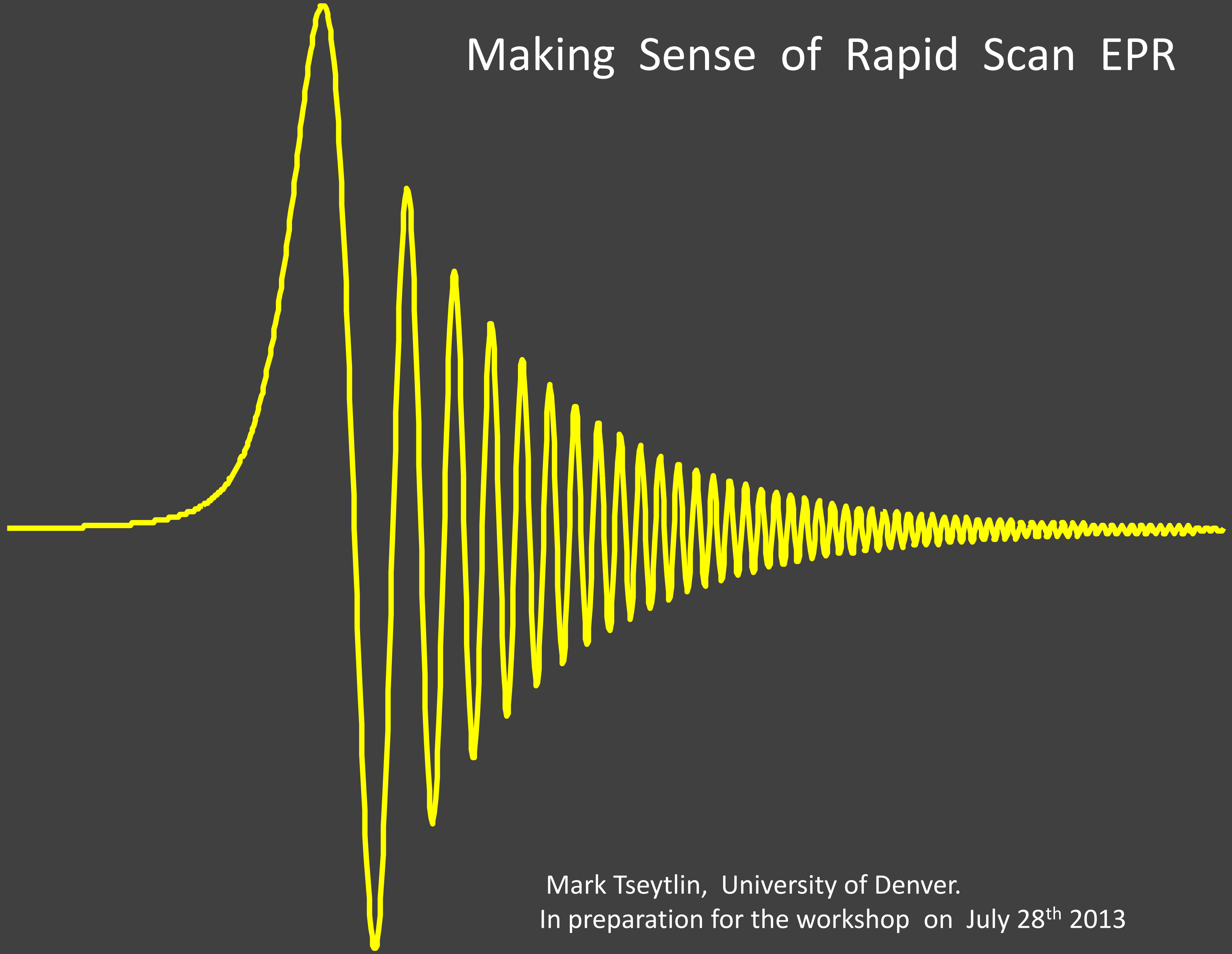
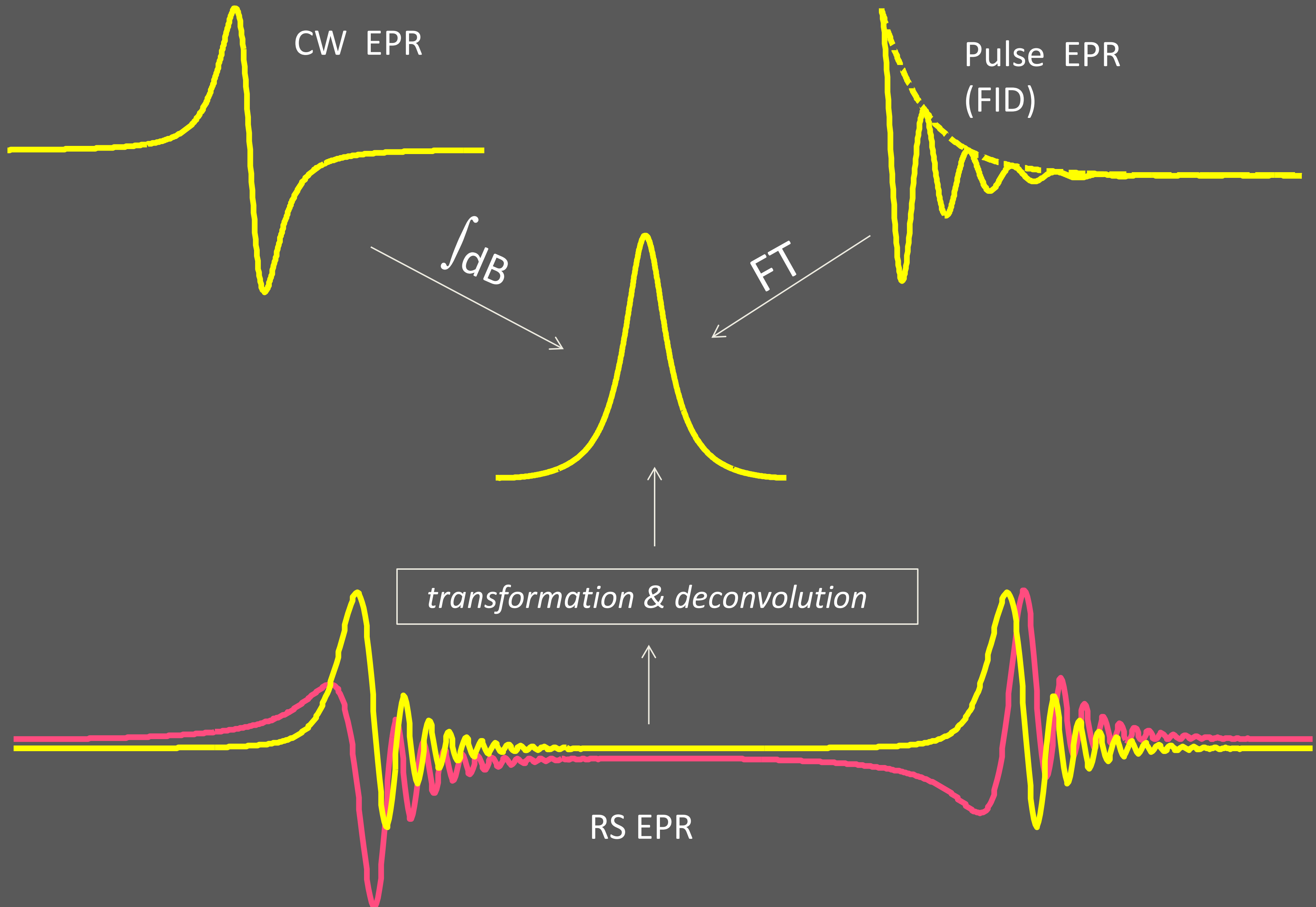
Making Sense of Rapid Scan EPR



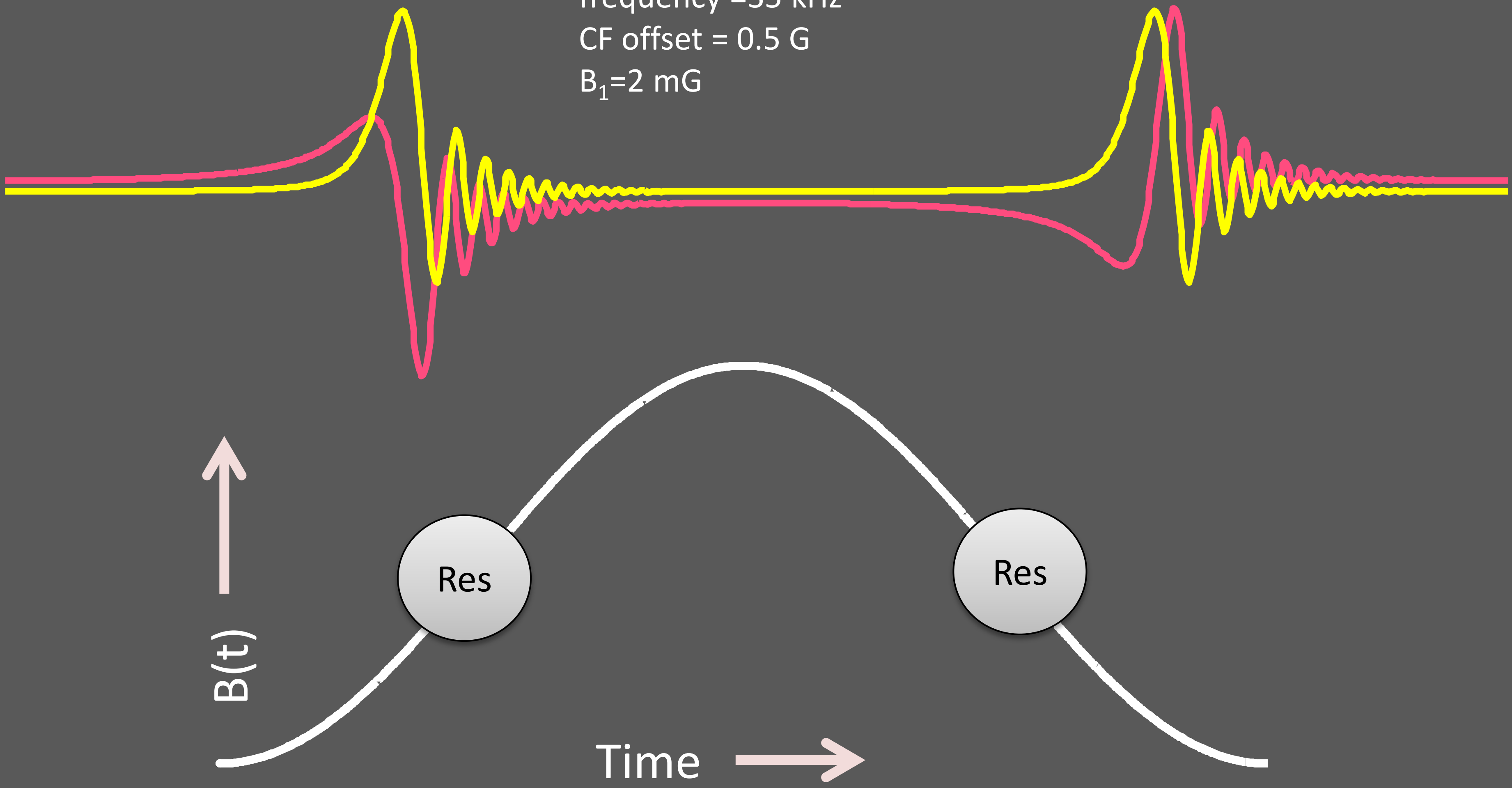
Mark Tseytlin, University of Denver.
In preparation for the workshop on July 28th 2013

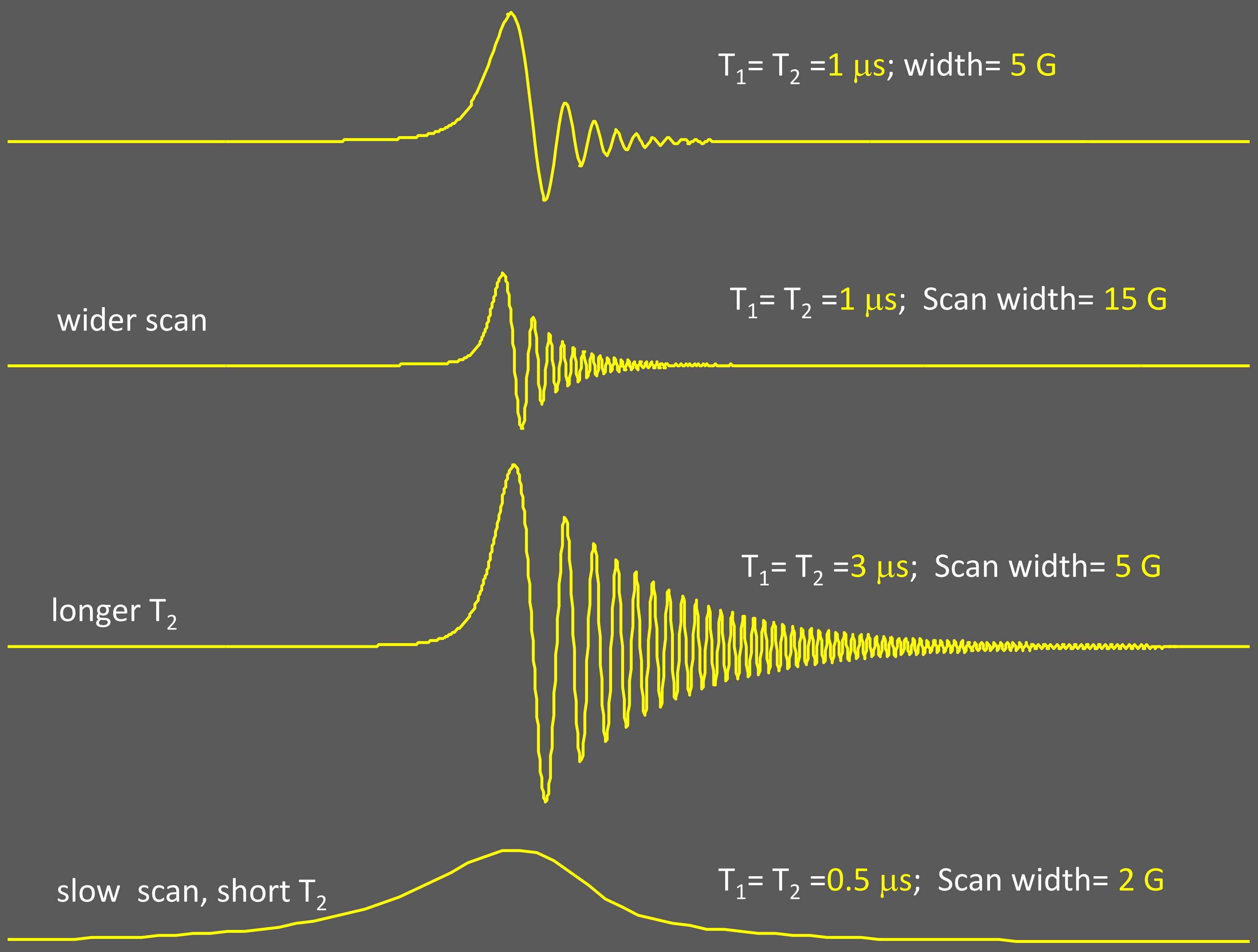

CW EPR
Pulse EPR
(FID)
∫dB
FT
transformation & deconvolution
RS EPR

Numerical Solution of Bloch Equations,

Full Sinusoidal Scan

$T_1 = T_2 = 1\ \mu s$
Sweep width= 3 G Sweep
frequency =35 kHz
CF offset = 0.5 G
B_1=2 mG



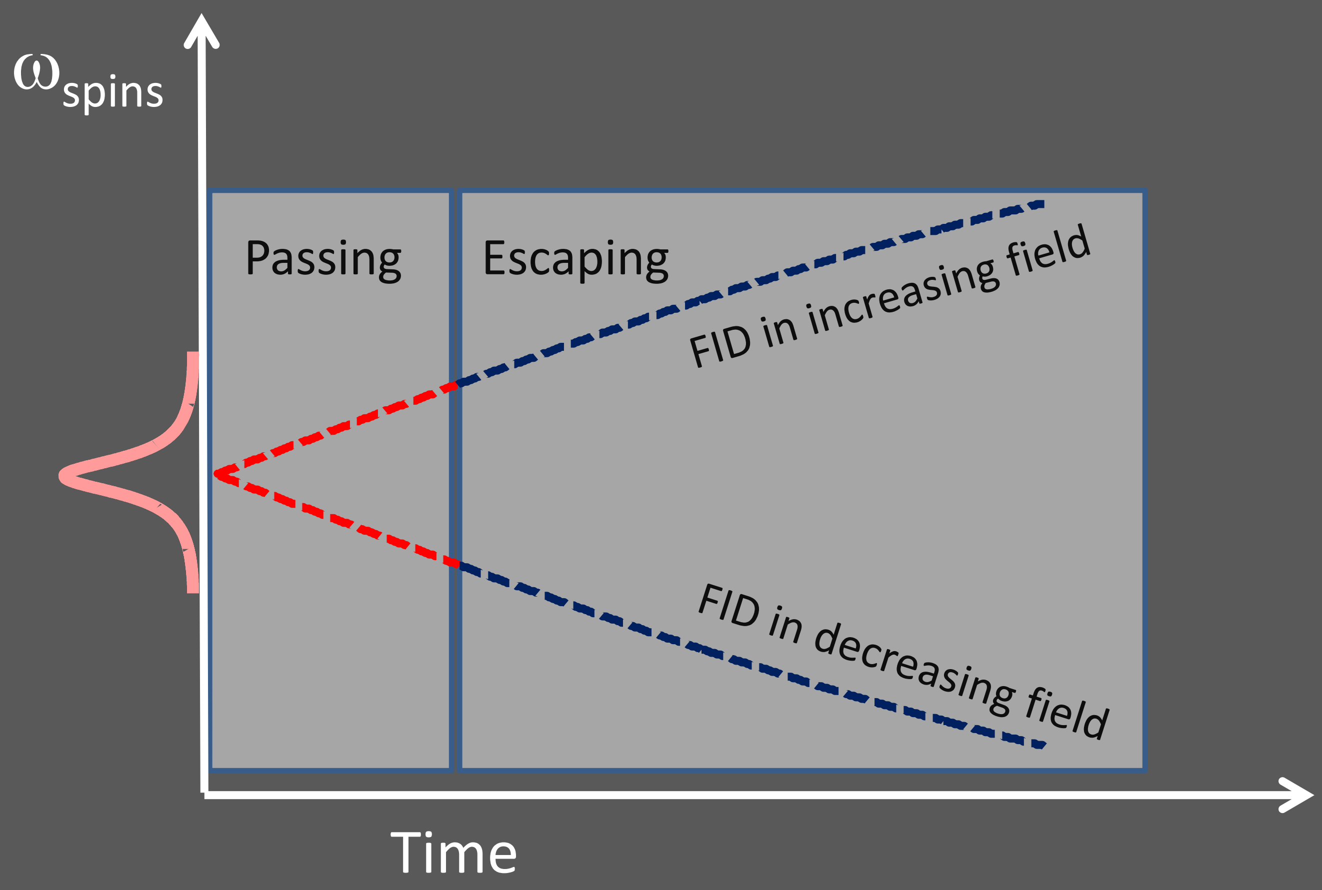


T1= T2 =1 μs; width= 5 G
wider scan
T1= T2 =1 μs; Scan width= 15 G
longer T2
T1= T2 =3 μs; Scan width= 5 G
slow scan, short T2
T1= T2 =0.5 μs; Scan width= 2 G

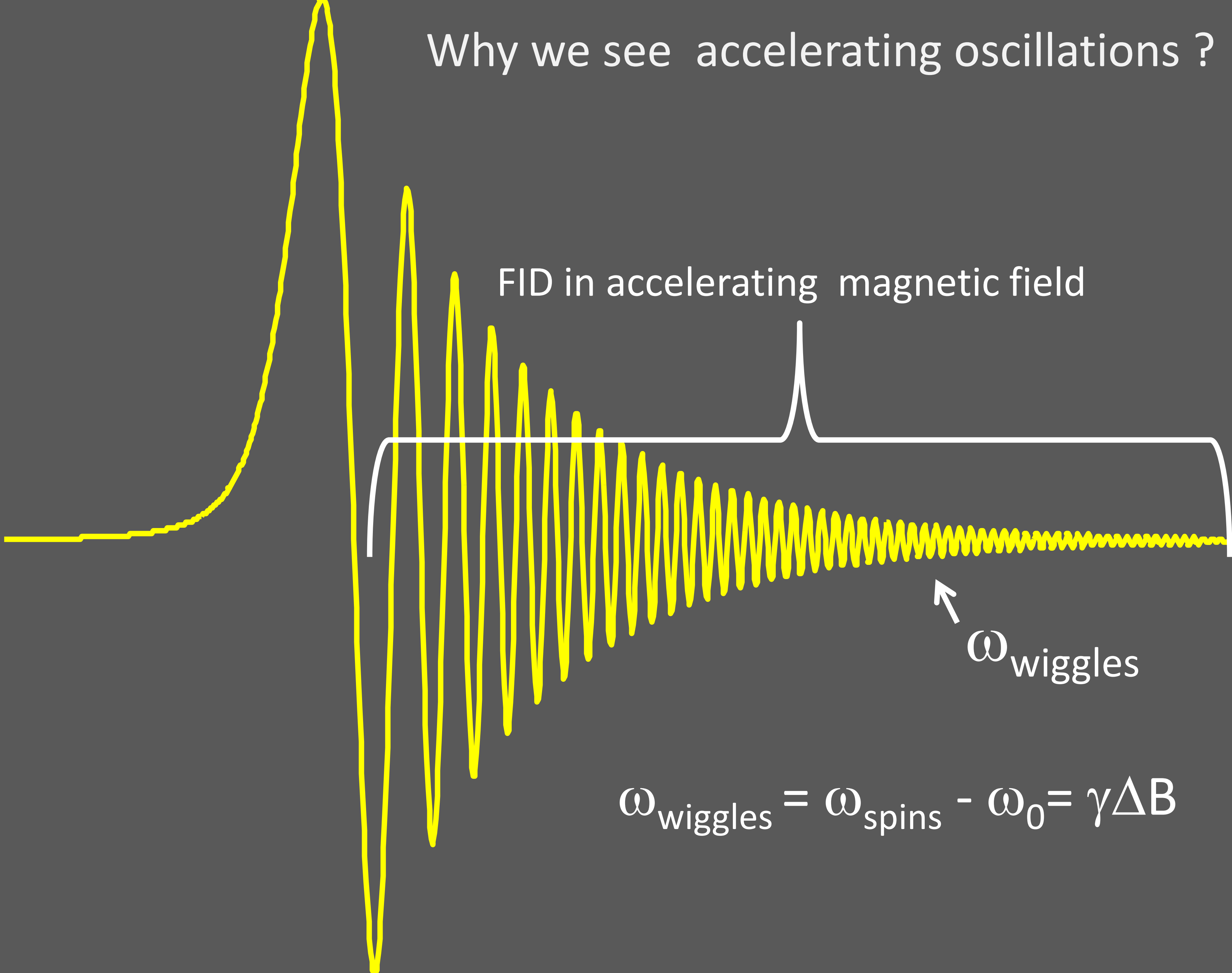
During a scan two time periods can be very roughly distinguished:

Passing through resonance (strong interaction with B_1)

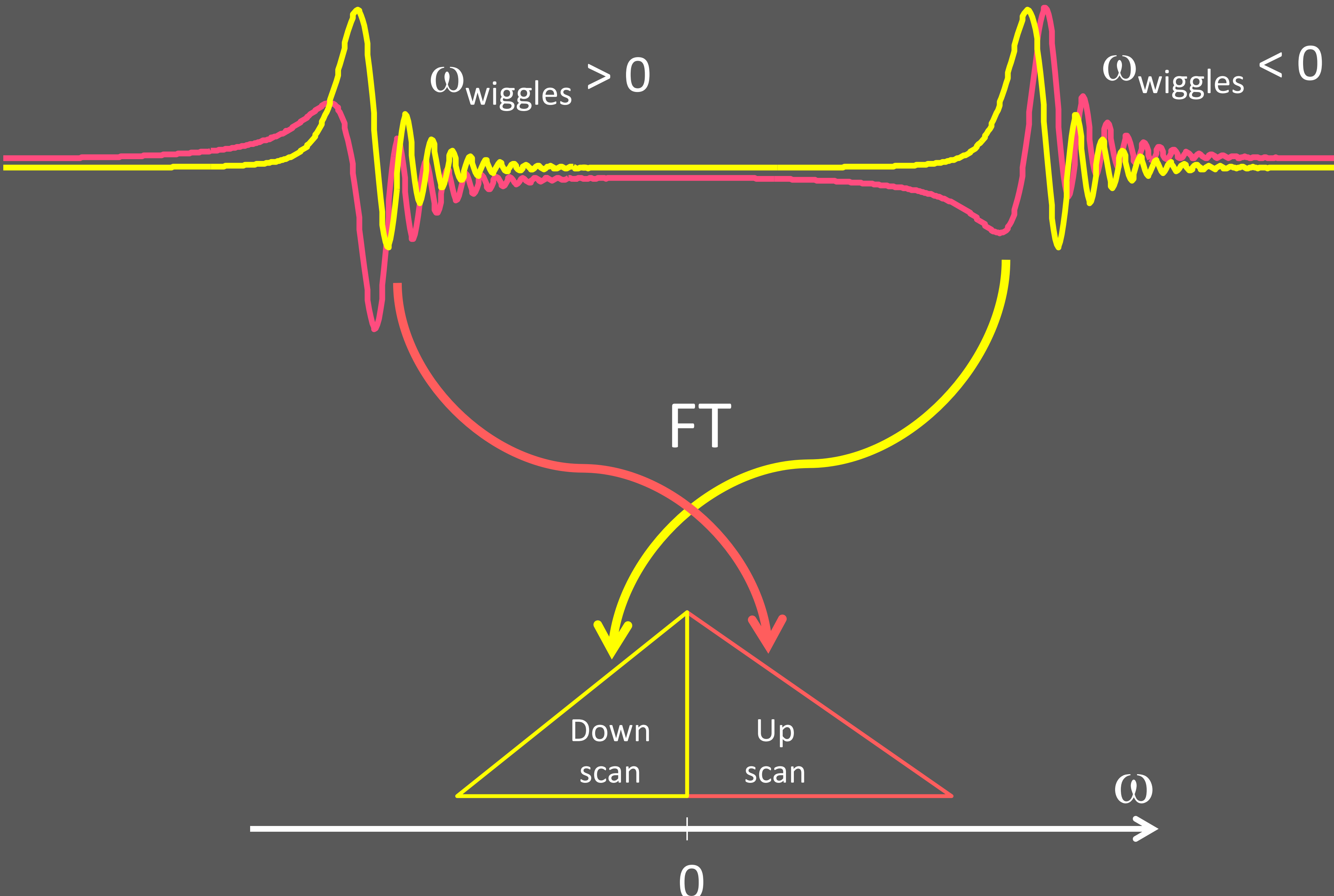
Escaping from the resonance (very weak interaction with B_1)



Why we see accelerating oscillations ?



$$\omega_{wiggles} = \omega_{spins} - \omega_0 = \gamma \Delta B$$

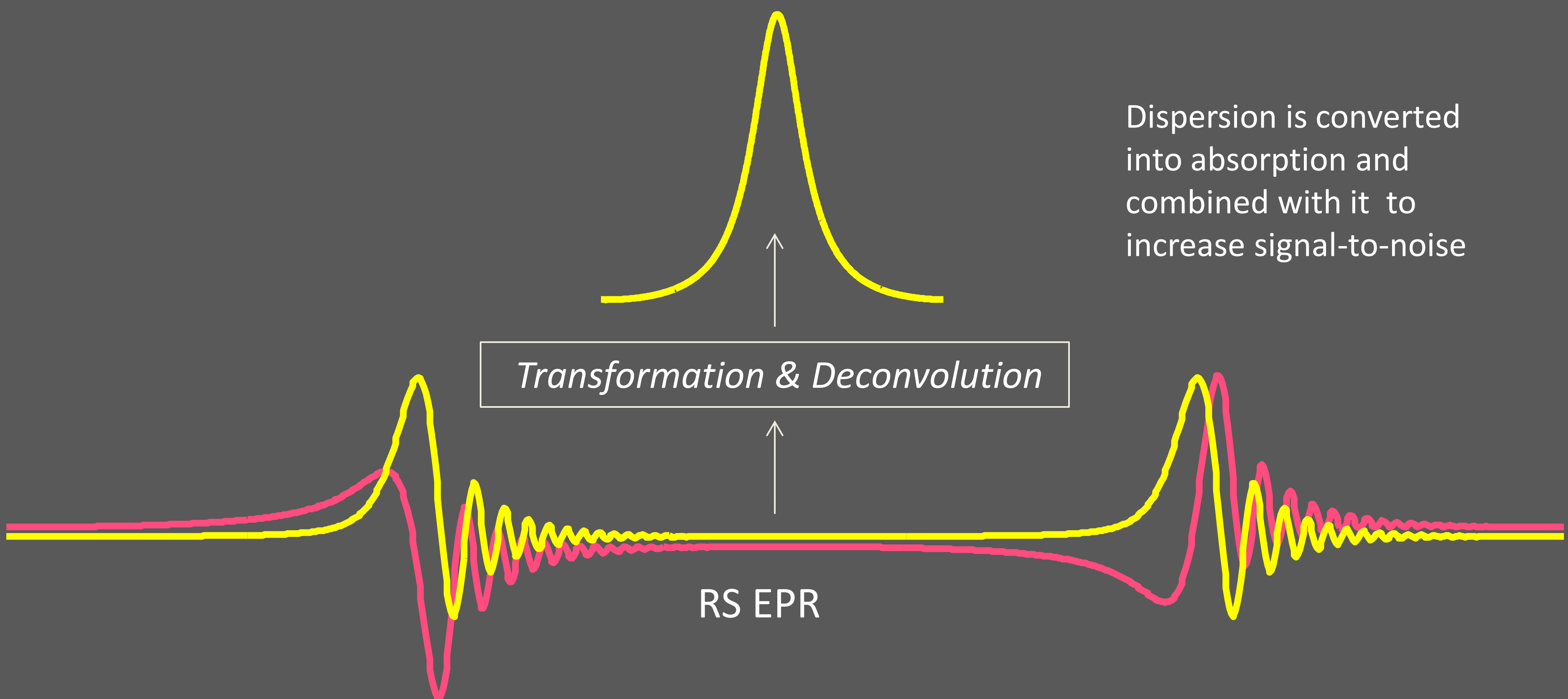


Up-field and down-field scans are separated in the ω-domain!

RS signal into EPR spectrum in two steps

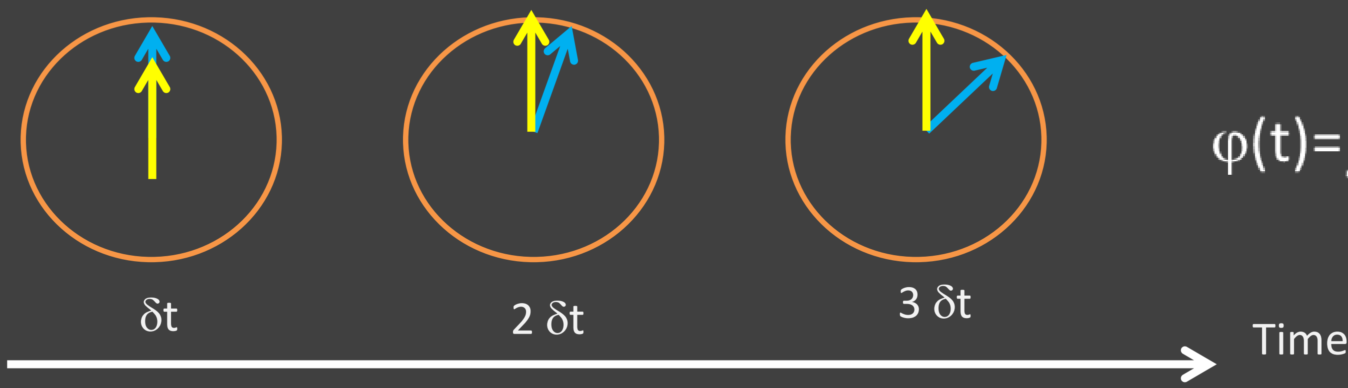
(1) Undo the effect of the changing magnetic field that manifests itself as accelerating oscillations. It is done by transformation of RS signal into an accelerating Larmor frequency frame.

(2) Deconvolution



We need to be in-phase with a vector that resides in an accelerating frame

$\varphi_1 \approx \omega_0(\delta t)\delta t$ $\varphi_2 \approx \varphi_1 + \omega_0(2\delta t)\delta t$ $\varphi_3 \approx \varphi_2 + \omega_0(3\delta t)\delta t$



$$\varphi(t) = \int_{t_0}^{t} \omega_0(\tau) d\tau$$

Transition into this frame is done by multiplication by $D(t) = \exp\{-j\varphi(t)\}$

Step 1: $RS'(t) = RS(t)\, D(t)$

This transformation is equivalent to changing:

From → To

Field scan experiment → Frequency scan experiment

$\omega_L = -½ \gamma B_S \cos(\omega_S t)$ → ω_L = const

ω_0 = const → $\omega_0 (t) = -½ \gamma B_S \cos(\omega_S t)$

$RS(t)$ → $RS'(t)=RS(t)\, D(t)$

B_1=const → $B_1 D(t)$

$\omega_L = ½ \gamma B_S \sin(\omega_S t)$, where B_S – scan amplitude, ω_S – scan frequency

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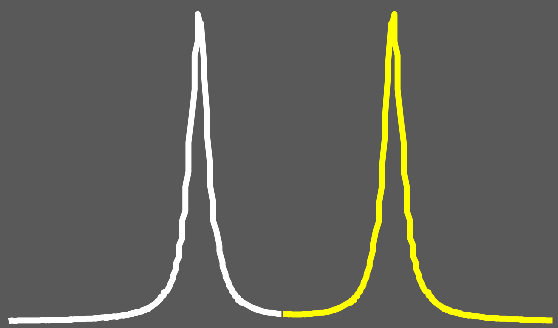
If the response of the spin $RS'(t)$ is linear with respect to $B_1(t)$

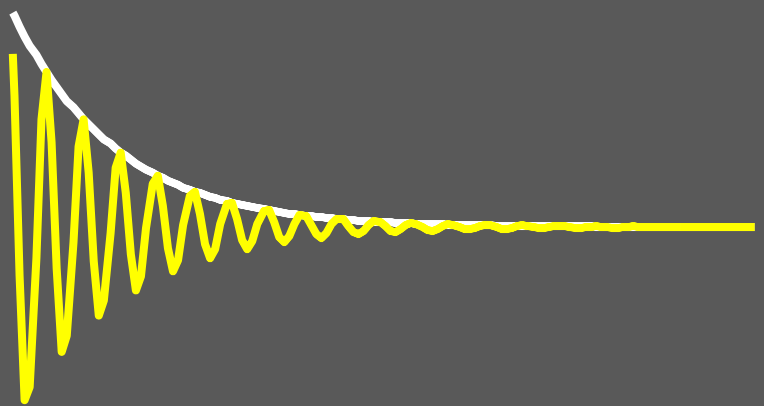
$RS'(t)=B_1 * FID(t) \otimes D(t)$ can be solved Spectrum = FT[RS'] / FT[D]

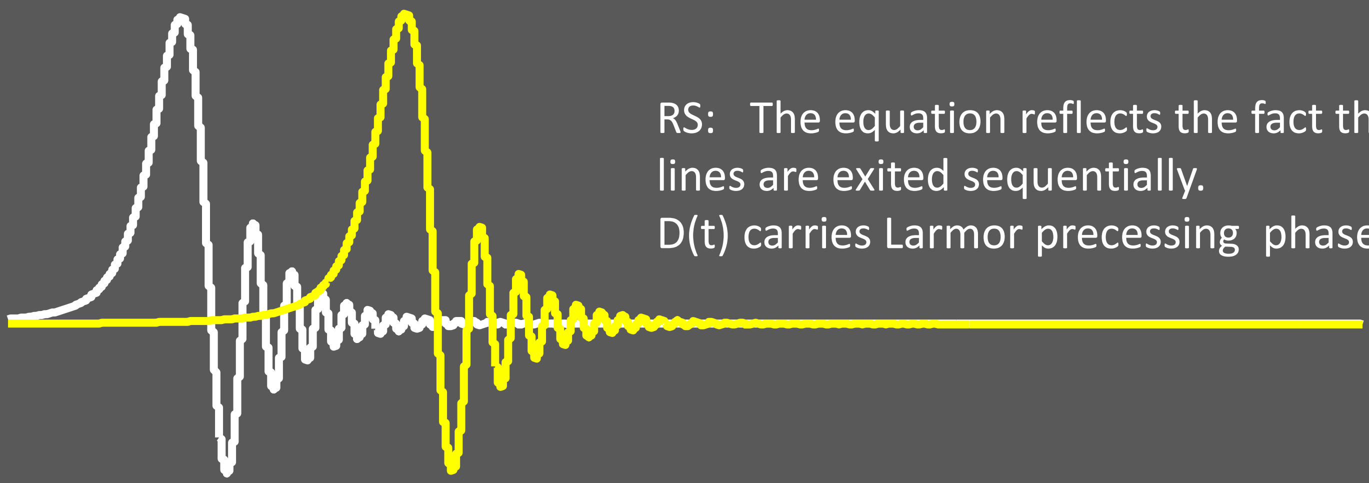
Stepping back to add some meaning to $RS'(t)=B_1 * FID(t) \otimes D(t)$

Two line spectrum:



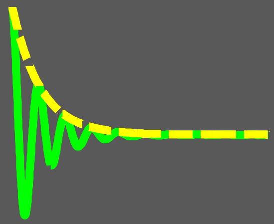
FID: two lines are excited at the same time



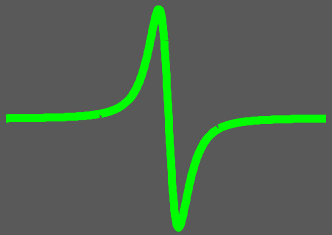


RS: The equation reflects the fact that two lines are exited sequentially.
D(t) carries Larmor precessing phase info.

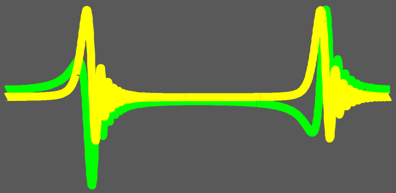
Background problem



In pulse EPR background signal is removed by phase cycling

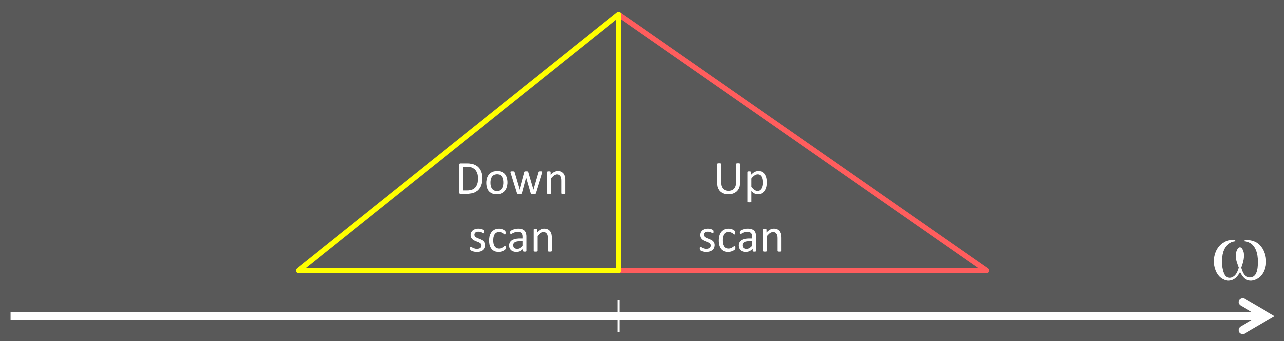


In CW EPR periodic background signal is removed by phase sensitive detection followed by baseline correction



The algorithm based on separation of EPR and background signals is the frequency domain has been developed.
It does not require off-resonance measurement.

Up-field and down-field scans are separated in the ω-domain



Background removal algorithm

Step 1. Fourier transformation of rapid scan signal plus background

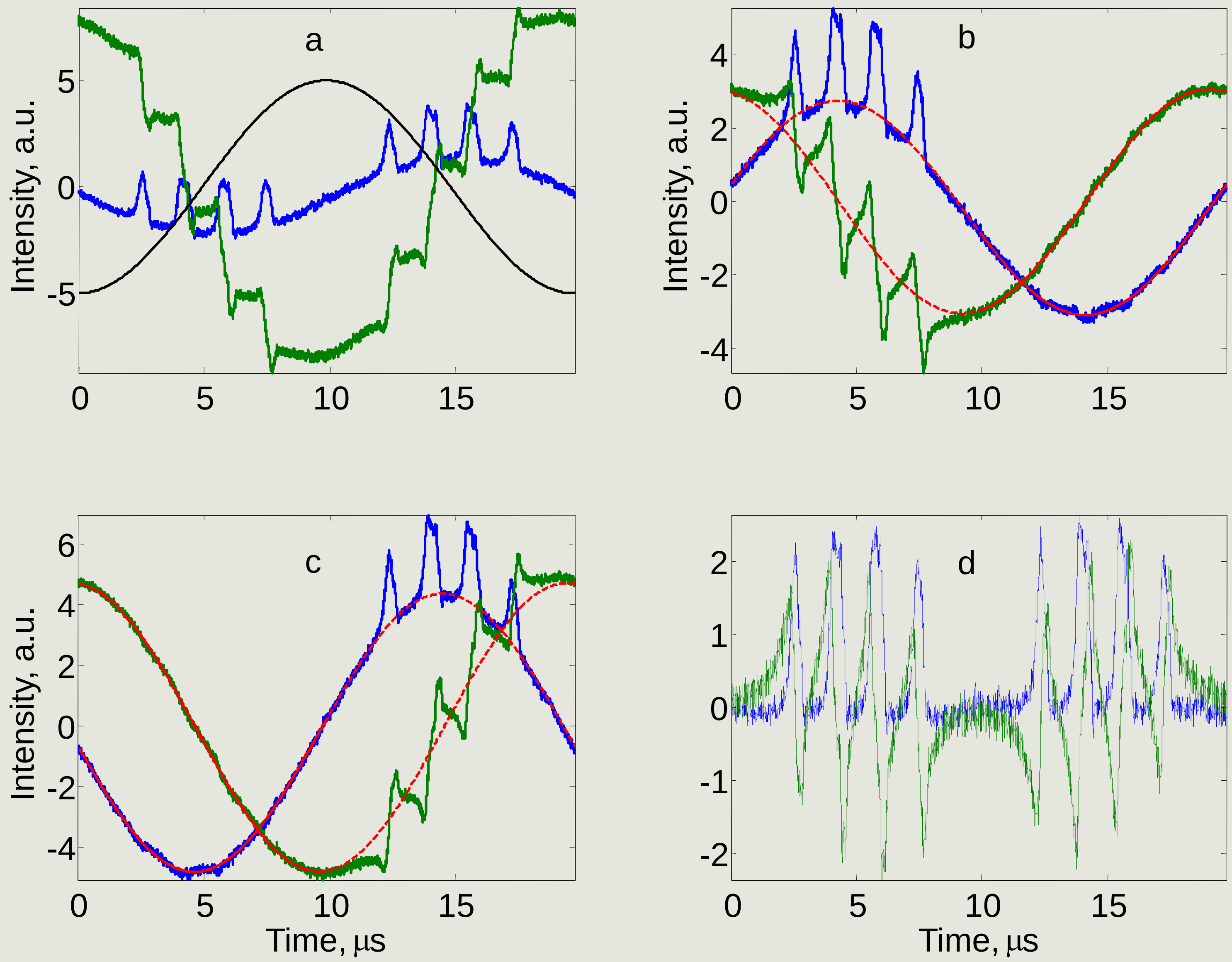
Step 2. Separation of up-field and down-field components.

The result is two frequency domain signals.

Step 3. These two signal s are Inverse Fourier transformed into the time-domain

Step 4. Background signals are fitted in the areas with no EPR , extrapolated into EPR containing areas and subtracted.

Example: background subtraction procedure to spectra of BMPO-OOH at X-band.



Summary

- Rapid scan signal exhibits features similar to both CW and pulse EPR
- The method has been developed to transform rapid scan signal into slow scan EPR
- Background signal can be removed by separating signals in the frequency domain