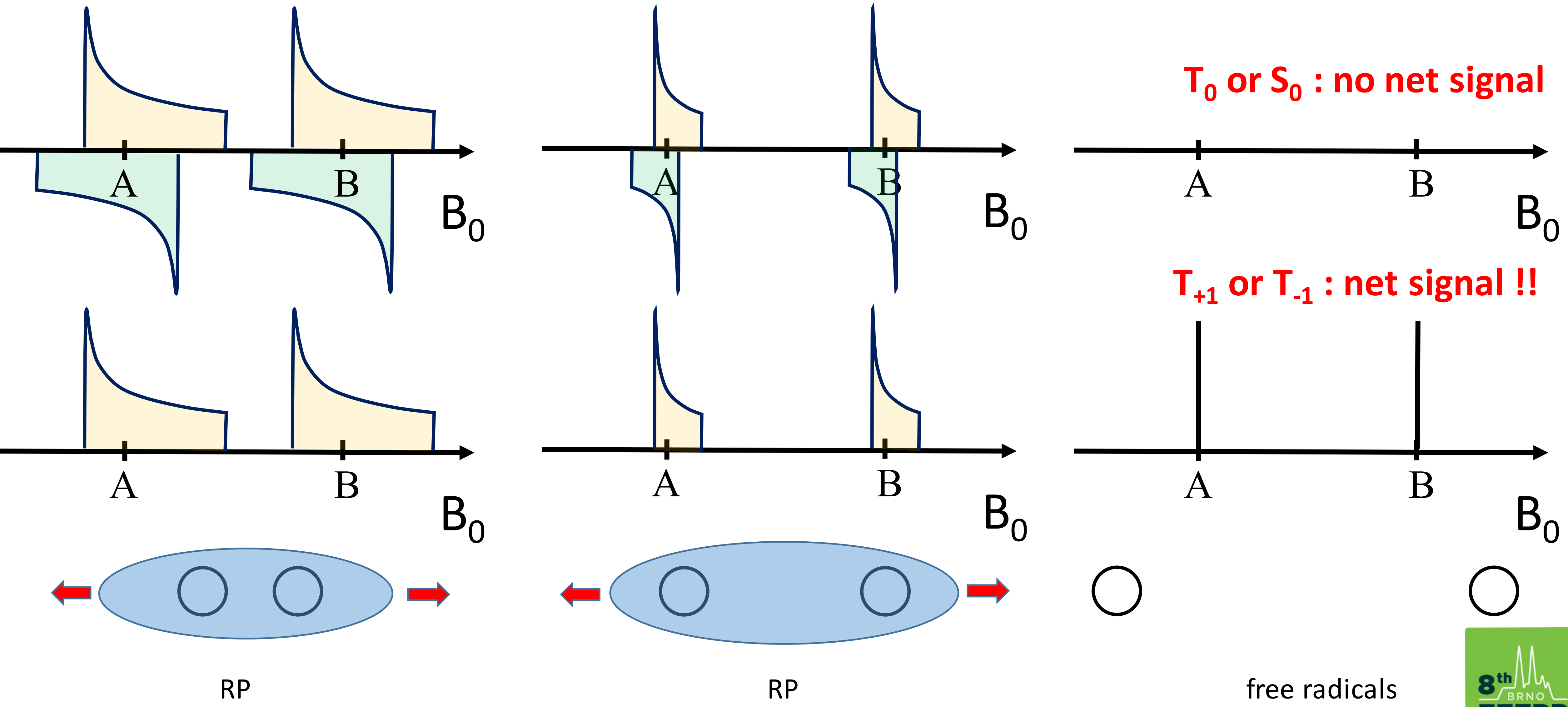


TM

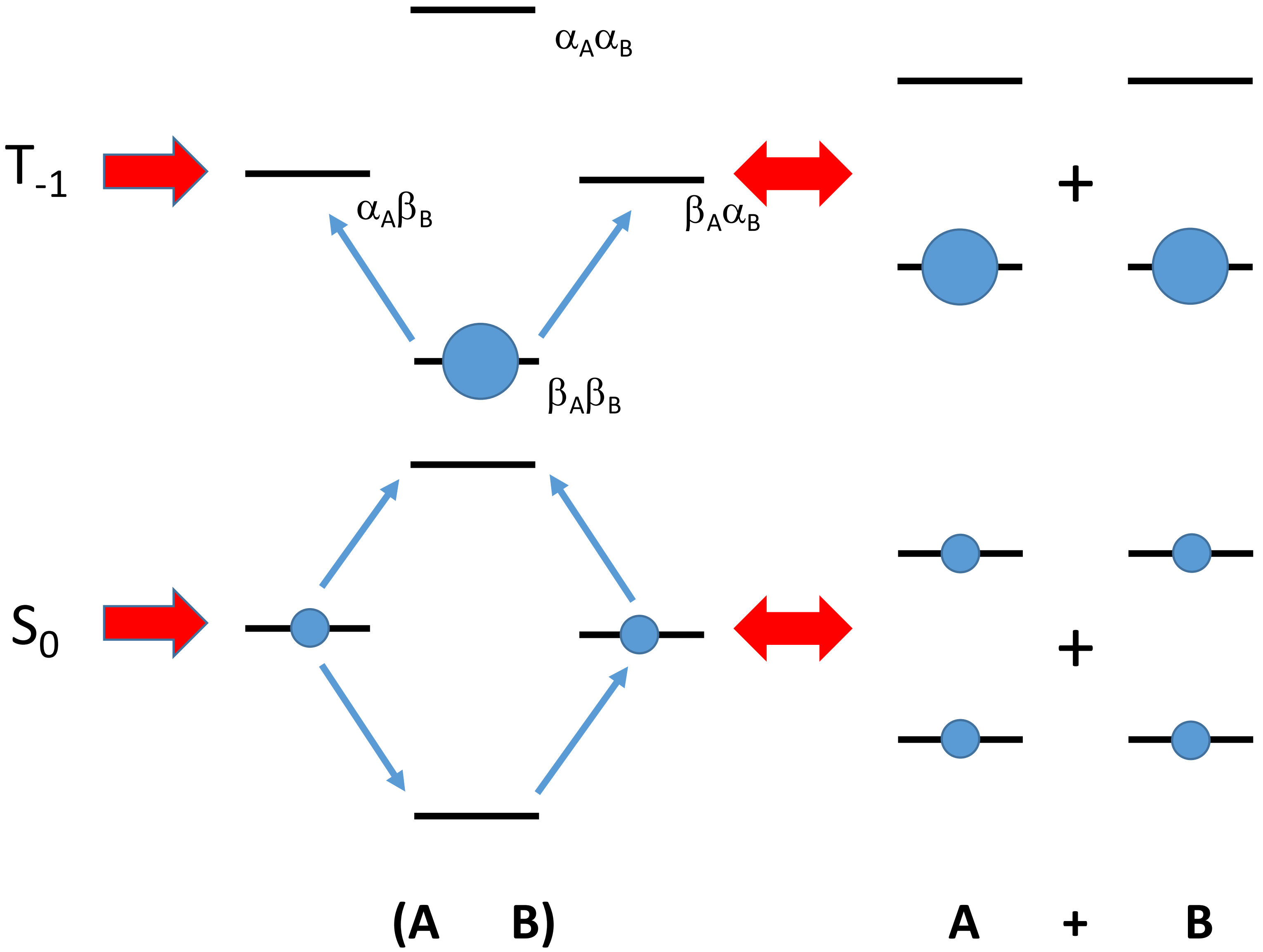


Forbes, Photochem Photobiol, 1997, 65, 73

CIDEP: naive picture

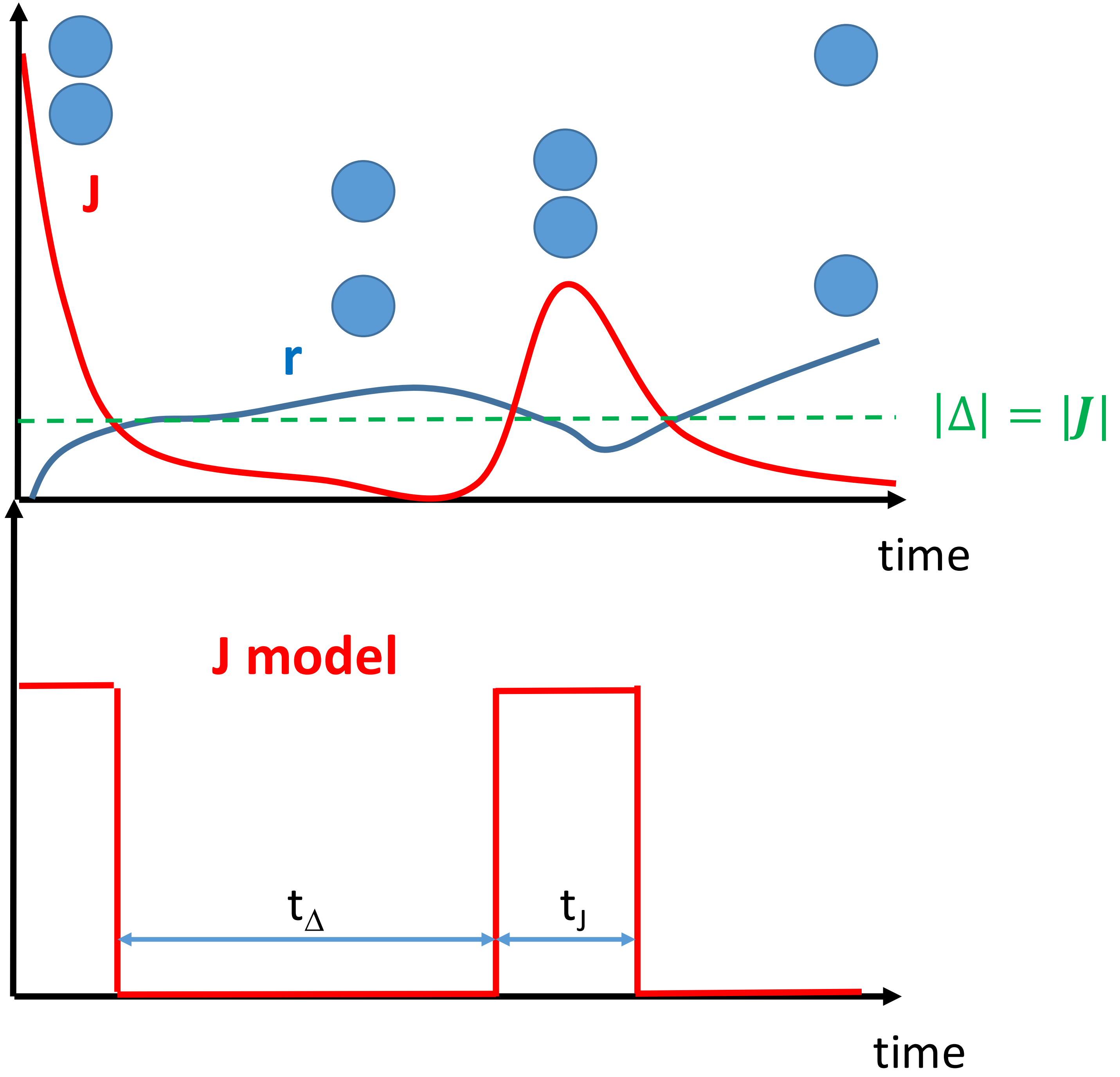


CIDEP: naive picture



$T_1 = \alpha_A\alpha_B$
$T_0 = (\alpha_A\beta_B + \beta_A\alpha_B)/2^{0.5}$
$T_{-1} = \beta_A\beta_B$
$S_0 = (\alpha_A\beta_B - \beta_A\alpha_B)/2^{0.5}$

(RPM) CIDEP: cornerstone



CIDEP: density matrix analysis

$$\rho^{S0} = 0.5\begin{pmatrix} +1 & -1 \\ -1 & +1 \end{pmatrix}$$

$$\rho^{T0} = 0.5\begin{pmatrix} +1 & +1 \\ +1 & +1 \end{pmatrix}$$

$\alpha_A\beta_B \quad \beta_A\alpha_B$

Population

Coherence

During RP ISC (T_0 initial state):

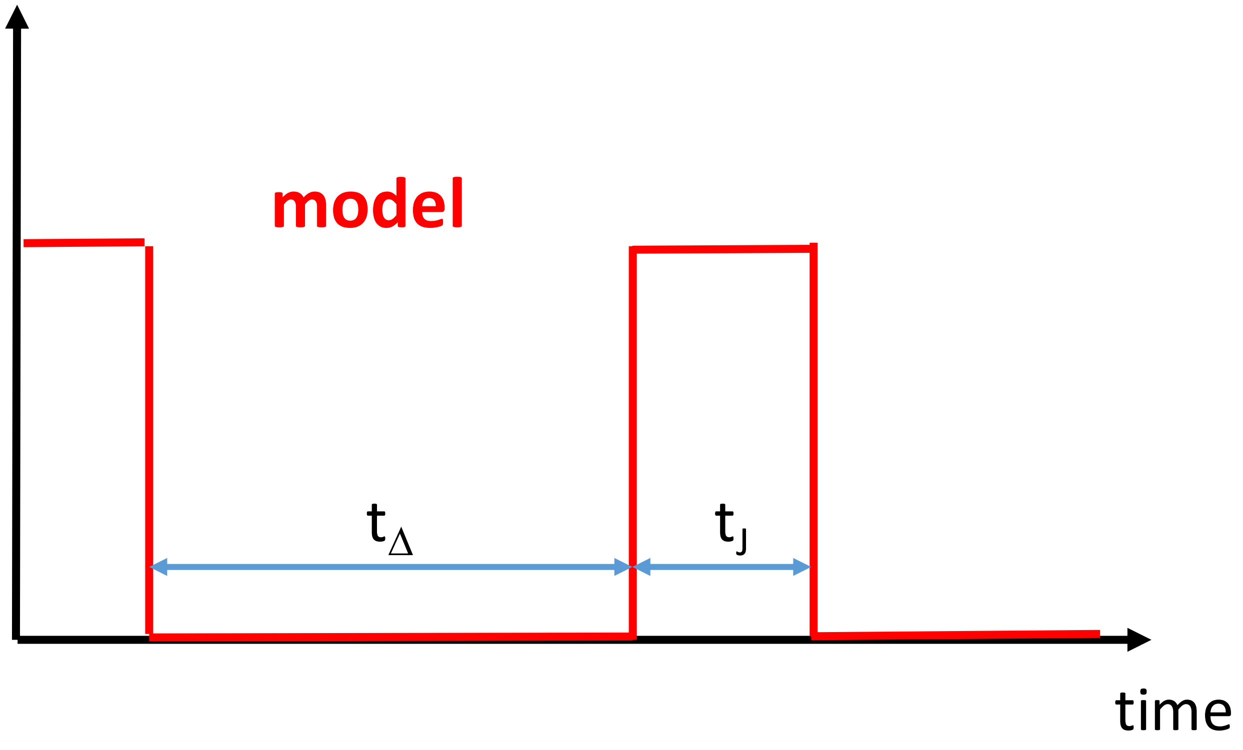
$$\rho(t) = \exp(-iHt)\ \rho(0)\ \exp(iHt)$$

$$H = \begin{pmatrix} \Delta & 0 \\ 0 & -\Delta \end{pmatrix}$$

$$\rho(t) = 0.5\begin{pmatrix} +1 & e^{-2i\Delta t} \\ e^{2i\Delta t} & +1 \end{pmatrix}$$

Again simple (RP) ISC does not change the population

(RPM) CIDEP: cornerstone



T_0 initial state

$$\rho(t) = \exp(-iHt_J)\ \exp(-iHt_\Delta)\ \rho(0)\ \exp(iHt_\Delta)\ \exp(-iHt_J)$$

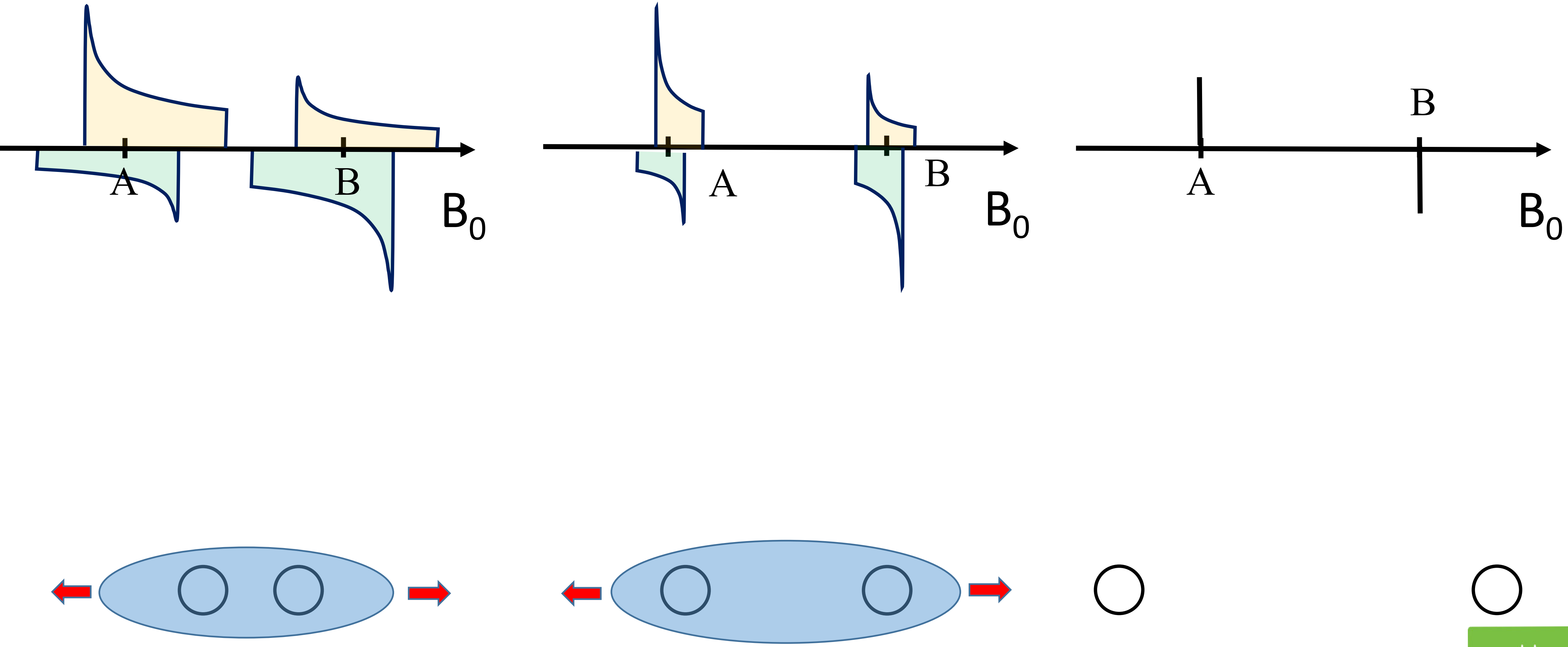
$$\rho(t) = 0.5\begin{pmatrix} a_{00} & a_{10} \\ a_{01} & a_{11} \end{pmatrix}$$

$$a_{00} = 1 + \sin(2Jt_J)\ \sin(2\Delta t_\Delta)$$
$$a_{11} = 1 - \sin(2Jt_J)\ \sin(2\Delta t_\Delta)$$

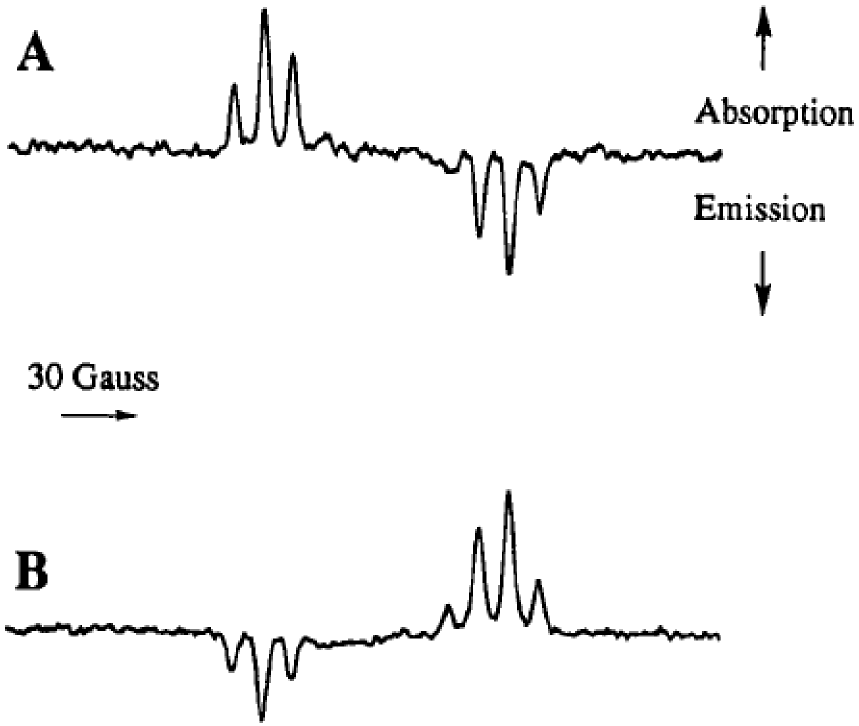
Populations change in this model!

- sign of J and D matter!
- time dependence
- same method with S_0

CIDEP (II)



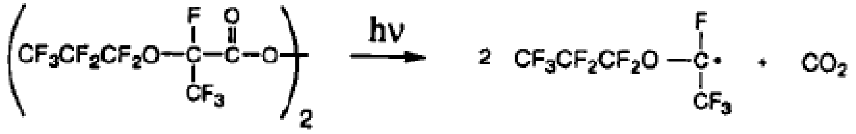
Singlet vs triplet precursor



Direct photolysis → Singlet state

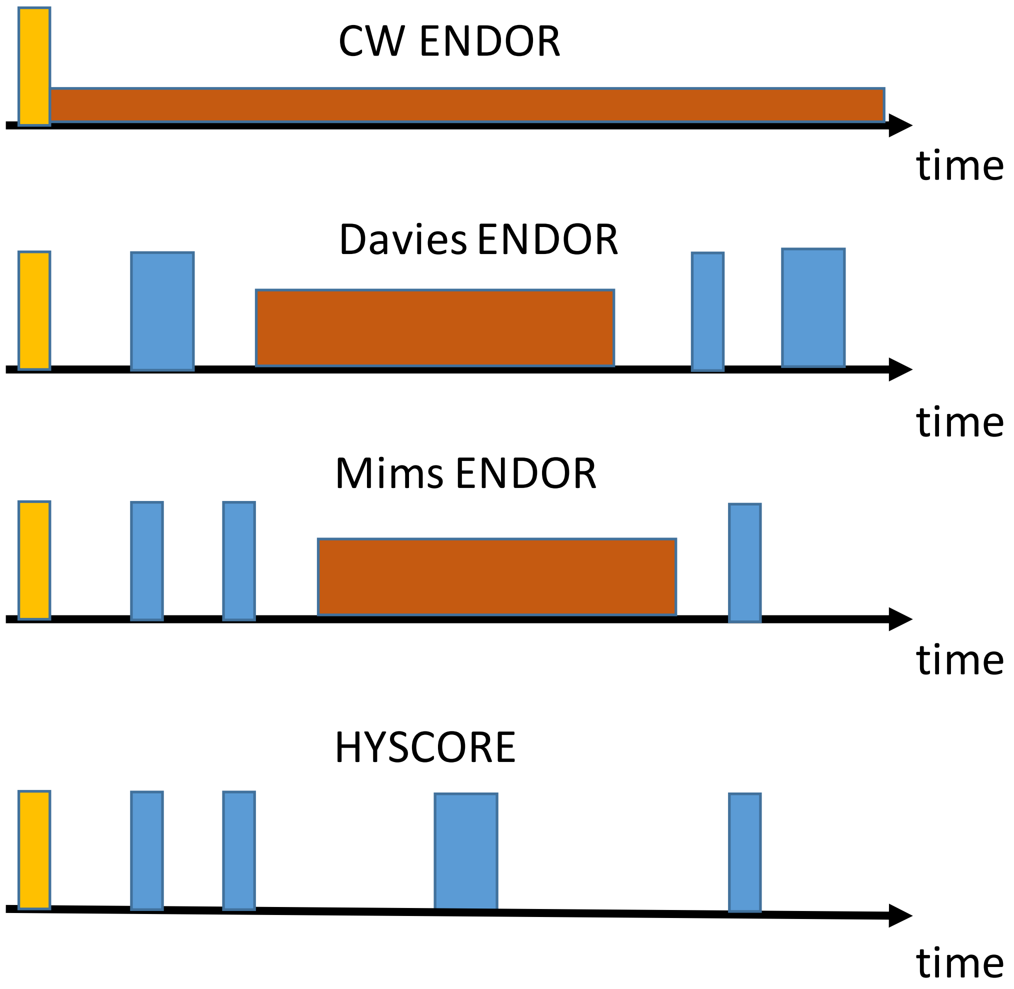
Initial state is not the same!

Triplet sensitization → Triplet state



Forbes, Photochem Photobiol, 1997, 65, 73

Advanced EPR with transient species



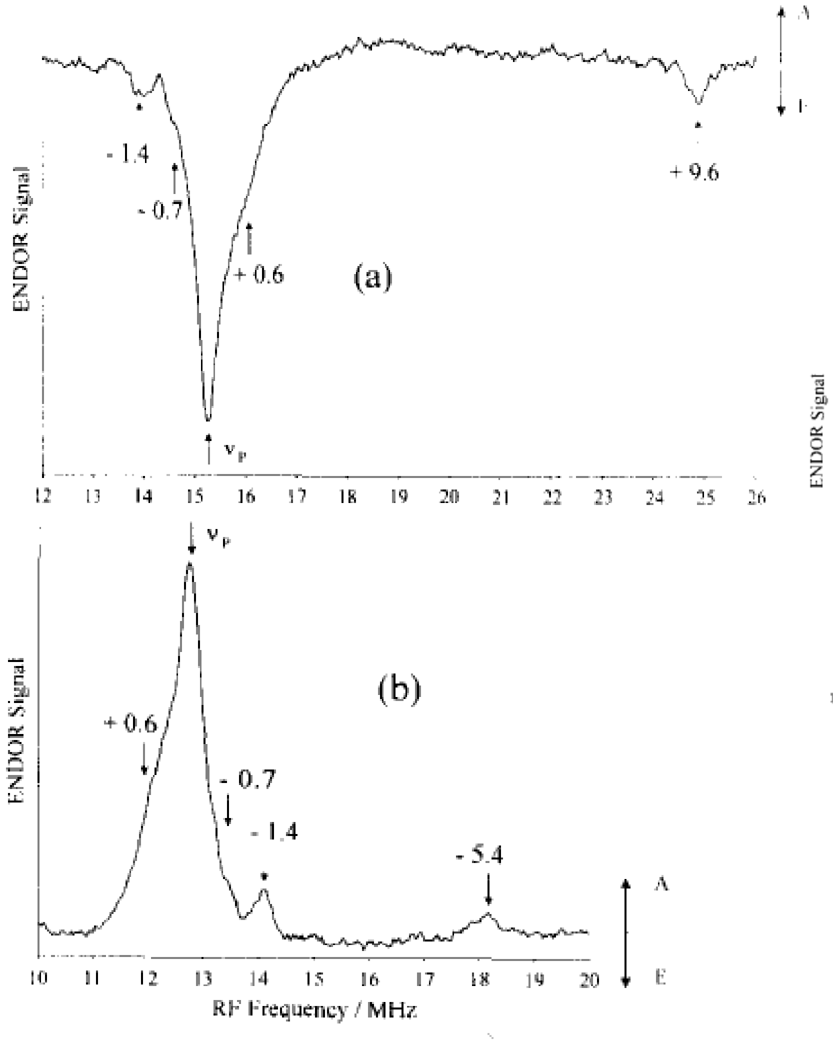
Classical pulsed EPR sequences and double resonance methods can be used.

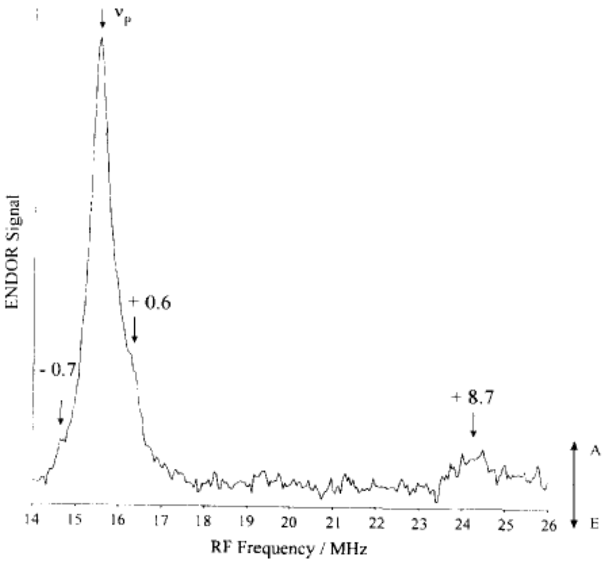
Transient species are generated following a laser flash

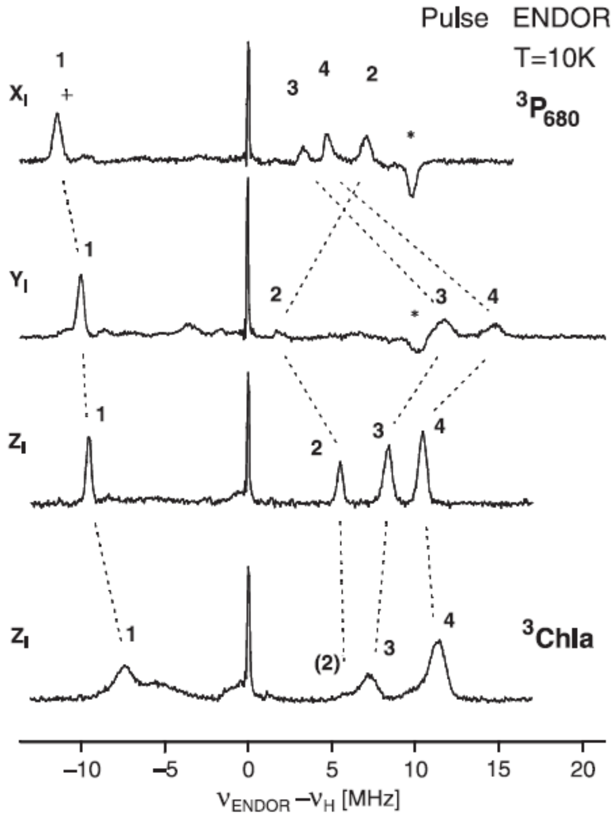
Take note of:

- T_1
- Laser repetition time
- A/E features

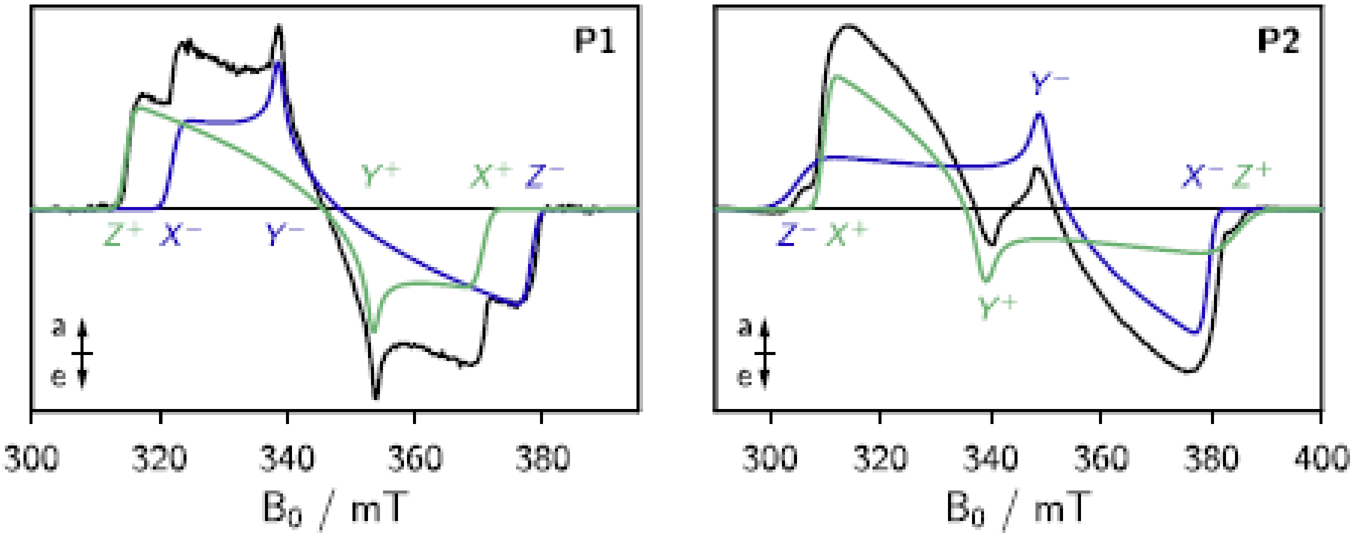
Advanced EPR with transient species

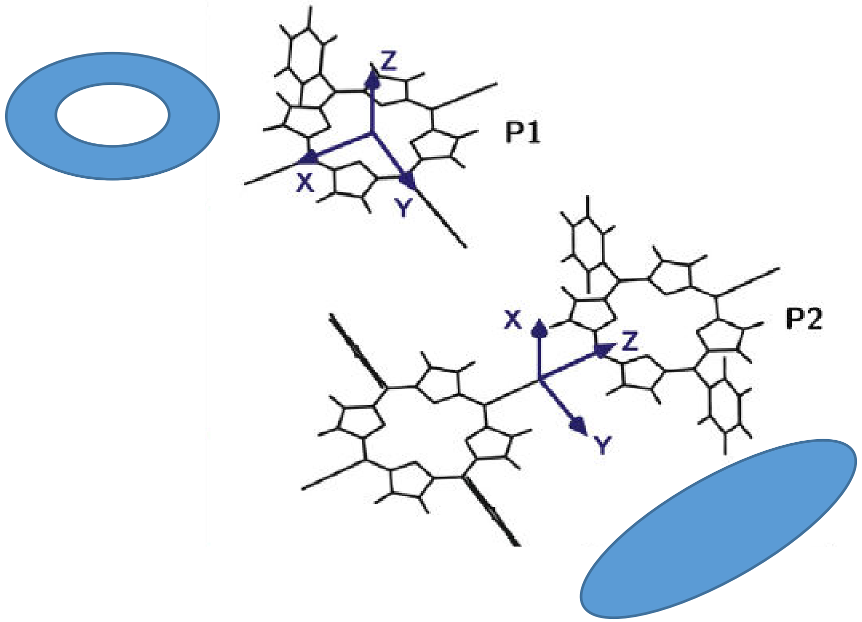






A complete (and complex) example



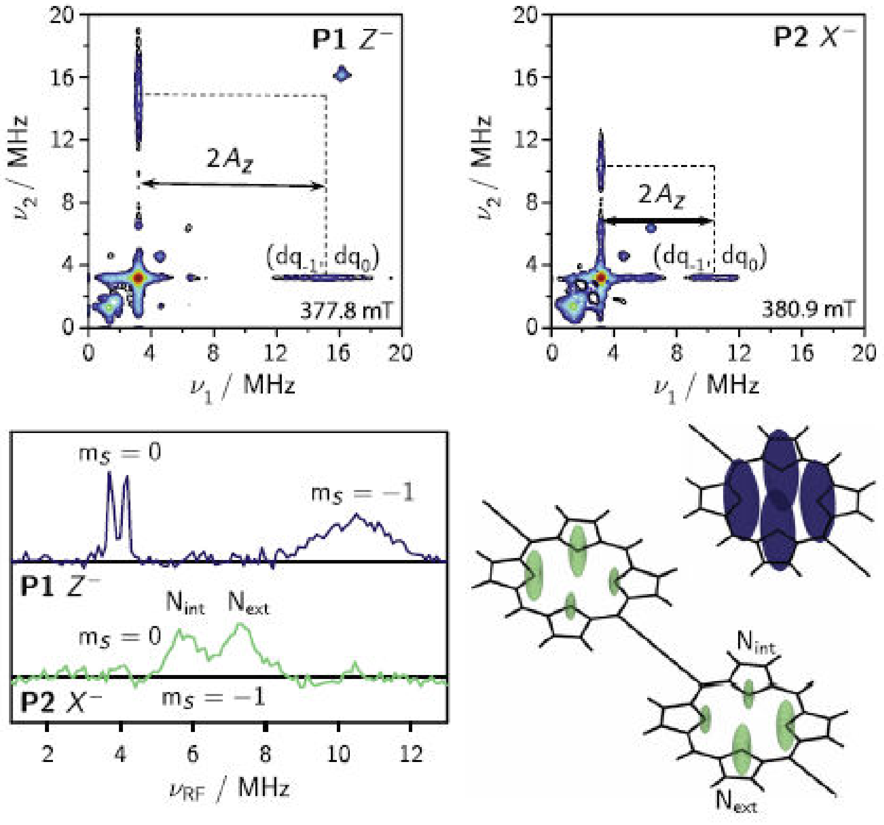


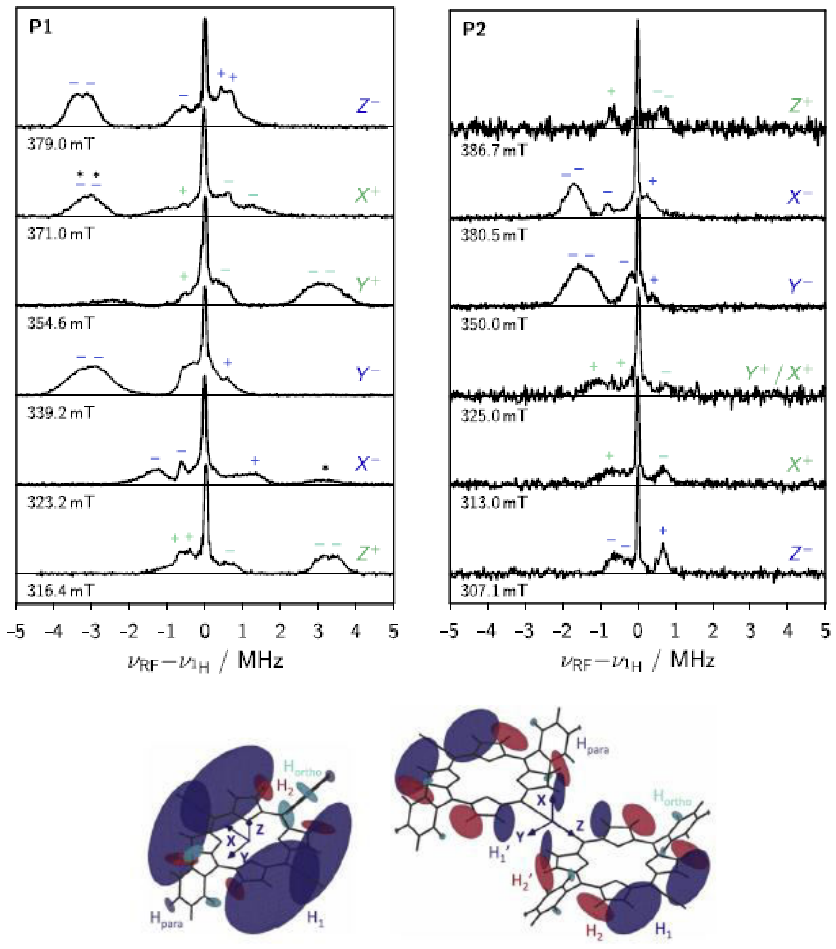
Electron distribution changes

- D changes sign from P1 to P2
- D principal axis changes
- Populated levels change

Richert, Tait, Timmel, JMR, 2017, 280, 103

A complete (and complex) example





- D principal axis changes
- Hyperfine coupling reduced

Richert, Tait, Timmel, JMR, 2017, 280, 103

Thanks for your attention!

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