A6

A Pulsed and CW S-Band (2-4 GHz) EPR-Spectrometer

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1. Introduction

Why do pulsed S-band EPR-spectroscopy?

Multi-frequency approach

for separation of different contributions to spin Hamiltonian

ESEEM (Electron Spin Echo Envelope Modulation)

Enhancement of modulation depth in ESE-spectroscopy at lower frequencies

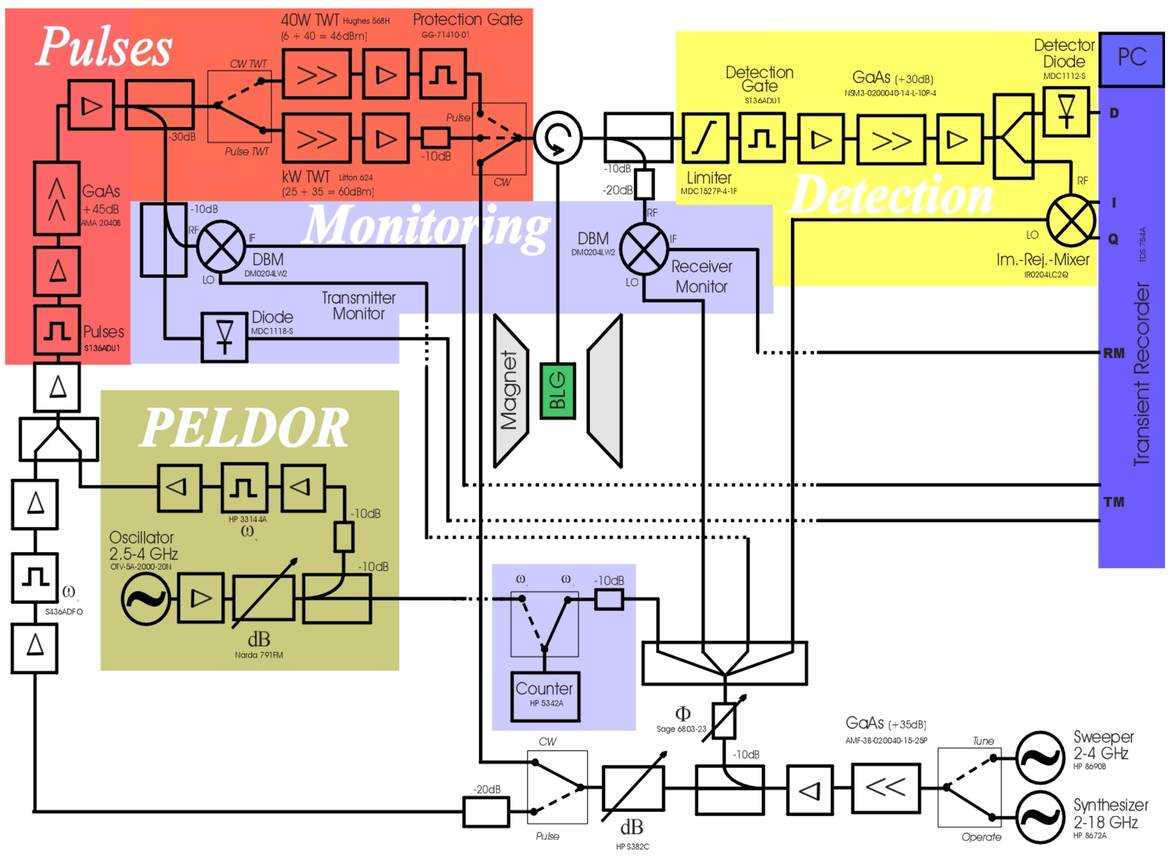
Forbidden transitions

Increased transition moments of forbidden transitions in High-spin systems

Zero-field splitting

Quantification of Zero-field splitting tensors in High-spin systems

2. Block Diagram



3. Specifications

microwave (mw) frequency n = 2.7 - 3.6 GHz
magnetic field (for g=2) B_0 = 960 - 1280 G

quality factor of bridged loop gap resonator (BLG) Q = 100 - 600
=> bandwidth $\Delta\nu$ = 5 - 30 MHz

conversion factor of BLG resonator c = 0.2 mT/√W
dead time after mw pulses t_d < 150 ns
$\pi/2$ pulse length (10W mw-power) $t_{\pi/2}$ = 10 ns

temperature range: 4 - 300 K

low noise broadband detection channel
(noise figure of det. amplifier < 1.5dB, typ. 1.0dB)

fast mw PIN diode (rise/fall time < 2 ns)

1 kW gated TWT ampifier (2-4 GHz)
duty cycle: 1%

repetition rate of experiment
transient recorder: 200 Hz
boxcar integrator: 10 kHz

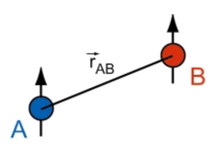
PELDOR-unit

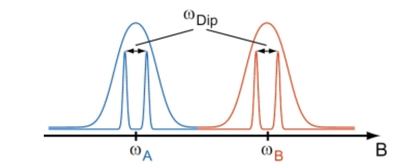
4. The PELDOR Experiment

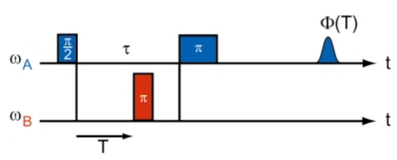
For spin-spin distances r_{AB} > 10Å the determination of the distance with cw methods is too inaccurate.

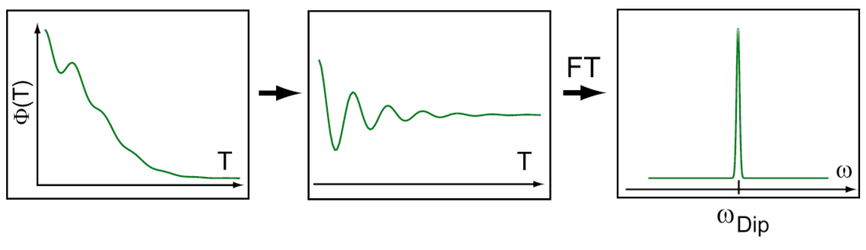
But with **PELDOR** (**P**ulsed-**El**ectron-**Do**uble-**R**esonance) it is possible to determine distances in the range of r_{AB} = 10Å - 50Å by evaluating the modulation of the electron spin echo caused by the dipolar coupling ω_{Dip} which gives the distance r_{AB} according to:

$$\omega_{Dip} = \text{const} \cdot |r_{AB}|^{-3}$$

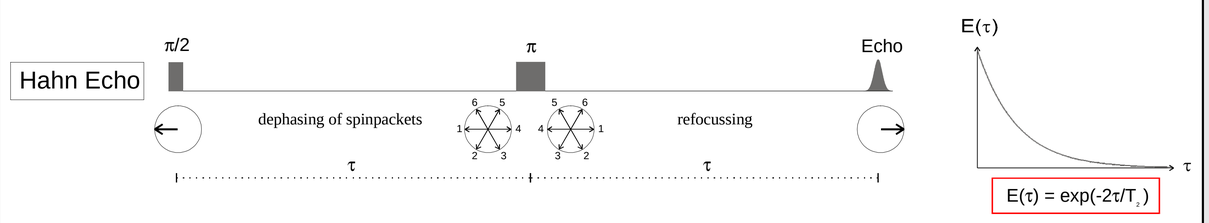


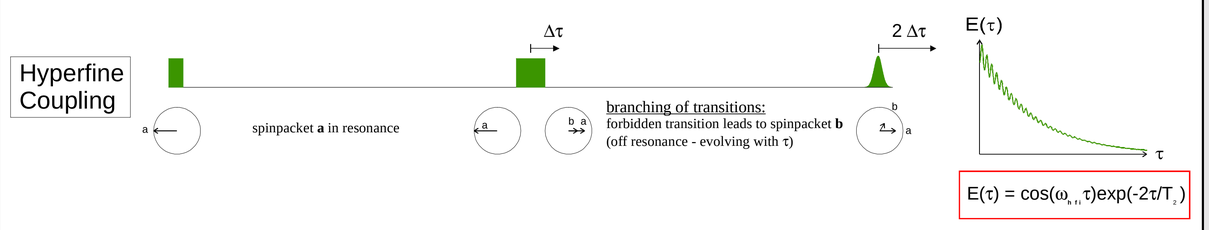


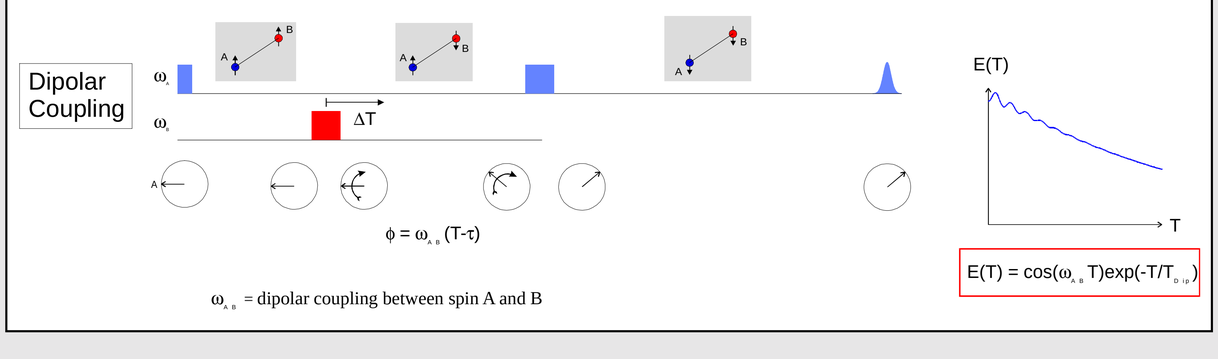




5. Echo Modulation due to Hyperfine and Dipolar Coupling

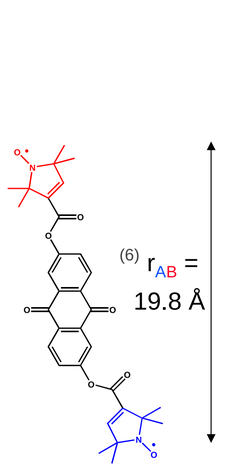




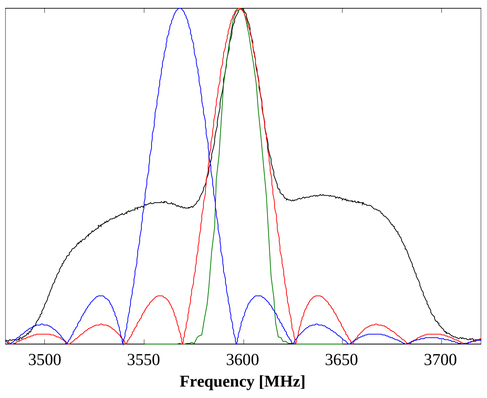


$\omega_{A\,B}$ = dipolar coupling between spin A and B

6. S-Band PELDOR



(6) r_{AB} = 19.8 Å



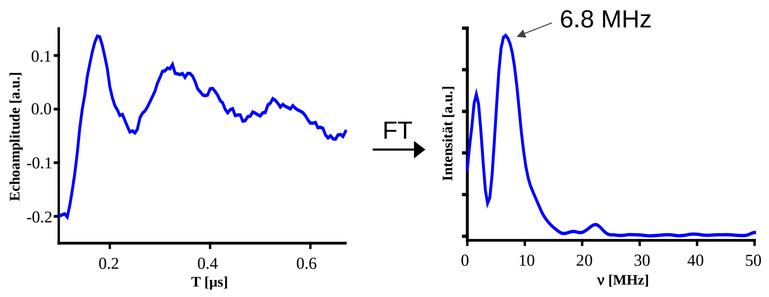
Resonator: f_0 = 3597.8 MHz
Δf ~ 40 MHz

Pumping: f_1 = 3597.8 MHz
t_P = 35 ns

Detection: f_2 = 3567.8 MHz
t_P = 35 ns

$f_1 - f_2$ = 60 MHz

Nitroxide Spectrum @ 1282G

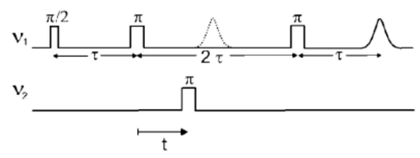


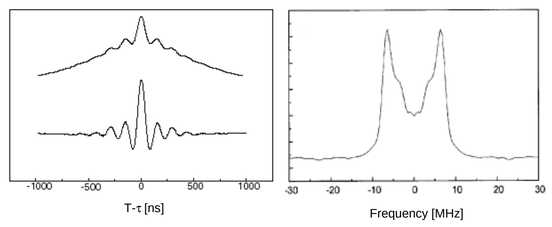
r_{AB} = 19.8Å

Comparison of S- and X-Band PELDOR enables to distinguish between hyperfine and dipolar interaction.

7. Deadtime Free 4-Puls PELDOR

Pannier, M.; Veit, S.; Godt, A.; Jeschke, G.; Spiess, H. W.
J. Magn. Res. **2000**, 142, 331.





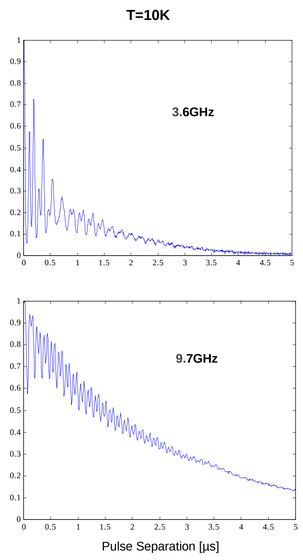
$\omega_{AB} = \omega_{Dip}(3\cos^2\Theta - 1)$

ω_{Dip} = 7.12 MHz r_{AB} = 19.4 Å

Advantage:
Broad electron-electron coupling distribution can be recovered so the angular-dependend part of the Pake pattern can be observed.

Disadvantage:
Detection after 4τ (not 2τ as in case of the 3 pulse sequence) => T_M-Limit

8. S- and X-Band ESEEM



Modulation Depth
k ~ 0.95

Phase memory time
T_M ~ 0.7µs

Modulation Depth
k ~ 0.40

Phase memory time
T_M ~ 3µs

The modulation amplitude increases with decreasing magnetic field for distant nuclei approximately according to:

$$k \sim (B/\omega_I)^2$$

B: field-independent parameter of hfi
ω_I: nuclear Zeeman frequency