

Accessing fast spin relaxation dynamics at (sub)millimetre wave frequencies via rapid-scan EPR spectroscopy

Oleksii Laguta

Brno University of Technology

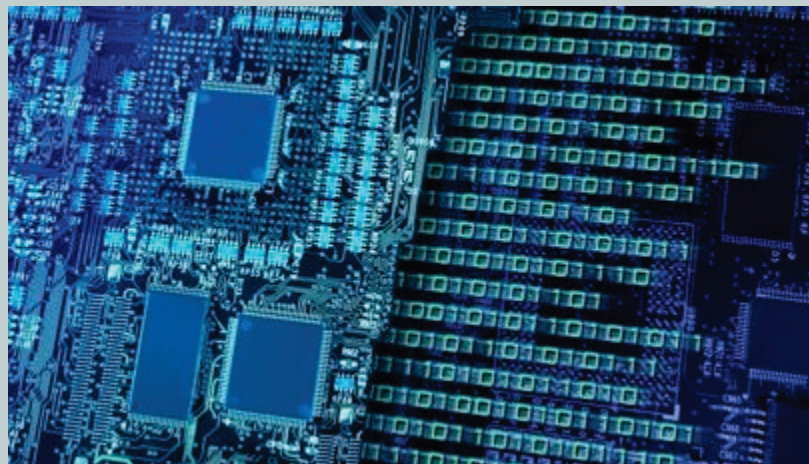
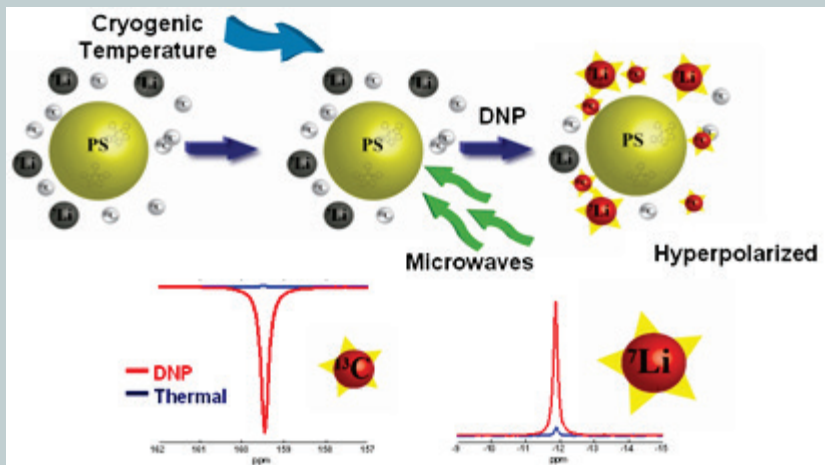


Introduction

Spin dynamics in THz frequency range

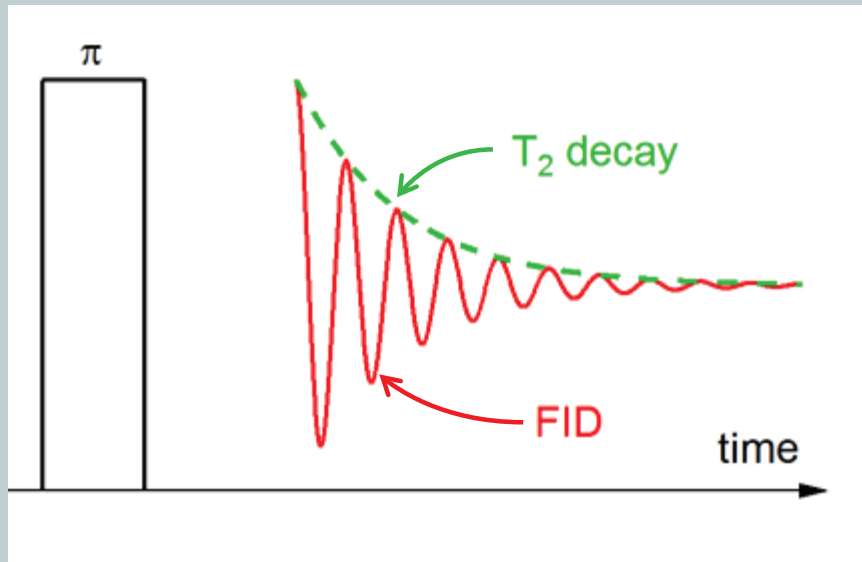
Dynamic Nuclear Polarization –
Nuclear Magnetic Resonance

Quantum computation – spin coherence time T_2



Introduction

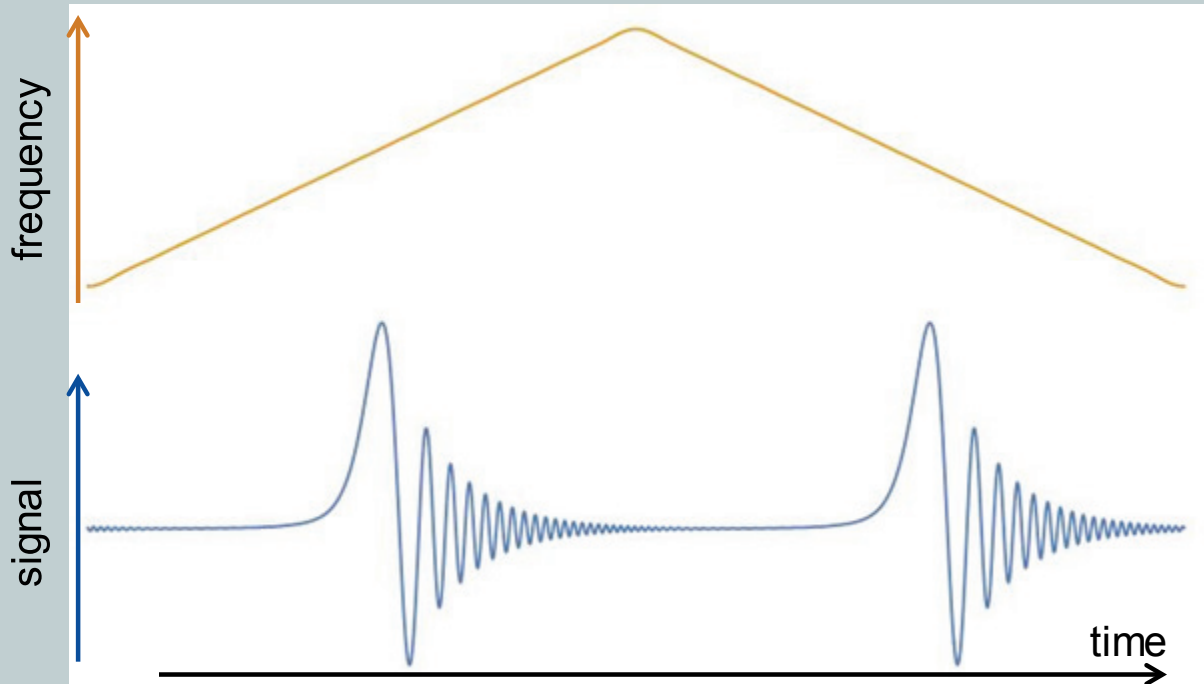
Pulse techniques



- Easy data processing
- Rather easy in technical aspects
- Requires high MW power

Introduction

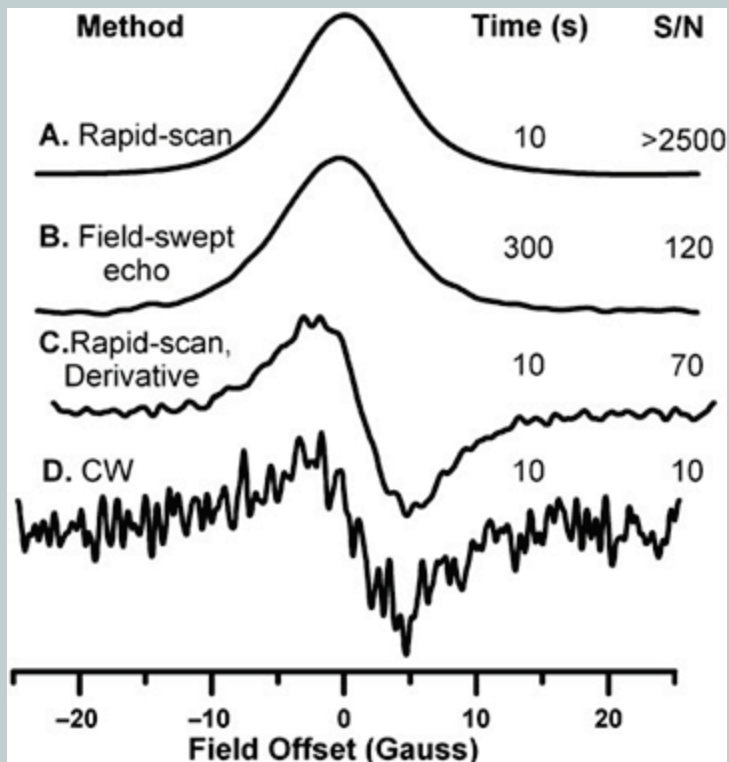
Rapid scan technique



- Does not require high MW power
- More complicate data processing
- Requires high sweep rates

Introduction

Rapid scan technique



- Does not require high MW power
- More complicated data processing
- Requires high sweep rates

Basics of rapid scan technique

- Rapid scan mode if $\left| \frac{df}{dt} \right| \gg T_2^{-2}, (T_1 T_2)^{-1}$
- Analysis is based on the modified Bloch equations

$$\begin{aligned}\frac{dM_x}{dt} &= \frac{-M_x}{T_2} - [\Delta\omega + f_m(t)]M_y \\ \frac{dM_y}{dt} &= [\Delta\omega + f_m(t)]M_x - \frac{M_y}{T_2} - \gamma B_1 M_z \\ \frac{dM_z}{dt} &= \frac{M_0}{T_1} + \gamma B_1 M_y - \frac{M_z}{T_1}\end{aligned}$$

Basics of rapid scan technique

- Rapid scan mode if $\left| \frac{df}{dt} \right| \gg T_2^{-2}, (T_1 T_2)^{-1}$
- Analysis is based on the modified Bloch equations

$$\begin{aligned}\frac{dM_x}{dt} &= \frac{-M_x}{T_2} - [\Delta\omega + f_m(t)]M_y \\ \frac{dM_y}{dt} &= [\Delta\omega + f_m(t)]M_x - \frac{M_y}{T_2} - \gamma B_1 M_z \\ \frac{dM_z}{dt} &= \frac{M_0}{dt} + \gamma B_1 M_y - \frac{M_z}{T_1}\end{aligned}$$

- Types of modulation
- Cosine



Basics of rapid scan technique

- Rapid scan mode if $\left| \frac{df}{dt} \right| \gg T_2^{-2}, (T_1 T_2)^{-1}$
- Analysis is based on the modified Bloch equations

$$\begin{aligned}\frac{dM_x}{dt} &= \frac{-M_x}{T_2} - [\Delta\omega + f_m(t)]M_y \\ \frac{dM_y}{dt} &= [\Delta\omega + f_m(t)]M_x - \frac{M_y}{T_2} - \gamma B_1 M_z \\ \frac{dM_z}{dt} &= \frac{M_0}{dt} + \gamma B_1 M_y - \frac{M_z}{T_1}\end{aligned}$$

Types of modulation

- Cosine



- Linear
- Triangular



Basics of rapid scan technique

- Rapid scan mode if $\left| \frac{df}{dt} \right| \gg T_2^{-2}, (T_1 T_2)^{-1}$
- Analysis is based on the modified Bloch equations

$$\begin{aligned}\frac{dM_x}{dt} &= \frac{-M_x}{T_2} - [\Delta\omega + f_m(t)]M_y \\ \frac{dM_y}{dt} &= [\Delta\omega + f_m(t)]M_x - \frac{M_y}{T_2} - \gamma B_1 M_z \\ \frac{dM_z}{dt} &= \frac{M_0}{dt} + \gamma B_1 M_y - \frac{M_z}{T_1}\end{aligned}$$

Types of modulation

□ Cosine



□ Linear

□ Triangular

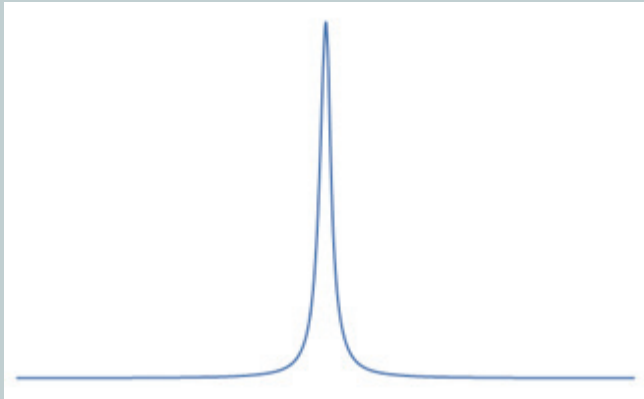


□ Trapezoidal

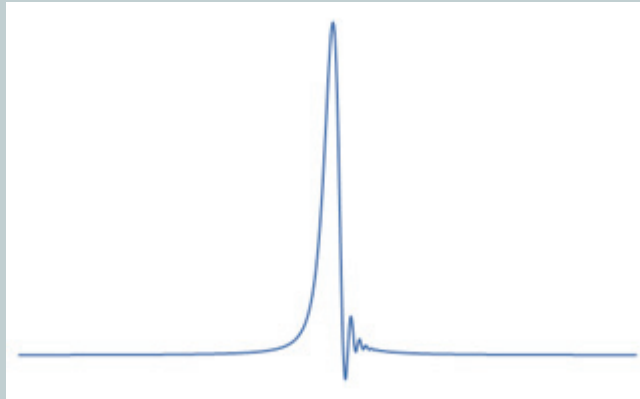


Basics of rapid scan technique

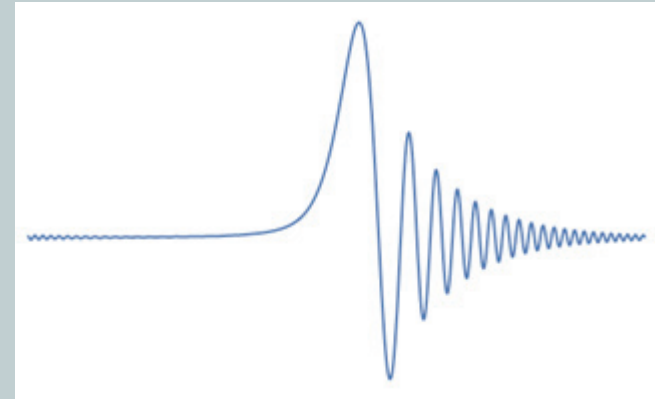
$$\left| \frac{df}{dt} \right| \ll T_2^{-2}$$



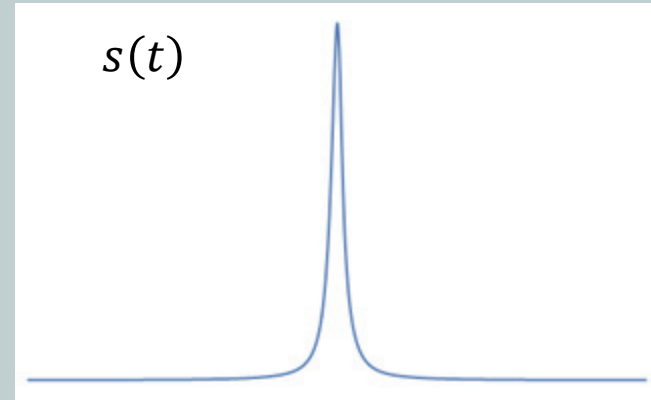
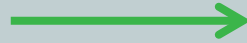
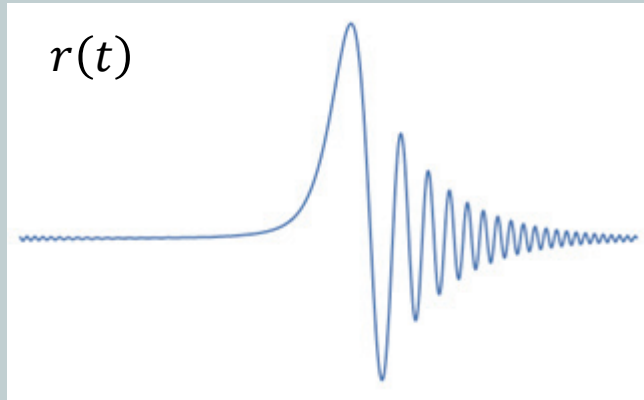
$$\left| \frac{df}{dt} \right| \approx T_2^{-2}$$



$$\left| \frac{df}{dt} \right| \gg T_2^{-2}$$



Basics of rapid scan technique. Deconvolution



Driving function Characteristic function

$$d(t) = \text{Exp}\left[i \int_0^t \omega(\tau) d\tau\right]$$

$$\begin{matrix} d(t) \\ D(\omega) \end{matrix}$$



$\begin{matrix} s(t) \\ S(\omega) \end{matrix}$

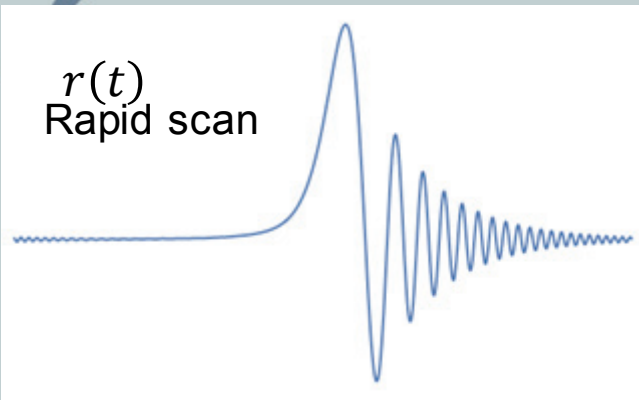


Response

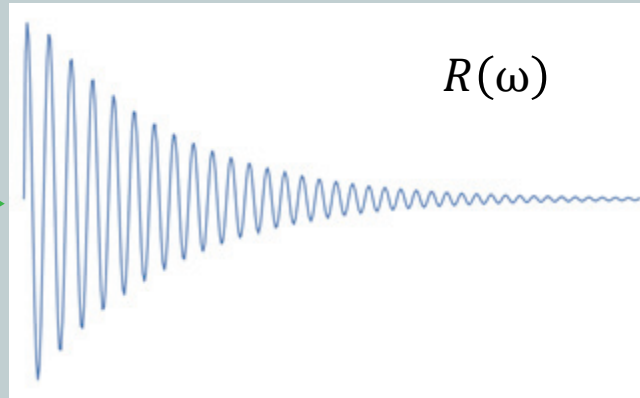
$$r(t) = \int_{-\infty}^{\infty} s(\tau) d(\tau - t) d\tau$$

$$R(\omega) = S(\omega) D(\omega)$$

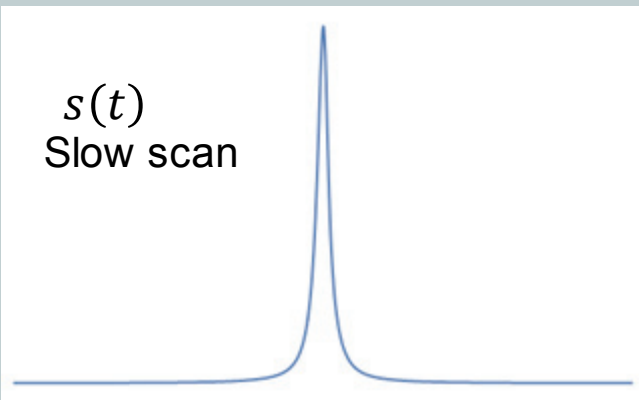
Basics of rapid scan technique. Deconvolution



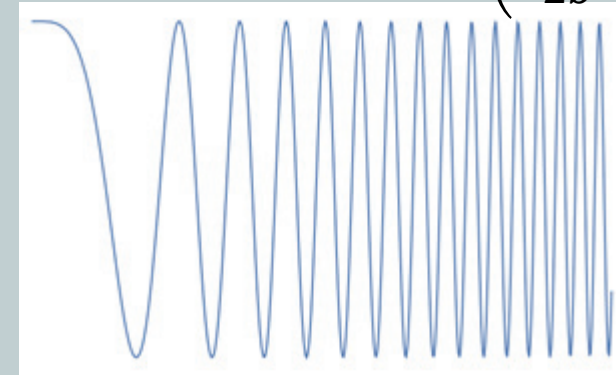
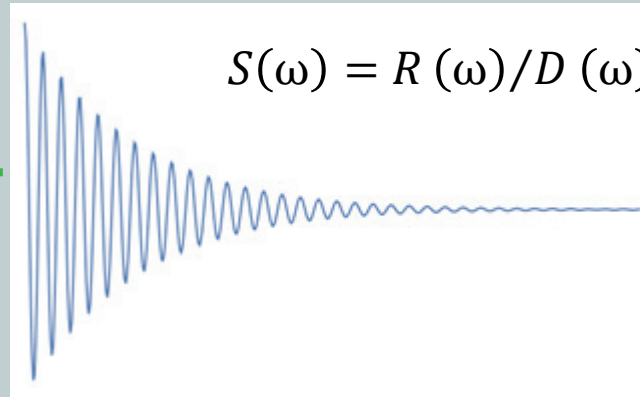
Fourier
→



$$D(\omega) = \exp\left(\frac{-i\omega^2}{2b}\right)$$



Inverse
Fourier
←



Basics of rapid scan technique. Practical considerations

Field domain

- + Relatively easy in development
- + No standing waves

- Low sweep rates!!!
- Narrow sweeps

Frequency domain

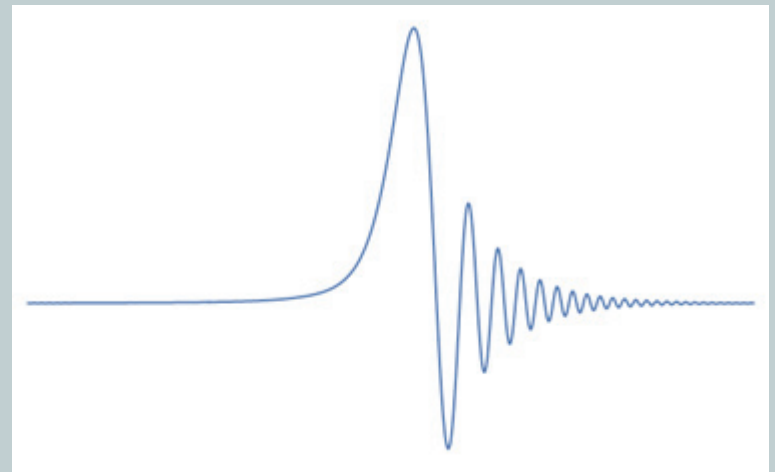
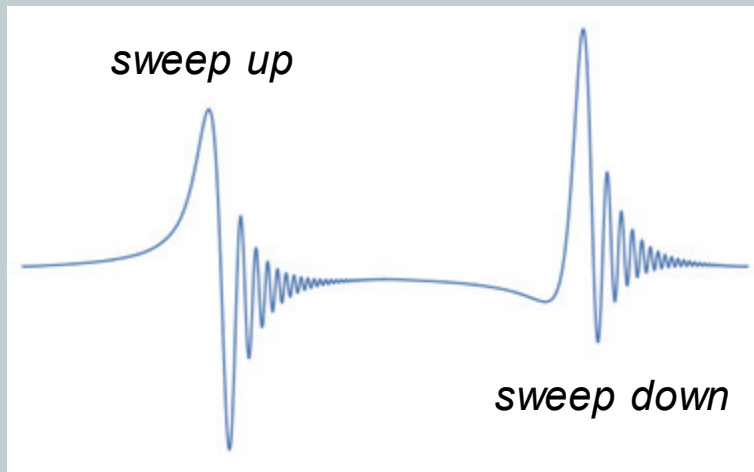
- + High sweep rates
- + Wide sweeps

- Standing waves
- Frequency dependent MW power
- Expensive MW generators

Basics of rapid scan technique. Practical considerations

Mixture of absorption and dispersion signals

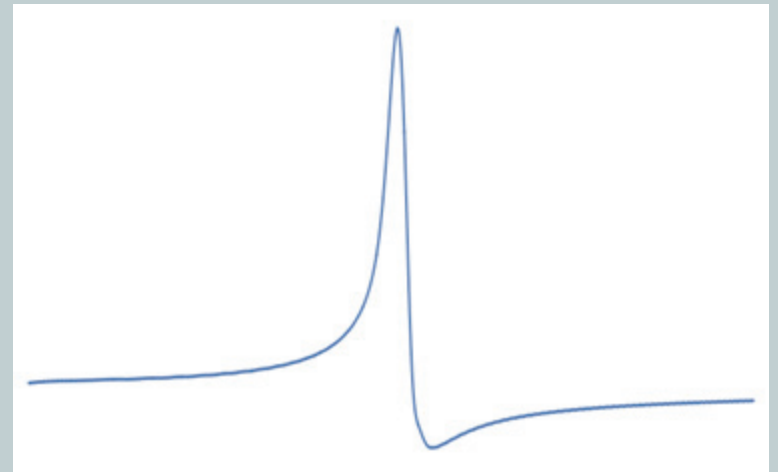
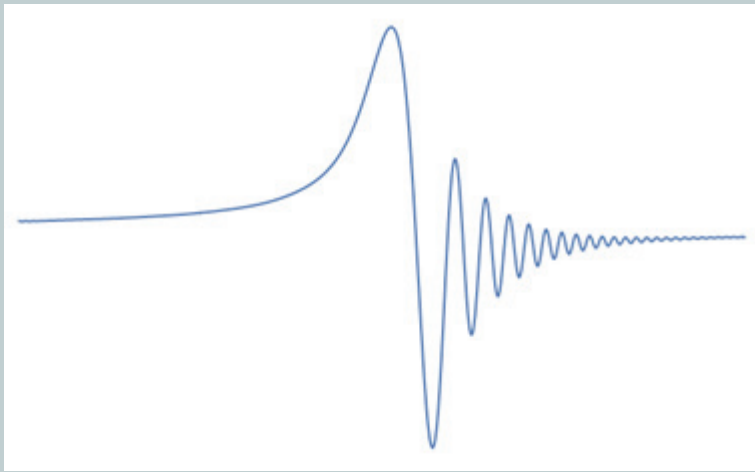
$$M_x(\text{sweepup}) = -M_x(\text{sweeplown})$$



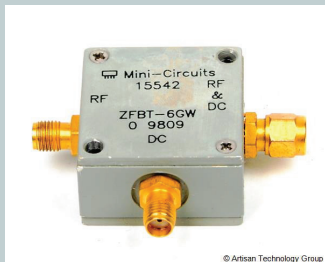
$$M_x + M_y - M_x + M_y = 2M_y$$

Basics of rapid scan technique. Practical considerations

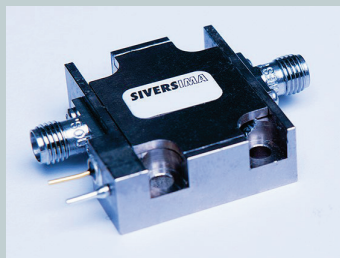
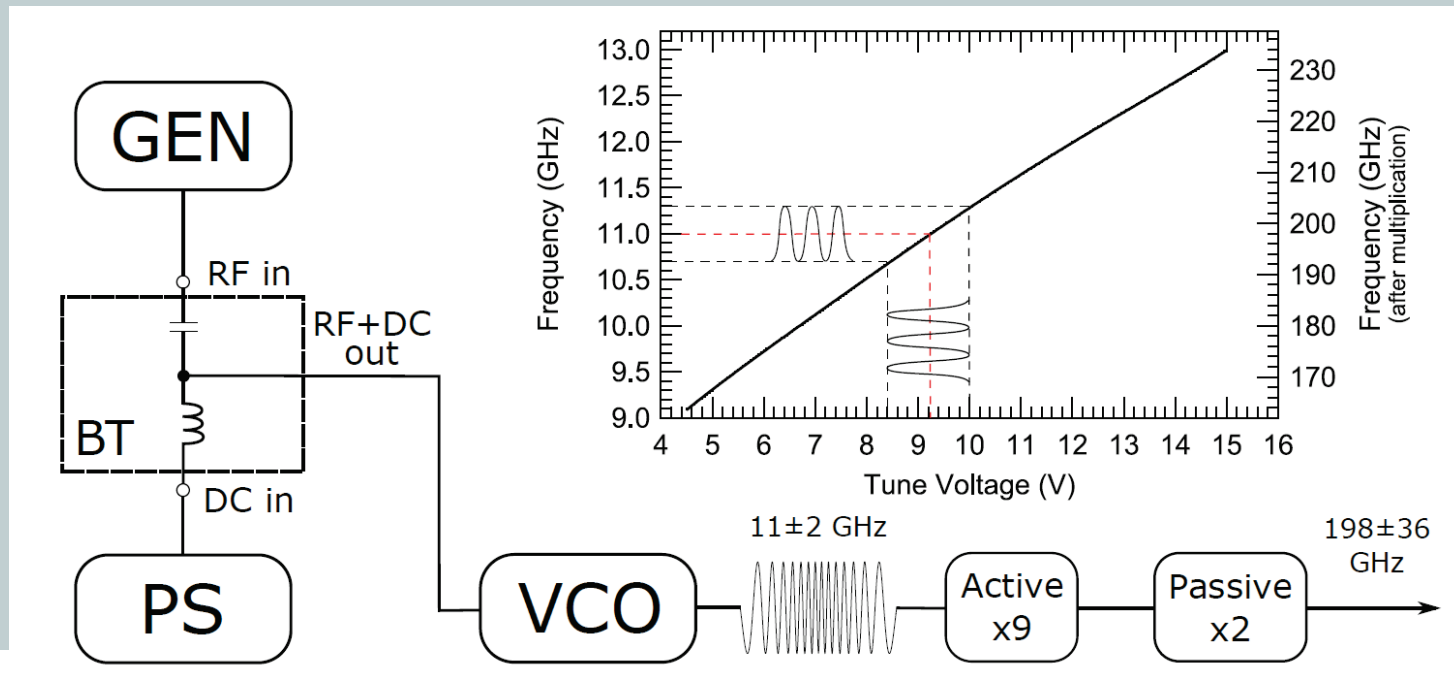
Mixture of absorption and dispersion signals



Experimental setup at Stuttgart University

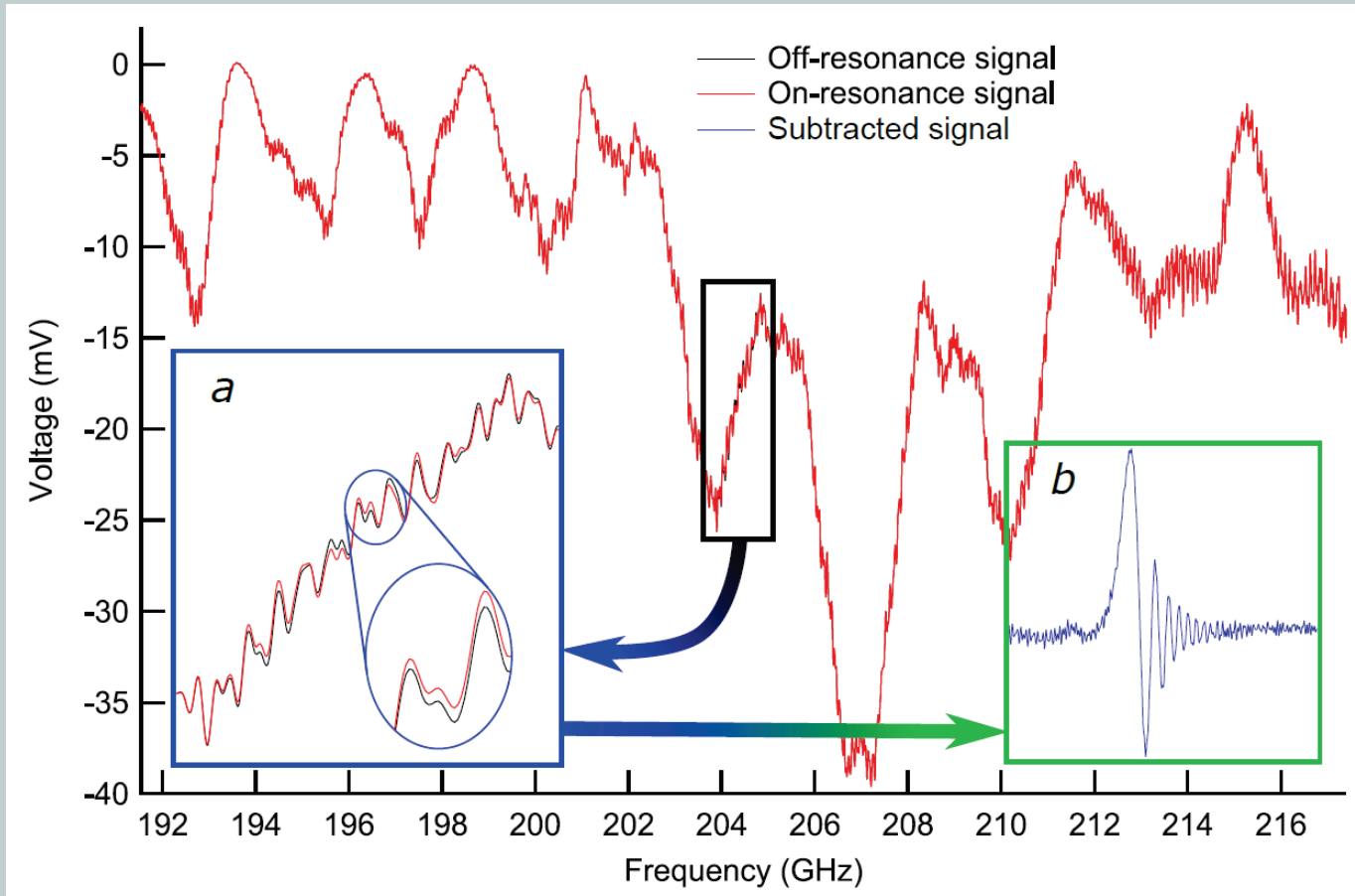


© Arisan Technology Group



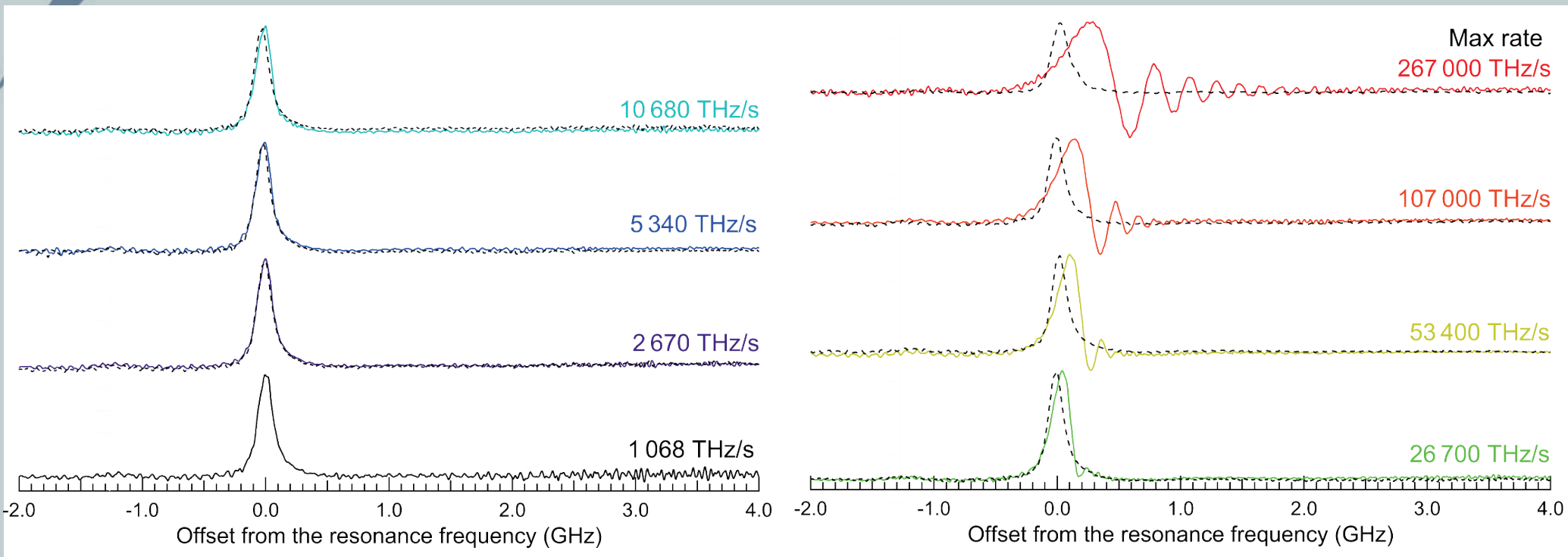
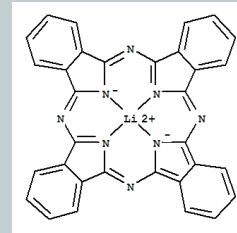
Experimental setup at Stuttgart university

Baseline correction



Experimental setup at Stuttgart university

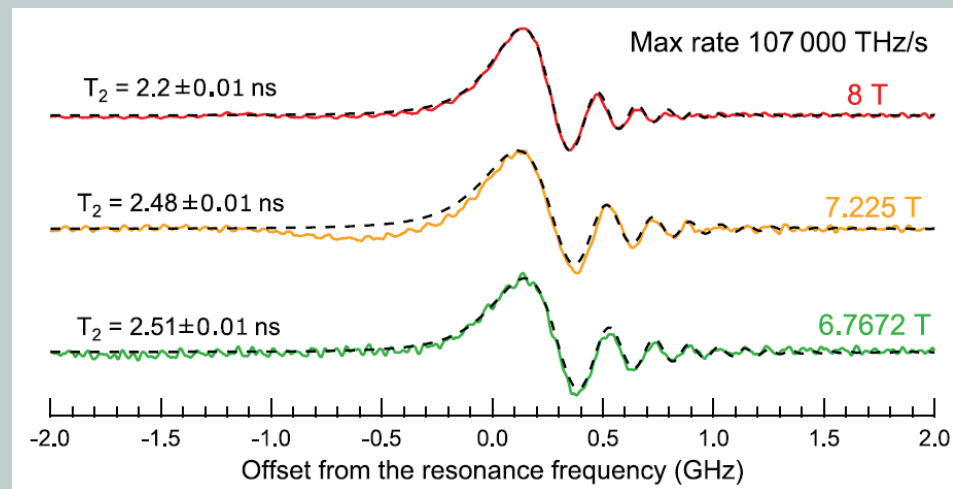
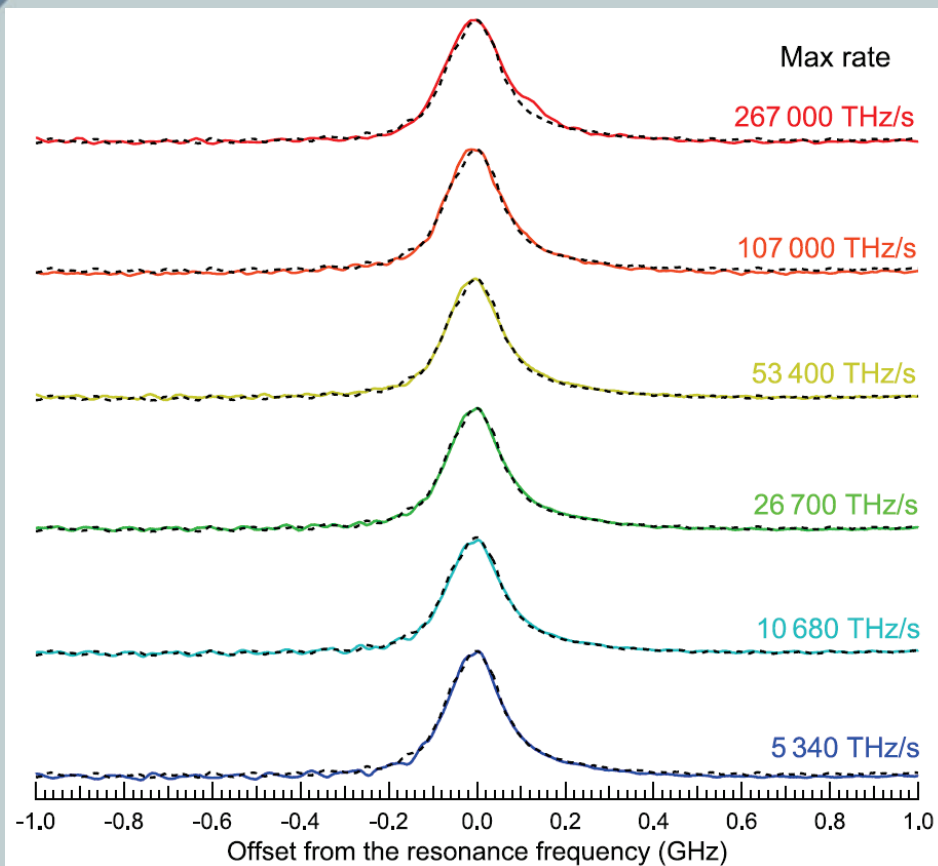
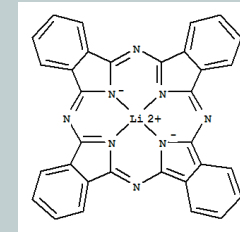
Lithium Phthalocyanine



Magnetic field **8 T** (resonance frequency \sim **224 GHz**), Temperature 13 K

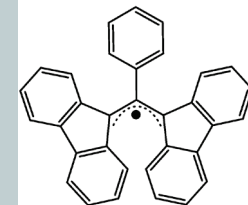
Experimental setup at Stuttgart university

Deconvolution and Bloch equations fit

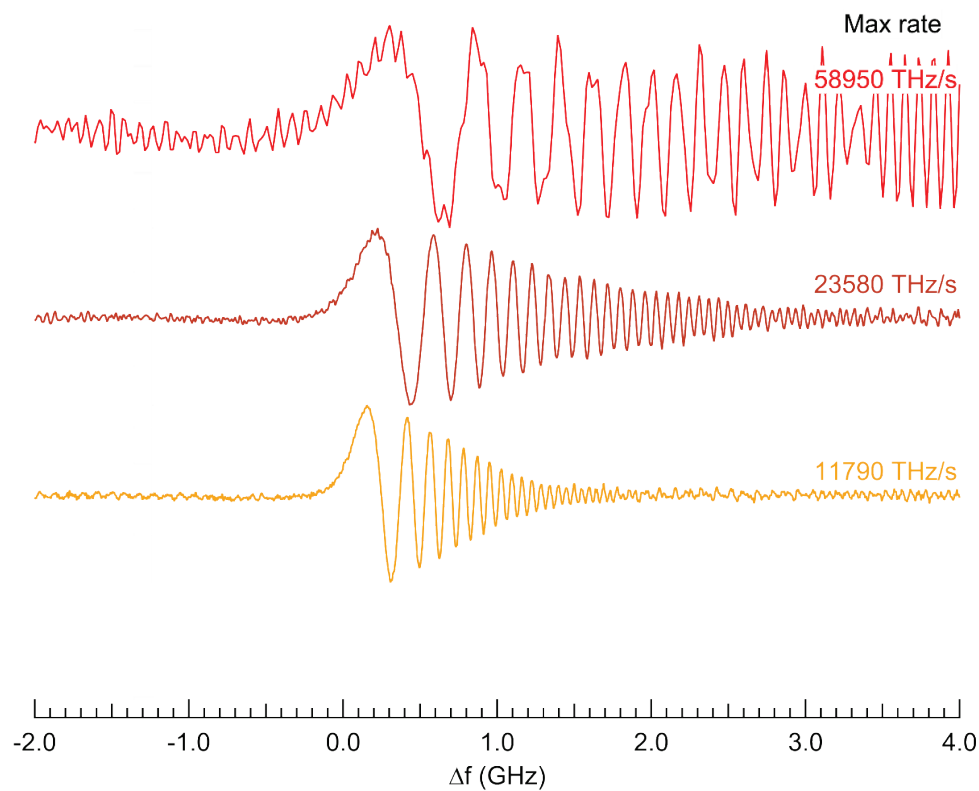
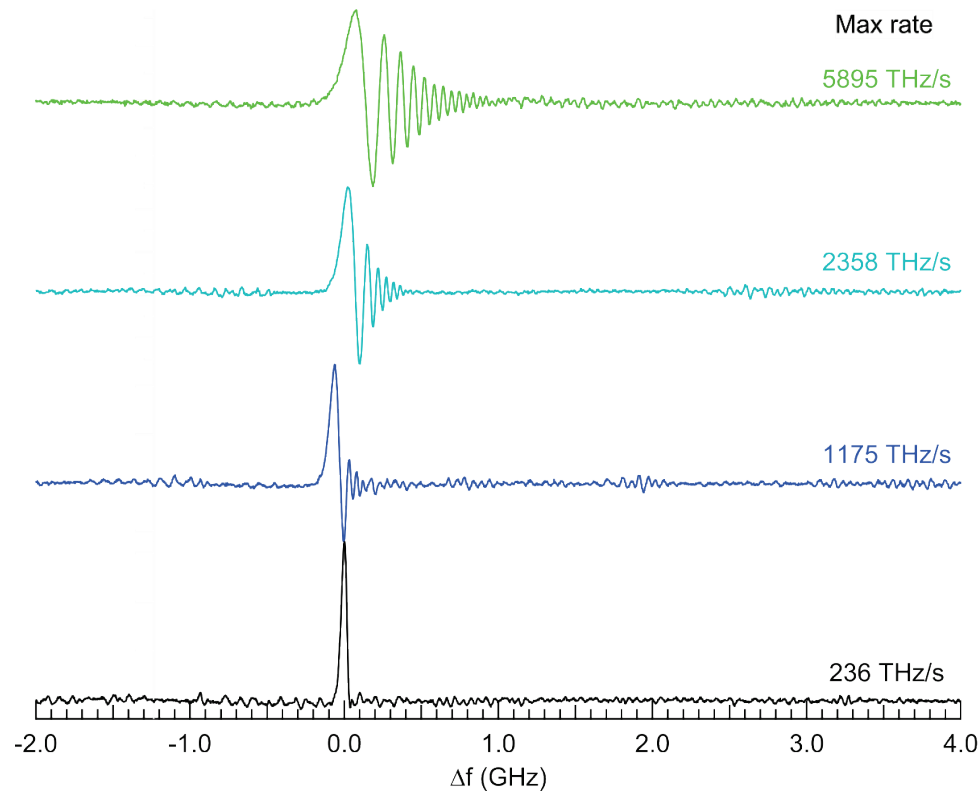


Experimental setup at Stuttgart university

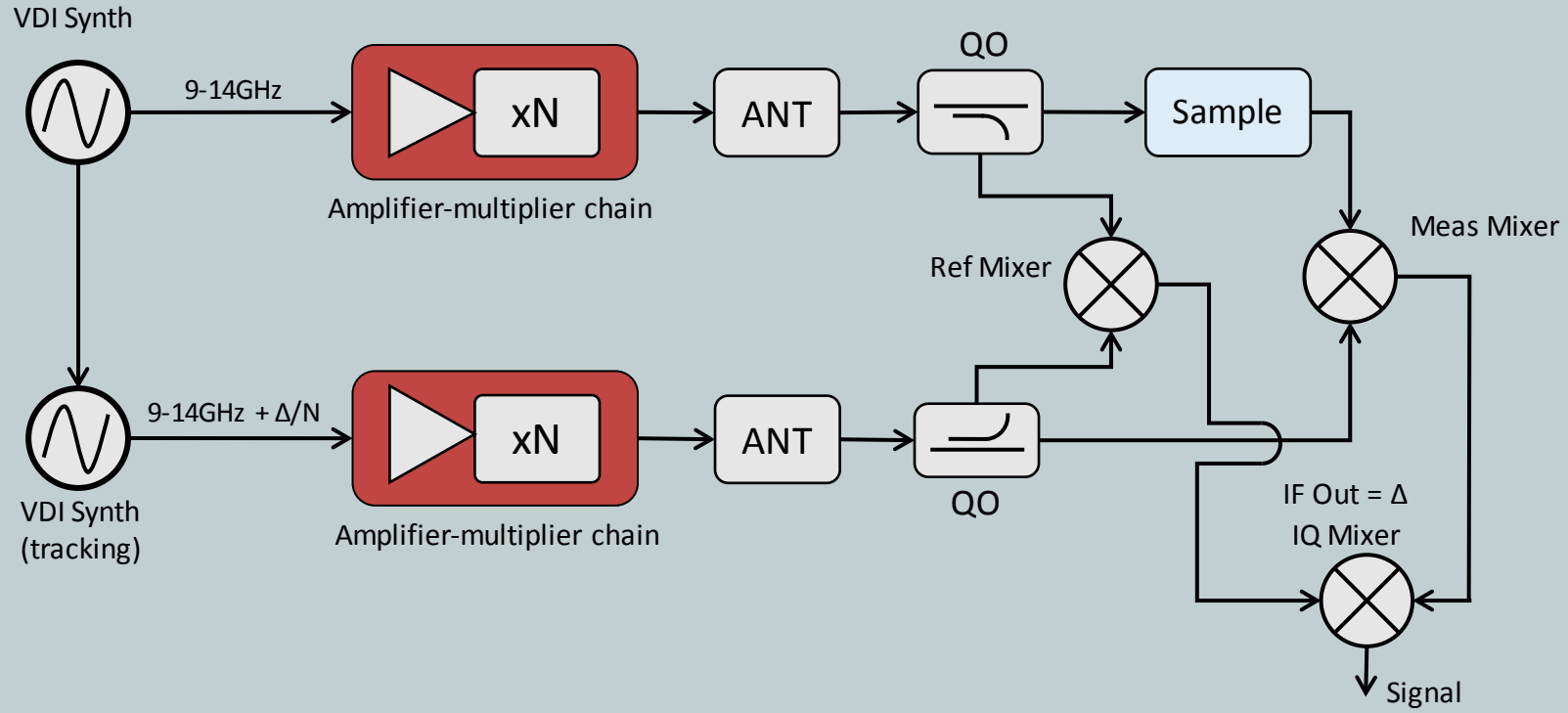
BDPA complex with benzene




1,3-bisdiphenylene-2-phenylallyl
(BDPA)



Experimental setup at Brno university





Thank you for your attention