# Shaped EPR pulse techniques with different type of spin labels

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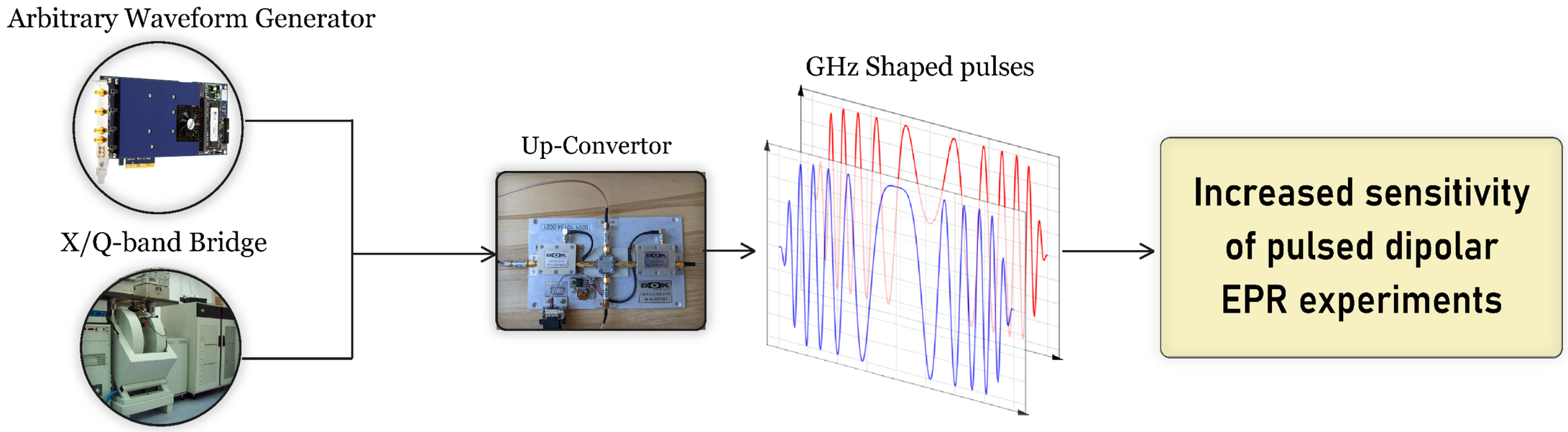



## BACKGROUND

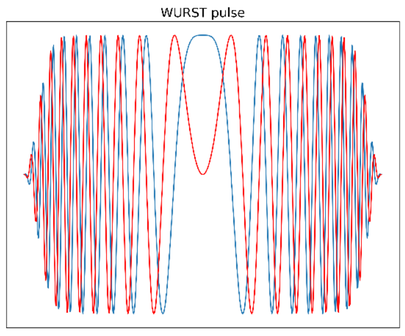
• Narrow excitation widebandth of conventional rectangular pulses often limits sensitivity of pulsed EPR experiments.

• By integrating Arbitrary Waveform Generator (AWG) in our spectrometer, we were able to introduce *shaped* pulses with user-defined amplitude and frequency modulations, allowing precise control of spin magnetization and increasing pulse bandwith.

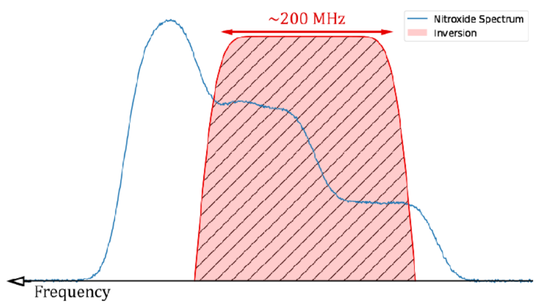
$$\Delta\omega(t) = kt$$

$$B(t) = B_m * (1 - |sin(\beta t)|^n)$$

WURST pulse



*Adiabatic pulses allow inversion bandwidth at hundreds of MHz and higher*




## AIM OF WORK

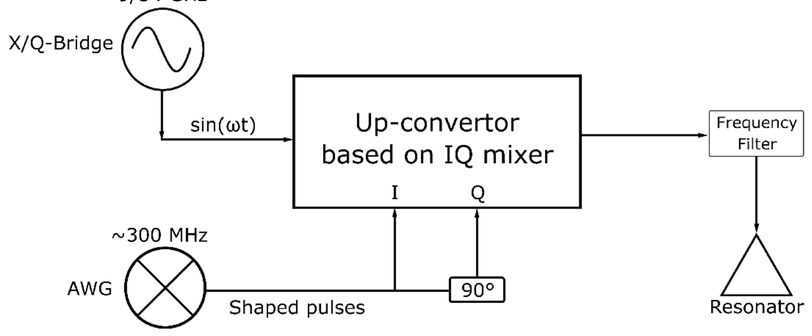
• Integrate support of shaped pulse techniques in Bruker E580 spectrometer

• Increase sensitivity of pulsed DEER experiments on nitroxide-nitroxide and copper-nitroxide pairs using adiabatic pulses

• Perform SIFTER experiment on photoexcited fullerene-trityle spin pair

## METHODS & MATERIALS

9/34 GHz




• User-defined waveforms were generated using Specturm Instrumentation M4i-6631x8 AWG and upconverted to GHz by custom -made unit

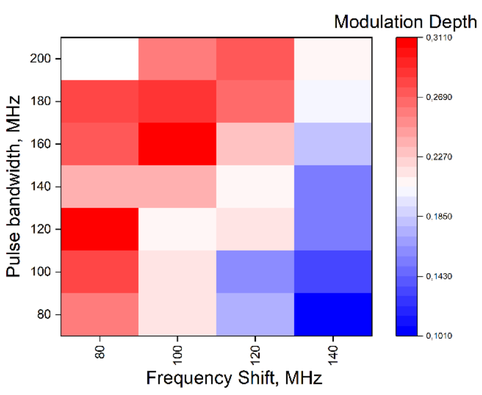
• Open-source software «Atomize» is used to control the AWG module

• Fullerene-trityl complex photoexcited by home-built laser source

• Pulses were adapted to limited resonator bandwith and other instrumental restrictions by varying their parameters

Model samples used in DEER experiments:

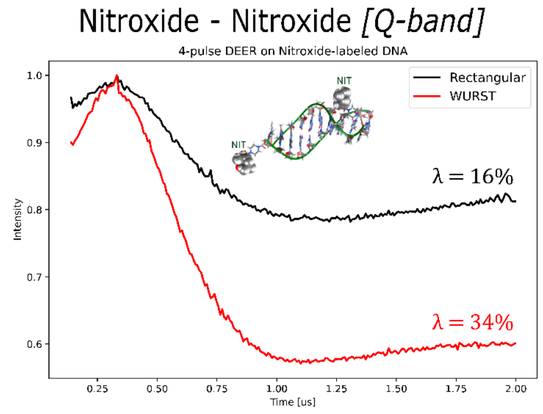
- Human DNA duplex labeled with nitroxide-nitroxide pair
- Human serum albumin (HSA) labeled with copper-nitroxide pair




## RESULTS

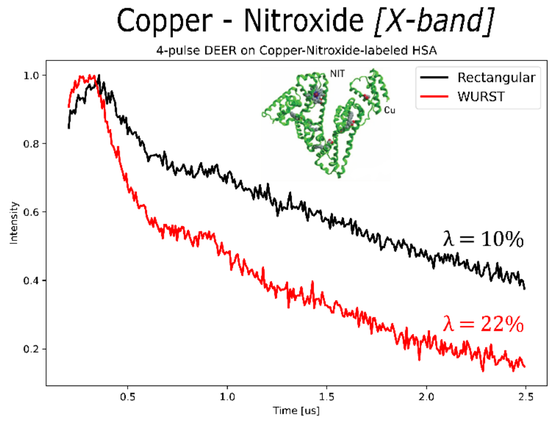
### DEER

Nitroxide - Nitroxide *[Q-band]*




Modulation depth increase in 2,12 times

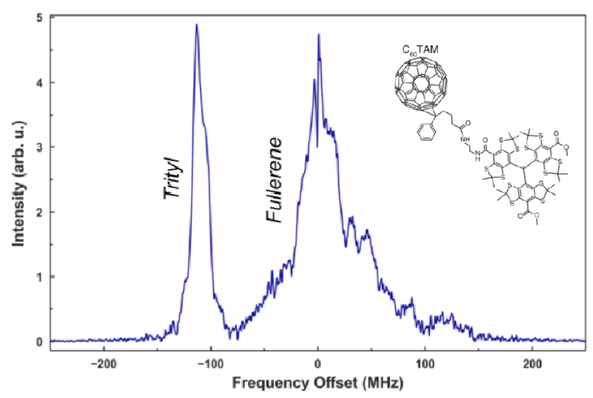
Copper - Nitroxide *[X-band]*



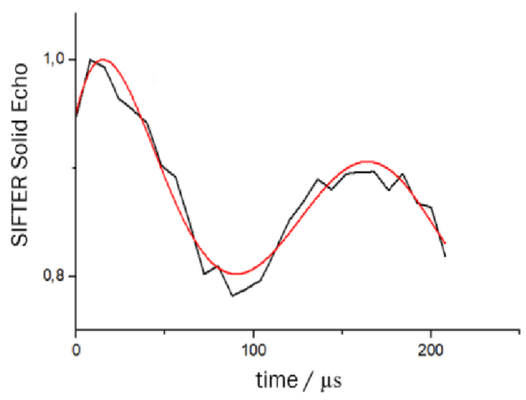

Modulation depth increase in 2,2 times

### SIFTER

Simultaneous excitation of Trityl and Fullerene




SIFTER effect observed




## CONCLUSION

1. Home-built high-frequency AWG has been successfully integrated in EPR spectrometer
2. Simple pulse optimization procedure has been used to compensate for instrumental distortions
3. Adiabatic pulses have shown more than double increase in modulation depth for Nitroxide-Nitroxide and Copper-Nitroxide spin pairs in DEER experiments
4. For the first time, shaped pulses were used in a SIFTER experiment on fullerene spin labels excited by the laser

Optimal control theory techinques are planned for implementation in the future works

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*[1] P.E. Spindler, Y. Zhang, B. Endeward, N. Gershernzon, T.E. Skinner, S.J. Glaser, T.F. Prisner. Shaped optimal control pulses for increased excitation bandwidth in EPR, J. Magn. Reso 218 (2012), pp. 49-58*

*[2] Doll, Andrin, Stephan Pribitzer, René Tschaggelar, and Gunnar Jeschke. 2013. "Adiabatic and Fast Passage Ultra-Wideband Inversion in Pulsed EPR." Journal of Magnetic Resonance 230 (May): 27–39.*