

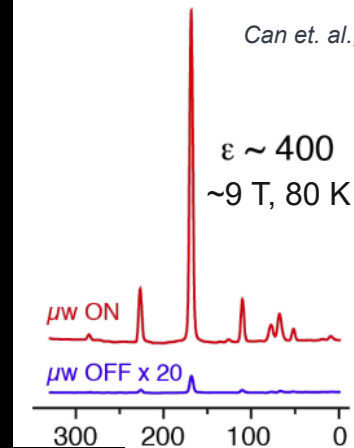
# Building a 263 GHz Pulsed DNP Microwave Bridge, Waveguides, Probe, and MAS Drive Caps



**Kong Ooi Tan**  
École Normale Supérieure  
MRPM 2022, Zhejiang

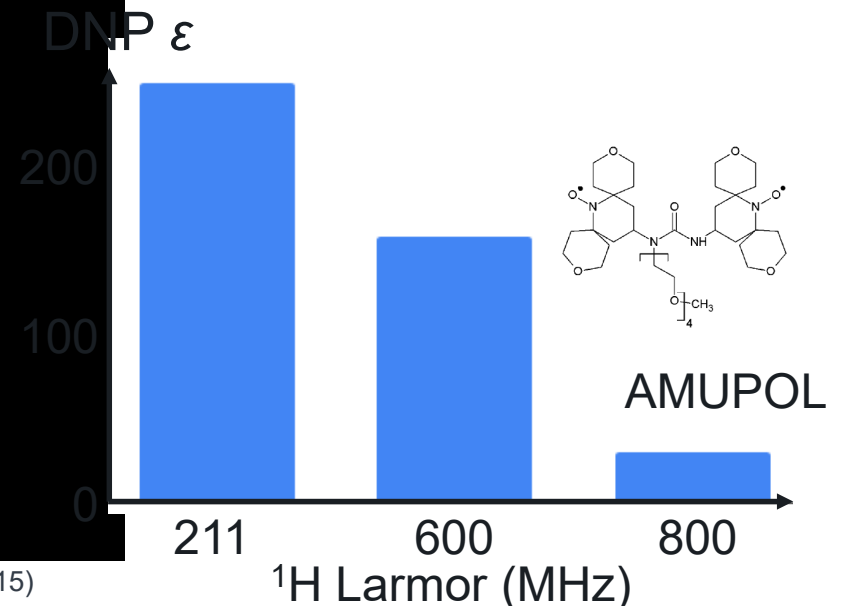
# Dynamic Nuclear Polarization (DNP)

Can et al., *J Magn Reson*, 253, 23-35, 2015



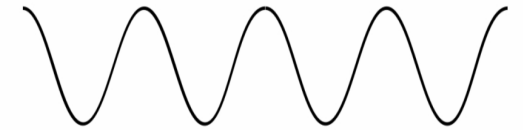
Problem

DNP  $\epsilon$  ↓ as  $B_0$  ↑

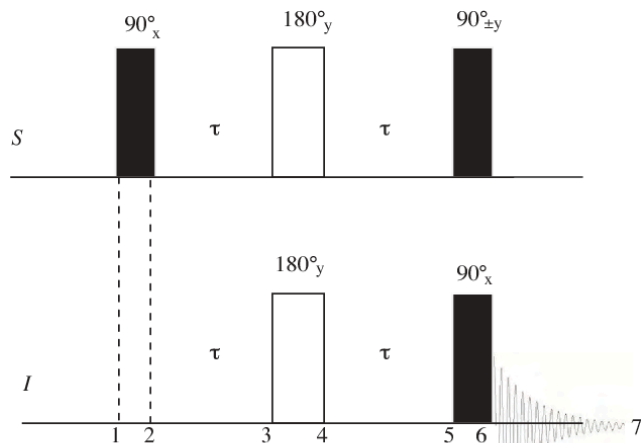


# Pulsed DNP

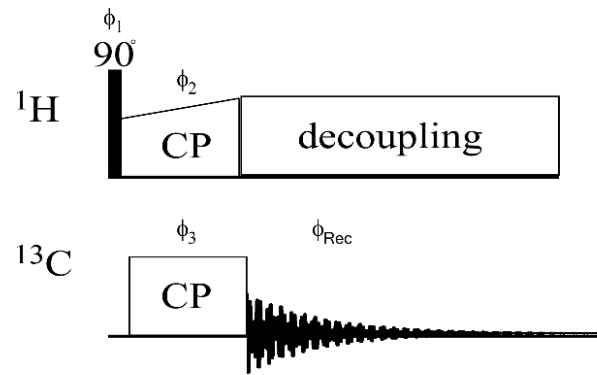
1. DNP using CW  $\mu\text{w}$  irradiation has  $\epsilon \sim \frac{1}{B_0^{n \geq 1}}$



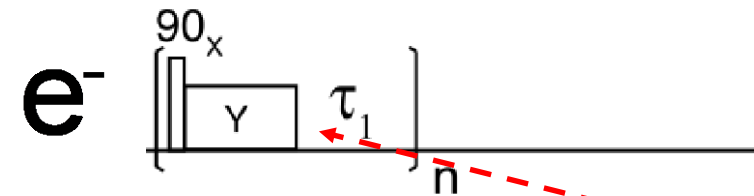
2. Pulsed DNP has **constant**  $\epsilon$  (in theory)



**INEPT**



**CP**

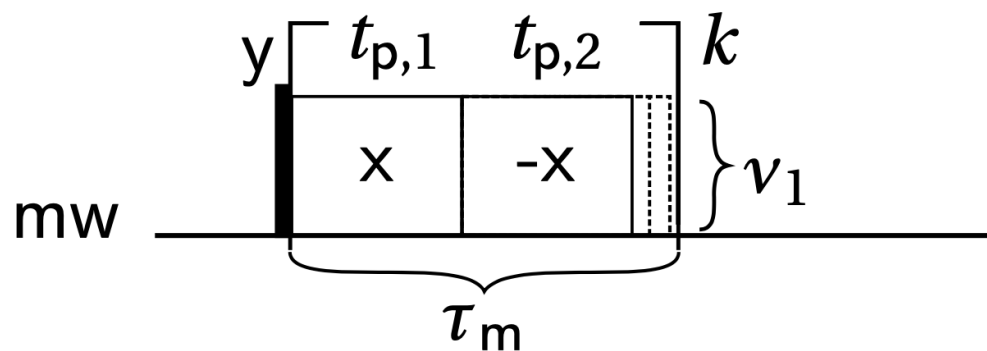


NOVEL: DNP version of CP ( $\omega_{1S} = \omega_{0I}$ )

😊: Remains efficient when  $B_0 \uparrow$

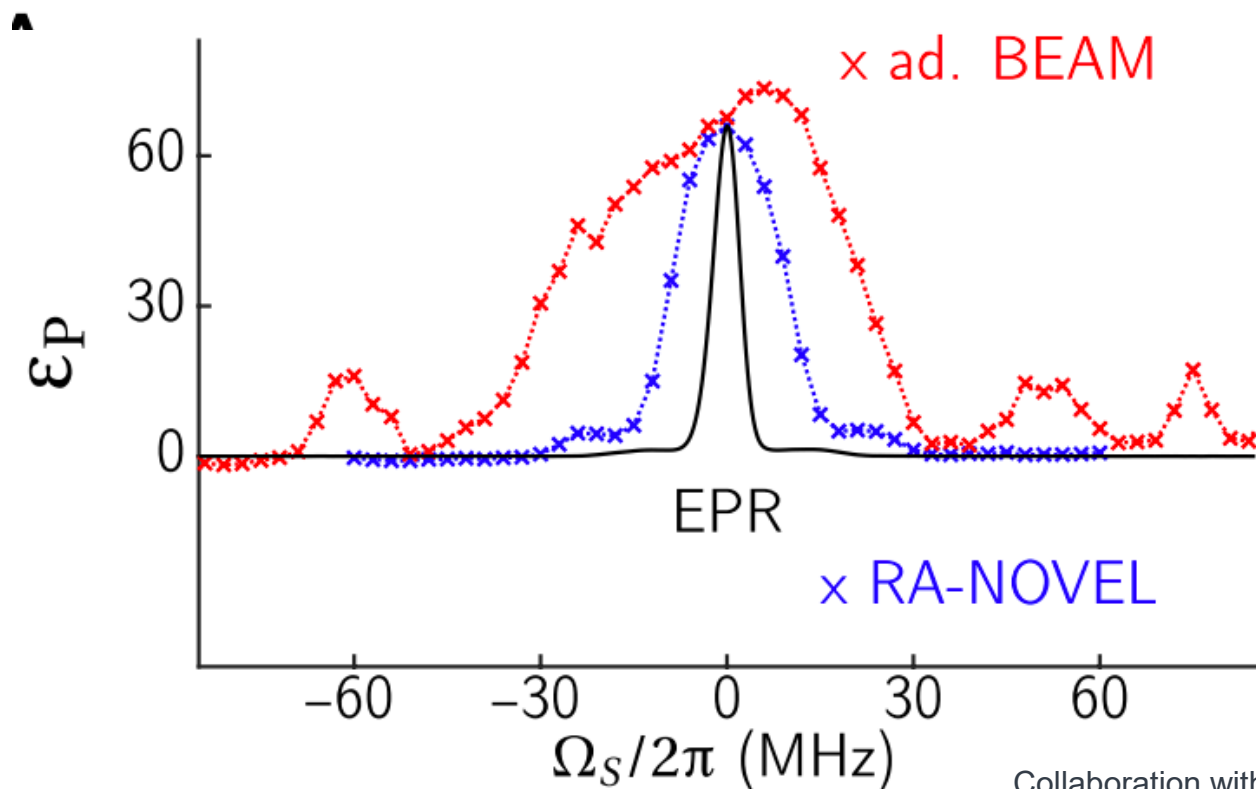
☹️: Need **HUGE**  $\mu\text{w}$  power when  $B_0 \uparrow$

# Broadband Excitation by Amplitude Modulation (BEAM) DNP @ 0.35 T

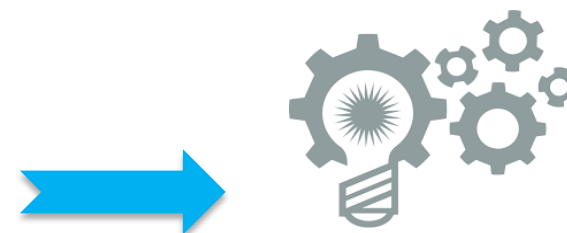


can be as efficient as nuclear orientation via electron spin locking (NOVEL),<sup>8,9</sup> the gold standard DNP mechanism. Concurrently, the ISE requires much less microwave power than NOVEL,<sup>4</sup> making it a promising method for high field experiments.

Yifan *et al.*, JPCL, 13, 5751-5757, 2022



We did better than **gold standard**, but needs **versatile & HUGE**  $\mu\text{w}$  power at high fields



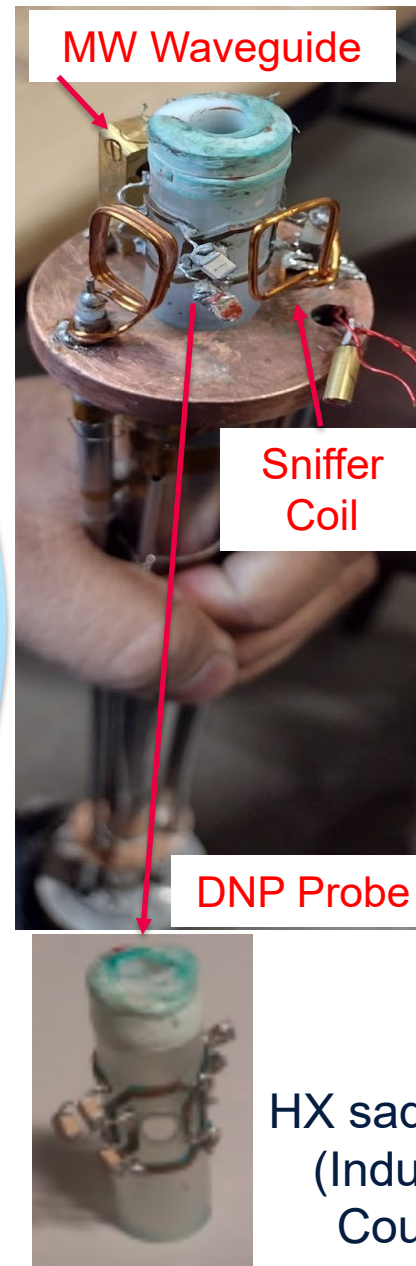
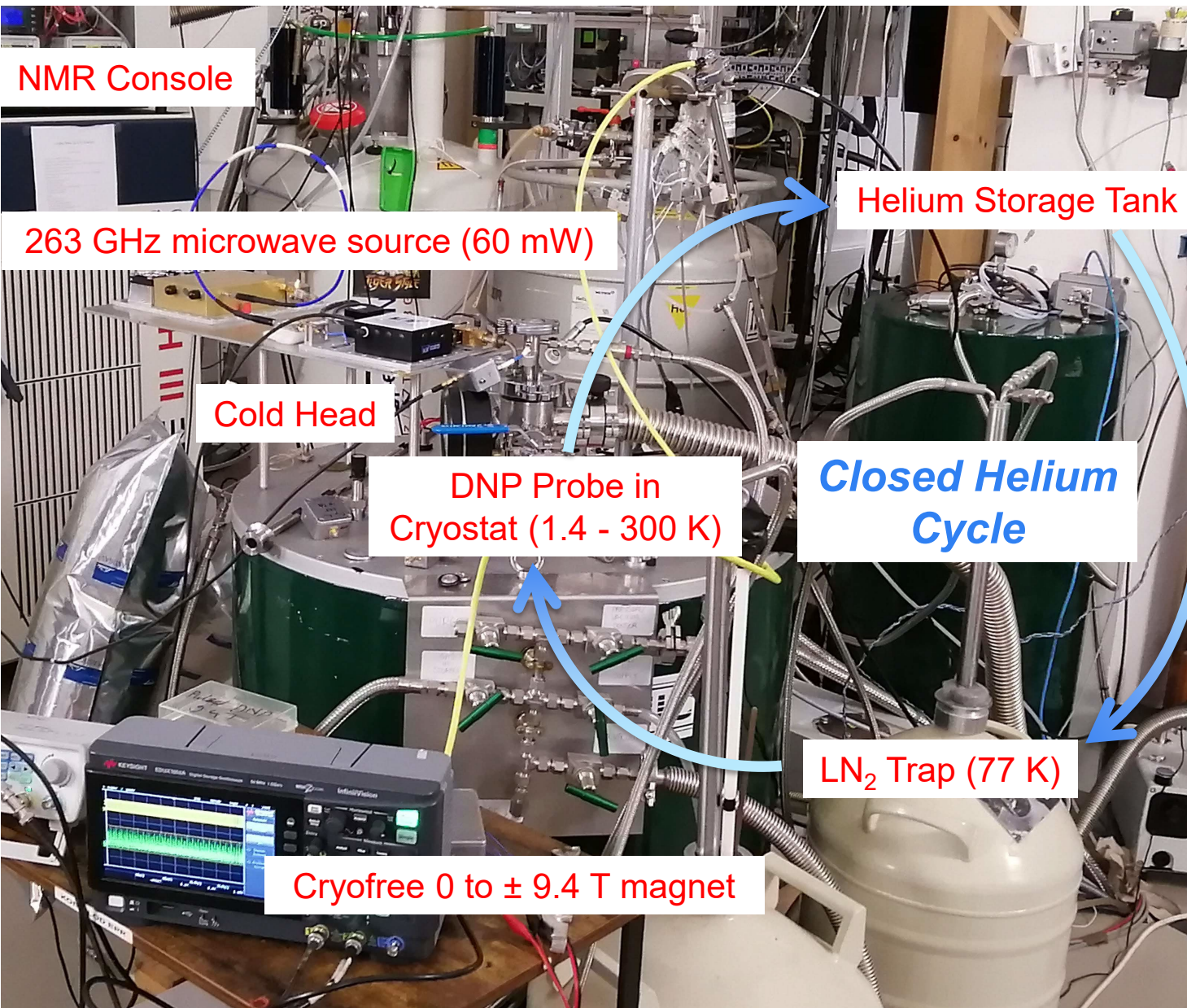
**Need new & better Instrumentation (MW/Probe/MAS)!**

Collaboration with ETH and Aarhus



Wili *et al.*, Science Advances 8, eabq0536, 2022

# A Homebuilt Cryofree 1.4 K / 9.4 T DNP Polarizer @ ENS



Cryofree (fridge) Magnet: Refilled He once in 6 years, no N<sub>2</sub>

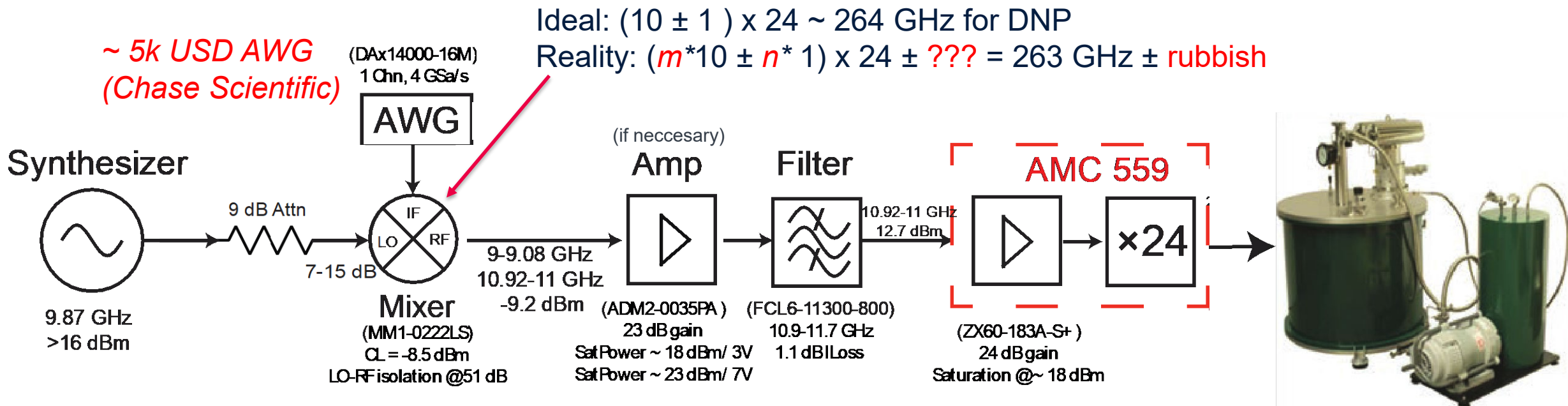
Closed He Operation: Stay cold for months without refill

$P(^1\text{H}) \sim 50\%$  with DNP at 1.4 K and 9.4 T

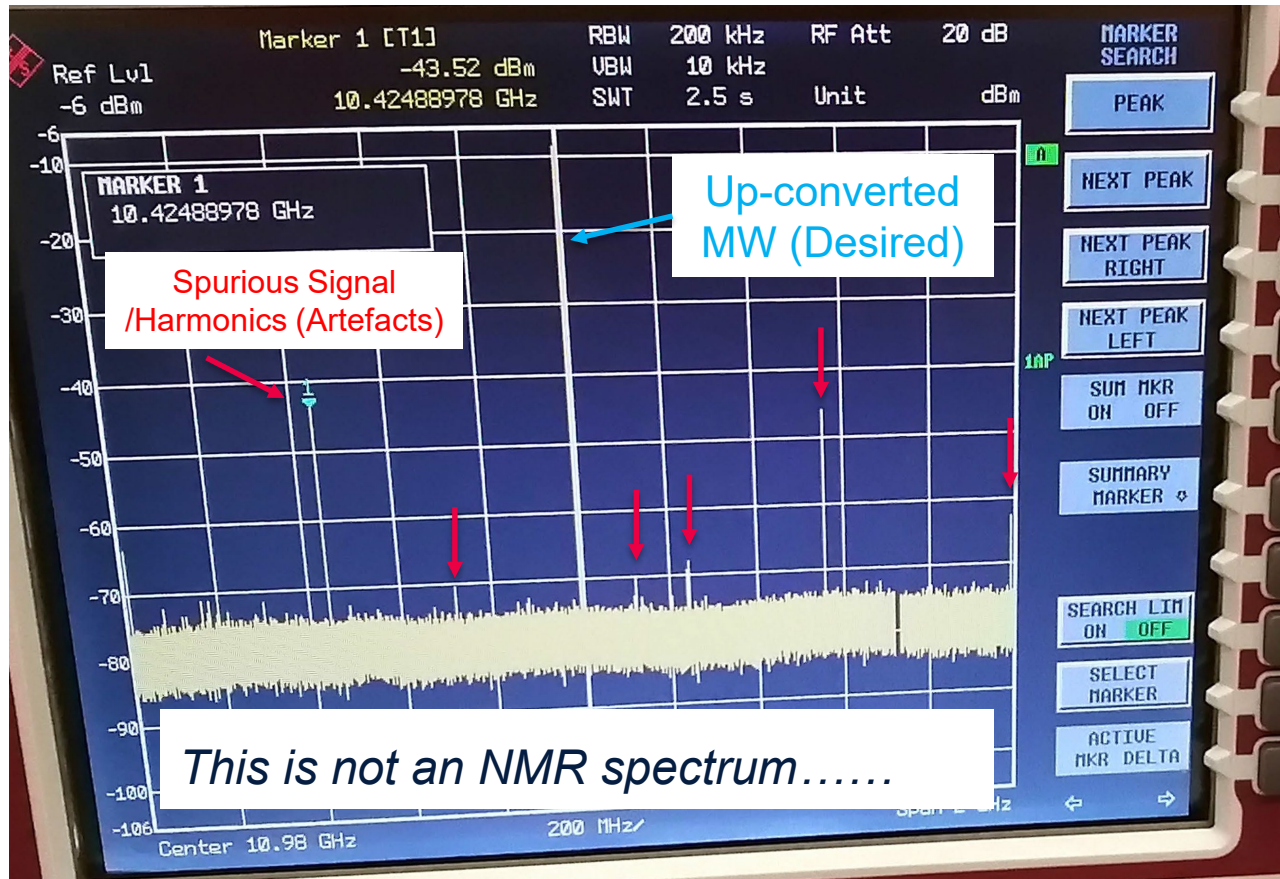


# 9.4 T / 263 GHz Pulsed DNP @ ENS

1. Incorporate arbitrary waveform generator (**AWG**) into the CW source to make MW *pulses* : Change *widths, frequencies, phases, and amplitudes* → Spin-locked e<sup>-</sup>
2. Similar design as NMR rf console (MHz → GHz transition), high multiplication factor (x 24) introduces artefacts (harmonics & power)



# Unwanted Spurs / Harmonics in MW Output

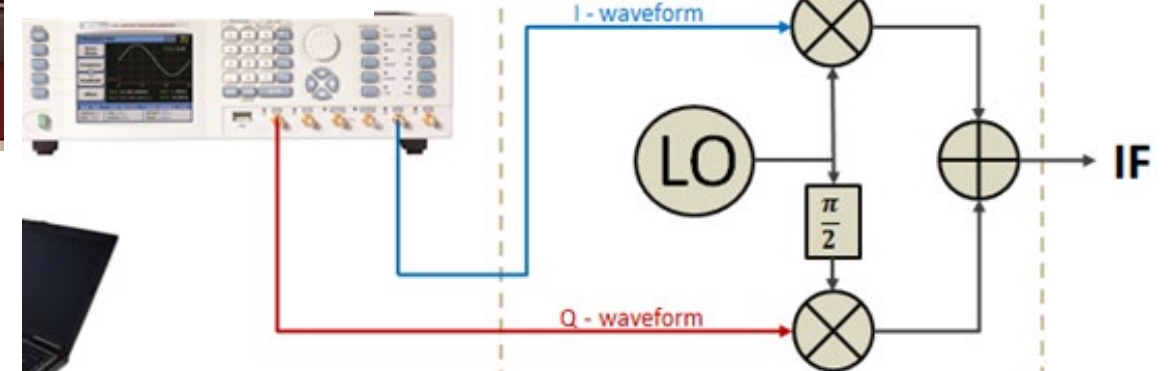


Spurious signals grow by  $20 \cdot \log(n) \sim 27$  dB (500x in power) after  $n=24$  multiplication.

**Solutions:** Use IQ Modulation (quadrature), filters, amplification bandwidth, high LO/IF...

We abandoned the IQ modulation used by most groups (\$\$, 1-chn AWG; IQ imbalance / perfect 90° introduces artefact).

2-chn AWG

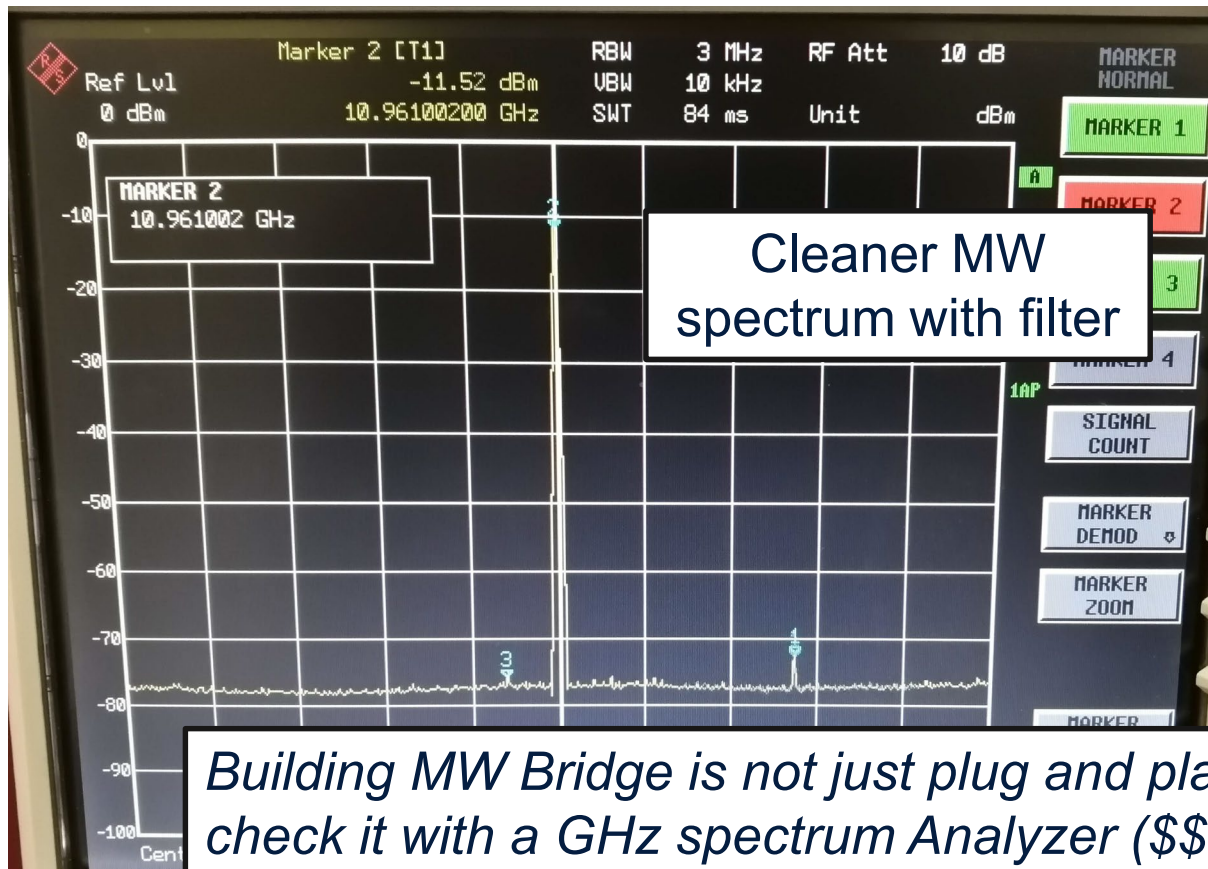


Use **custom-made bandpass filter** for high-quality  $\mu W$

# Customized MW Narrow Bandpass Filter

1. Specify the  $f_{\text{center}}$  (~11 GHz) and bandwidth (~0.3 GHz) to company (*Sirius Microwave*, Estonia), costs ~400 €
2. Harmonics suppressed by > 40 dB, net: 40-27= 13 dB

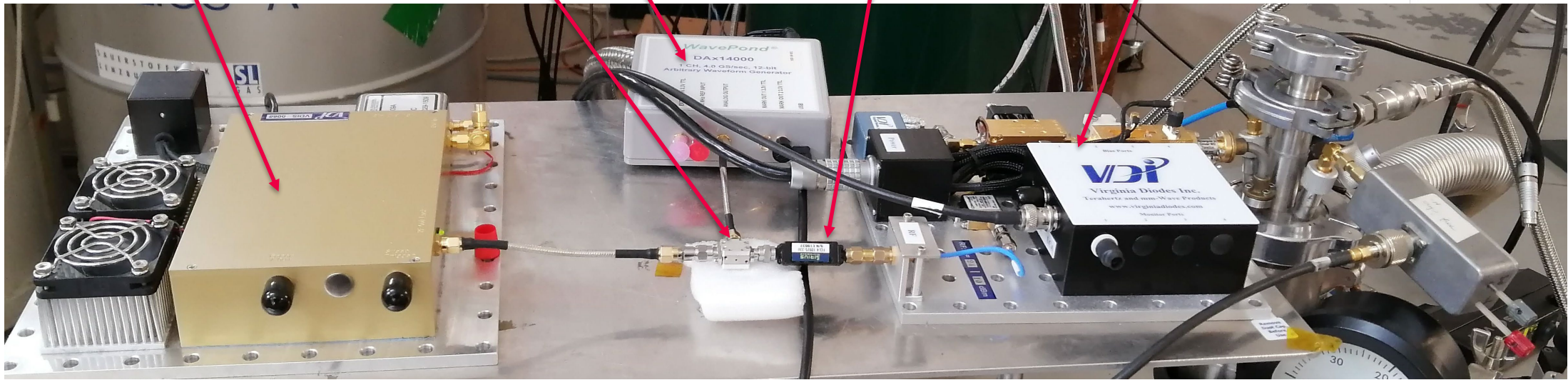
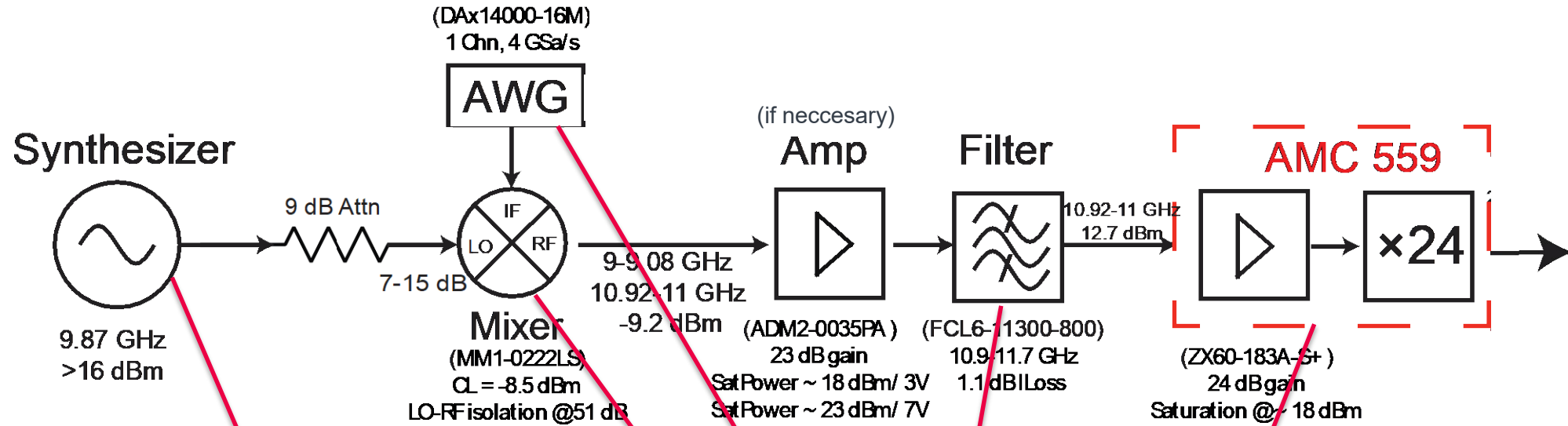
Spurs /  
Harmonics



*Building MW Bridge is not just plug and play,  
check it with a GHz spectrum Analyzer (\$\$\$)*



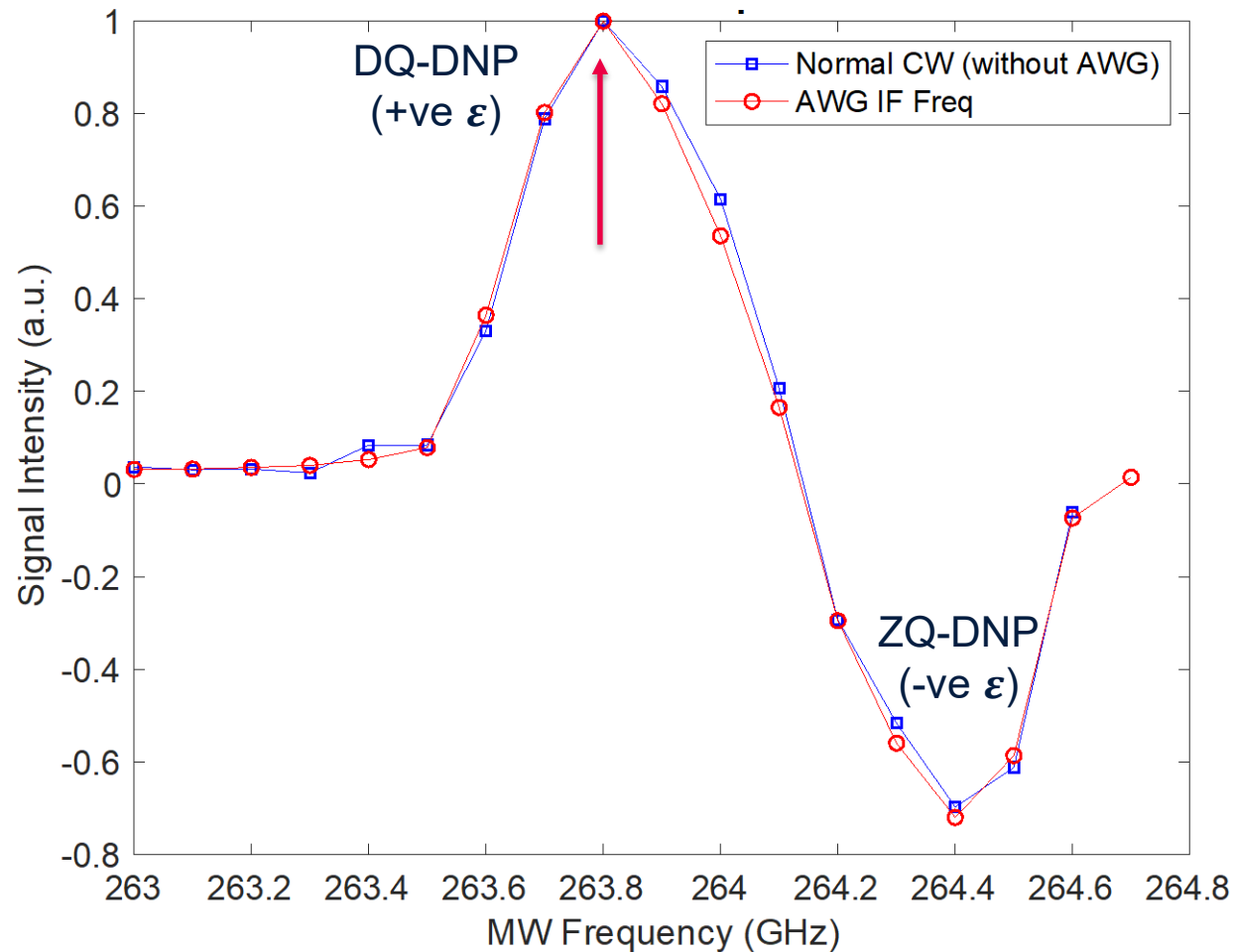
# 9.4 T/ 263 GHz Pulsed DNP @ ENS



Highest Frequency (263 GHz) AWG-Based Pulsed DNP

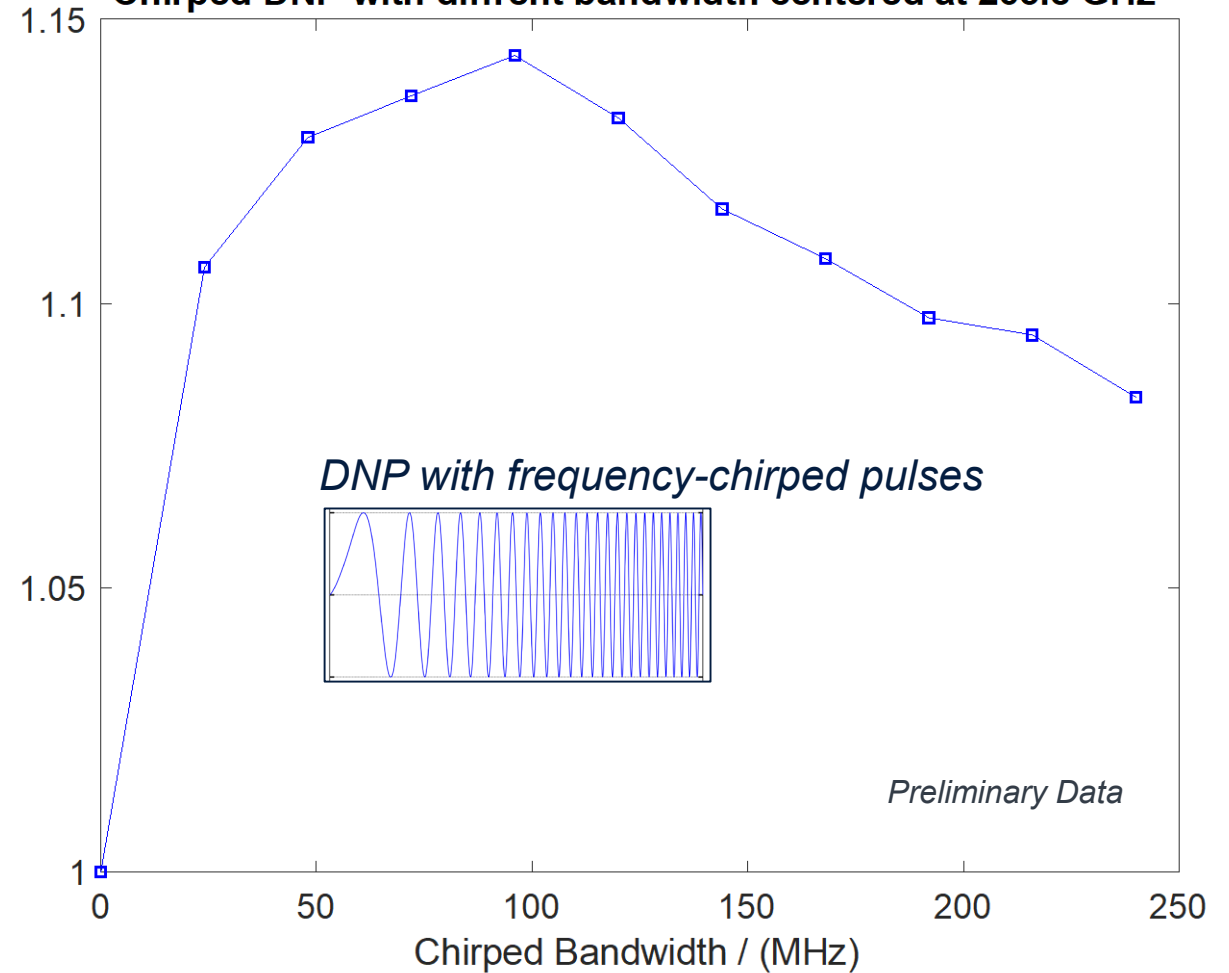
# 9.4 T/ 263 GHz Pulsed DNP Performance

Standard 50 mM TEMPOL in DNP Juice



Similar DNP field profile ensures proper AWG installation

Chirped DNP with different bandwidth centered at 263.8 GHz



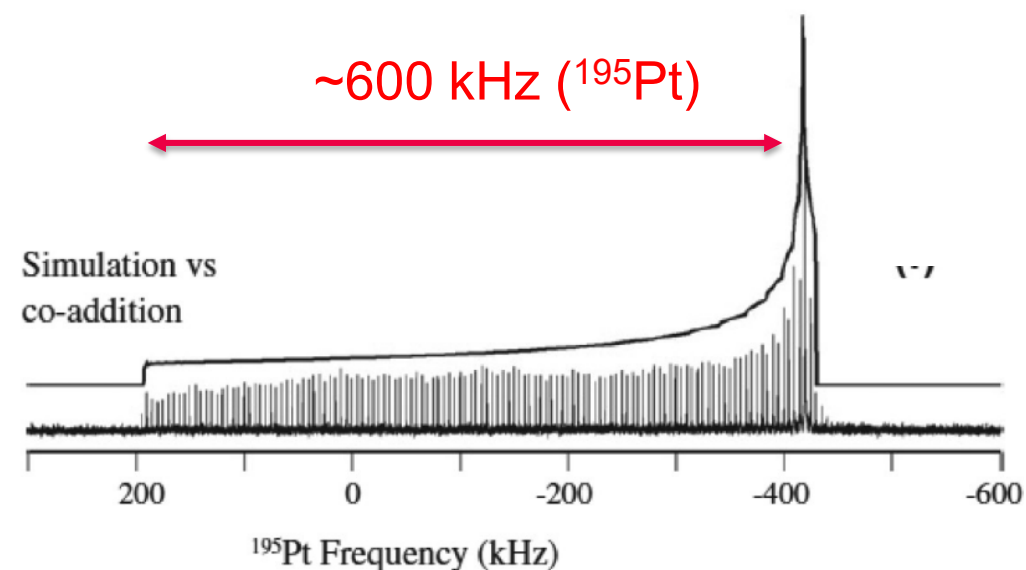
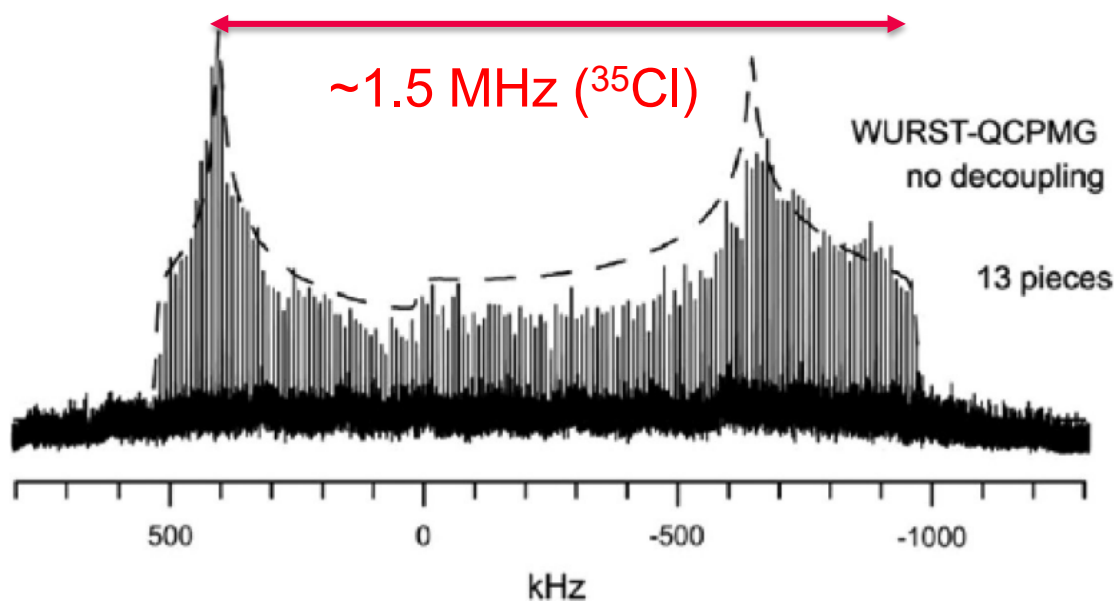
Field- or frequency-modulation technique is not new  
DNP improves **~14 %** with chirped pulses (unoptimized)

Tycko et. al, JMR, 204, 303 (2010)

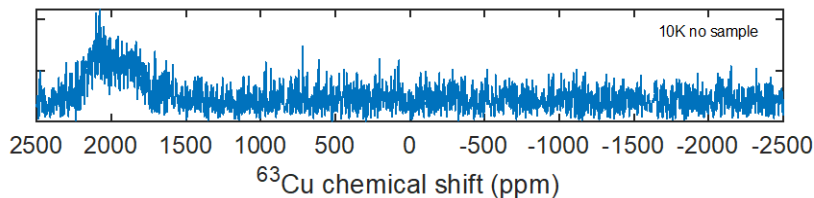
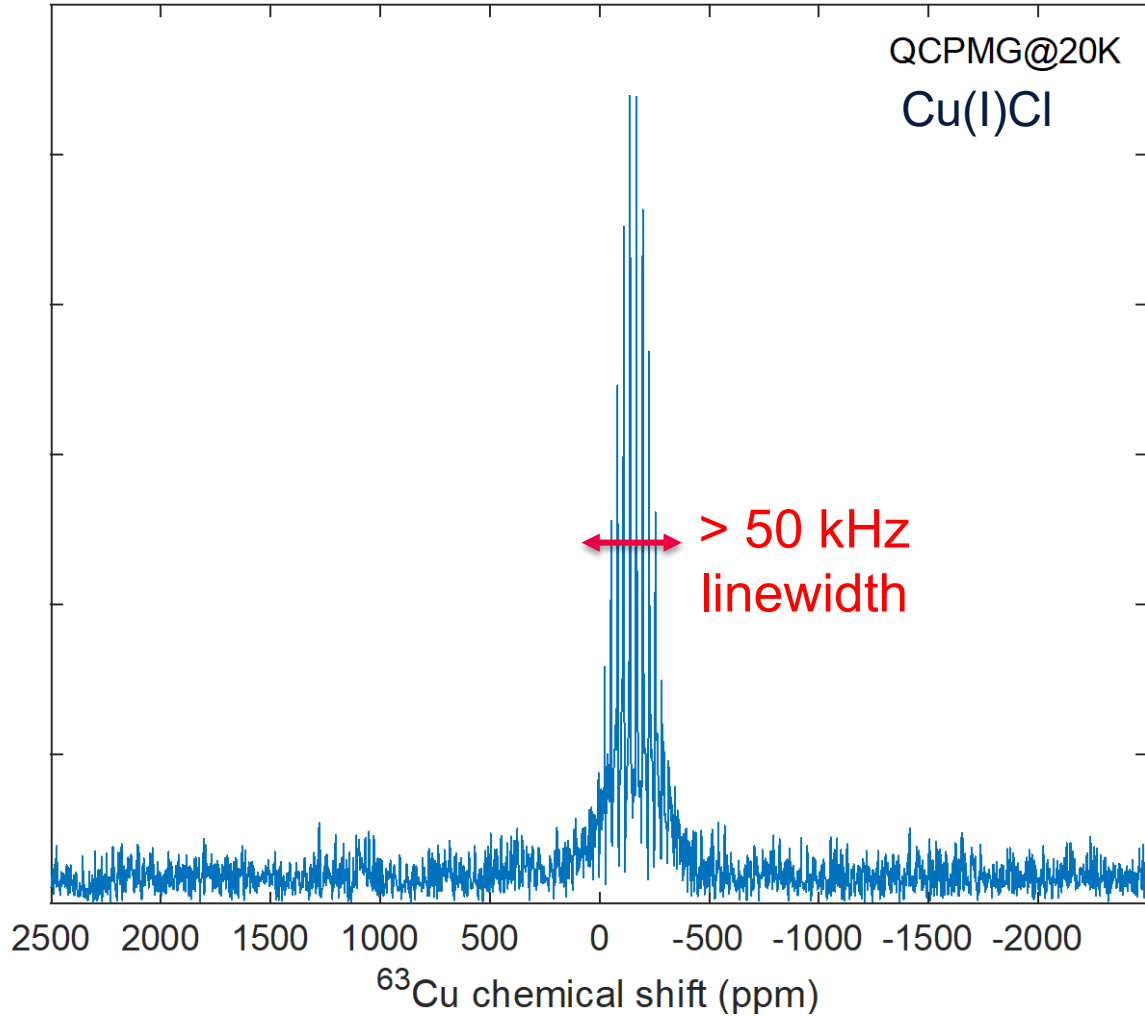
Hovav et. al, JMR, 238, 94 (2014)

# Application on Ultra Wideline Low-Gamma Nuclei ( $^{63}\text{Cu}$ , $^{91}\text{Zr}$ , $^{33}\text{S}$ , etc)

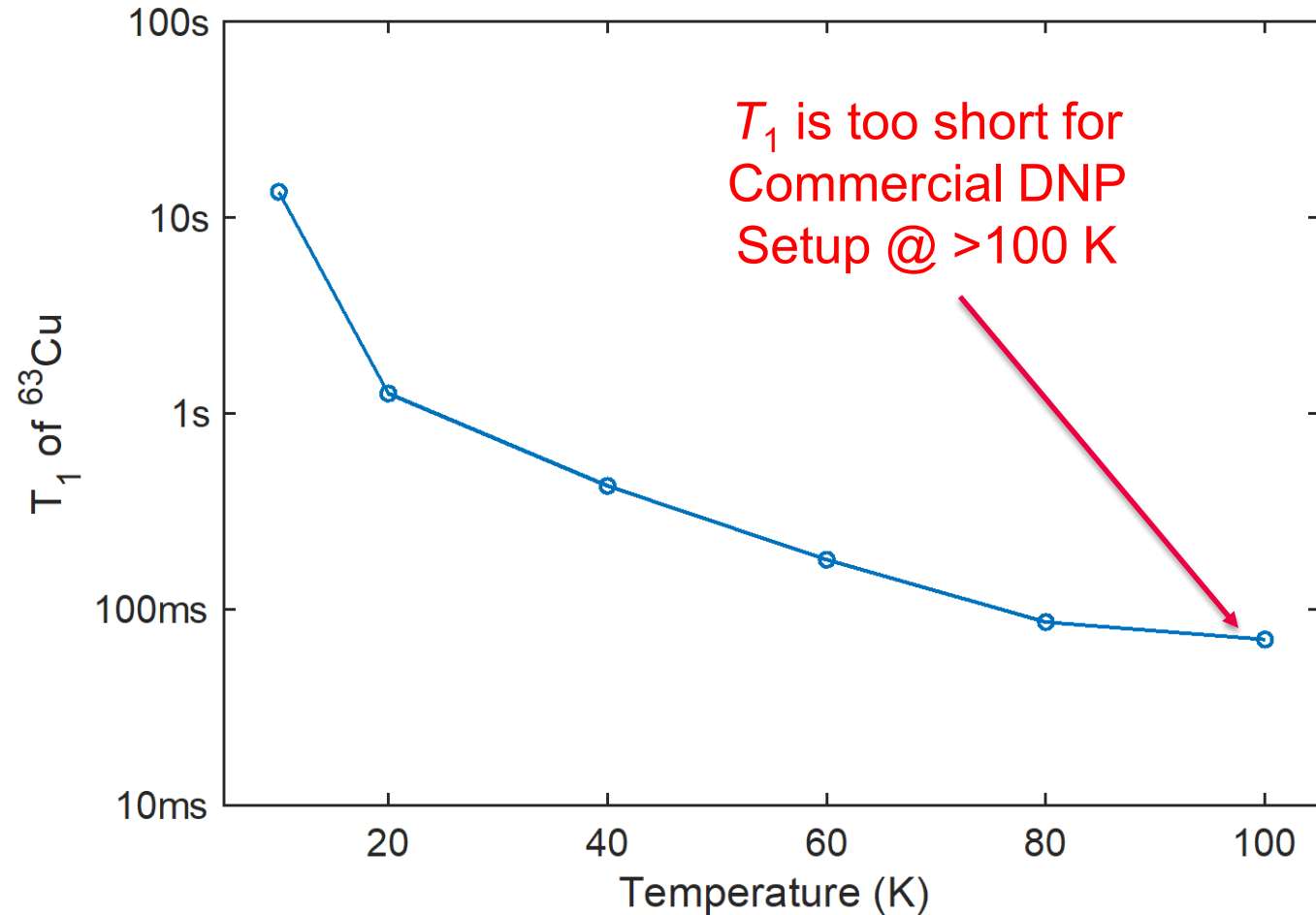
1. Low-gamma nuclei usually have low sensitivity because of (i) large **quadrupolar** coupling (and/or CSA) (beyond MAS) (ii) low **abundance** and (iii) low **gyromagnetic ratio**
2. Examples:  $^{195}\text{Pt}$ ,  $^{35}\text{Cl}$ ,  $^{91}\text{Zr}$ ,  $^{63}\text{Cu}$ ,  $^{207}\text{Pb}$ ,  $^{33}\text{S}$ , etc., and they play important roles in functional materials (catalysts / gas adsorption / perovskites / batteries)
3. Enhance sensitivity with DNP or study dynamics with our unique setup



# Ultra Wideline Low-Gamma Nuclei ( $^{63}\text{Cu}$ , $^{91}\text{Zr}$ , $^{33}\text{S}$ , etc.) @ 9,4 T



Note the metallic Cu signal @ 2000 ppm (Knight Shift)



Soon  
DNP on Cu/Pb/Zr/S  
Dynamics 1-300 K

Zhenfeng Pang



# Making RF Coils with CNC Machining in Lab

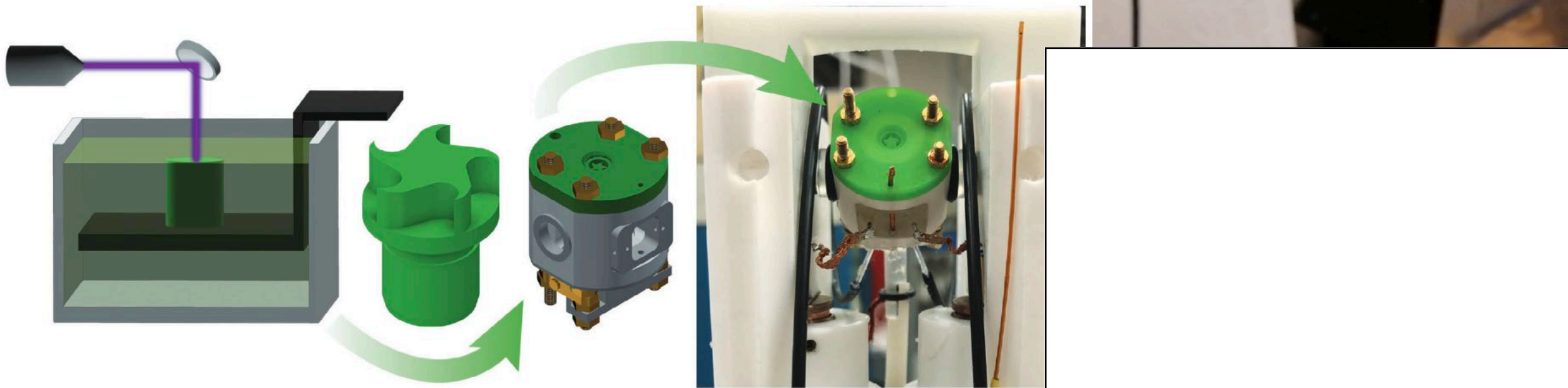
Tool Path Simulation (Fusion 360)

CNC Machining (Genmitsu 4030)



Changeable saddle coil (Inductively Coupled)

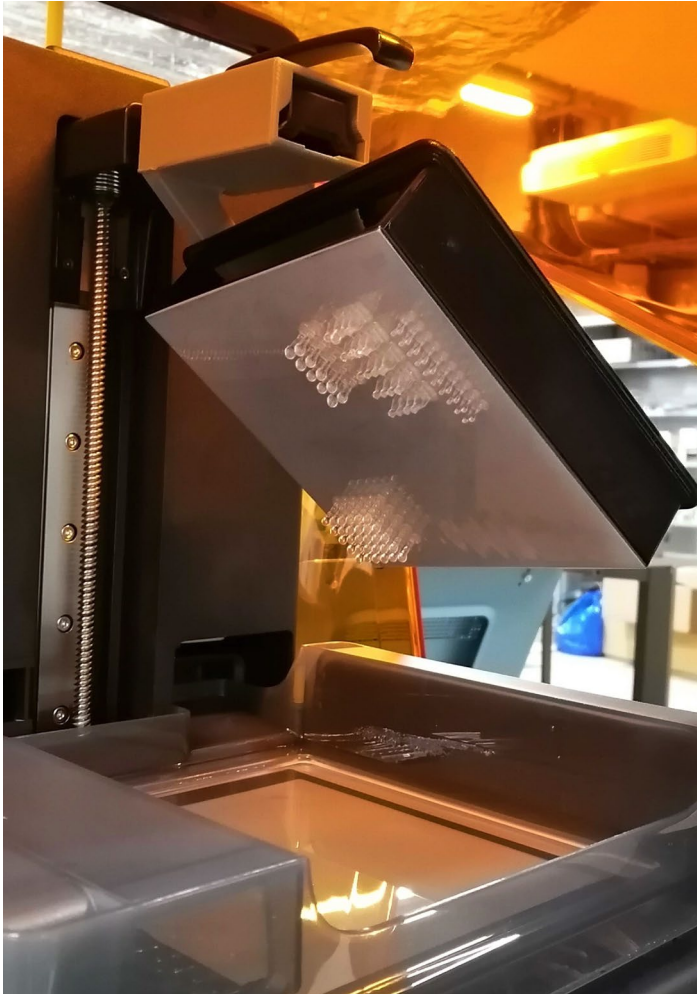
# 3D-Printing Drive Caps (Industrial)



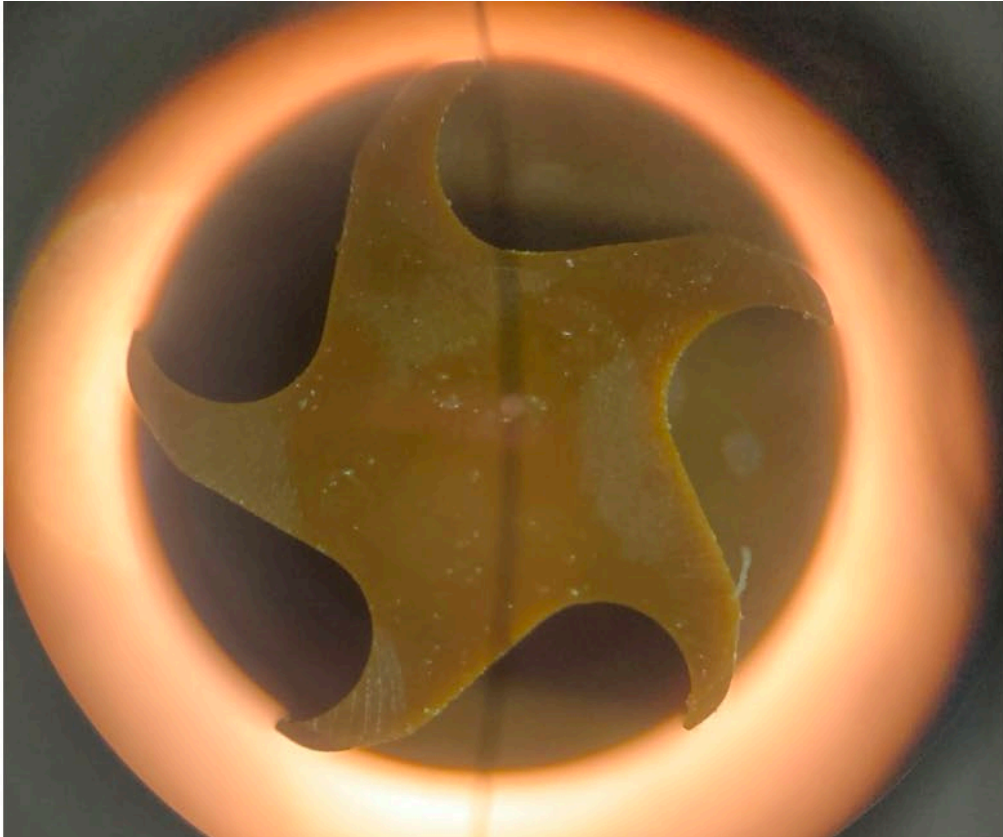
Most plastic components of the MAS assembly, including the gas inlet bushings (Fig. 1g), coil block (Fig. 1i), bottom plate (Fig. 1j), and fiber optic block (Fig. 1n) were 3D printed in-house using clear resin on a Formlabs (Somerville, MA) Form 3 printer at a resolution setting of 25  $\mu\text{m}$ . The Form 3 printer **was not capable of producing the drive caps** (Fig. 1a) and drive plate (Fig. 1d)

However, *quality varies* with batches  
I want to make them *in our own lab!*

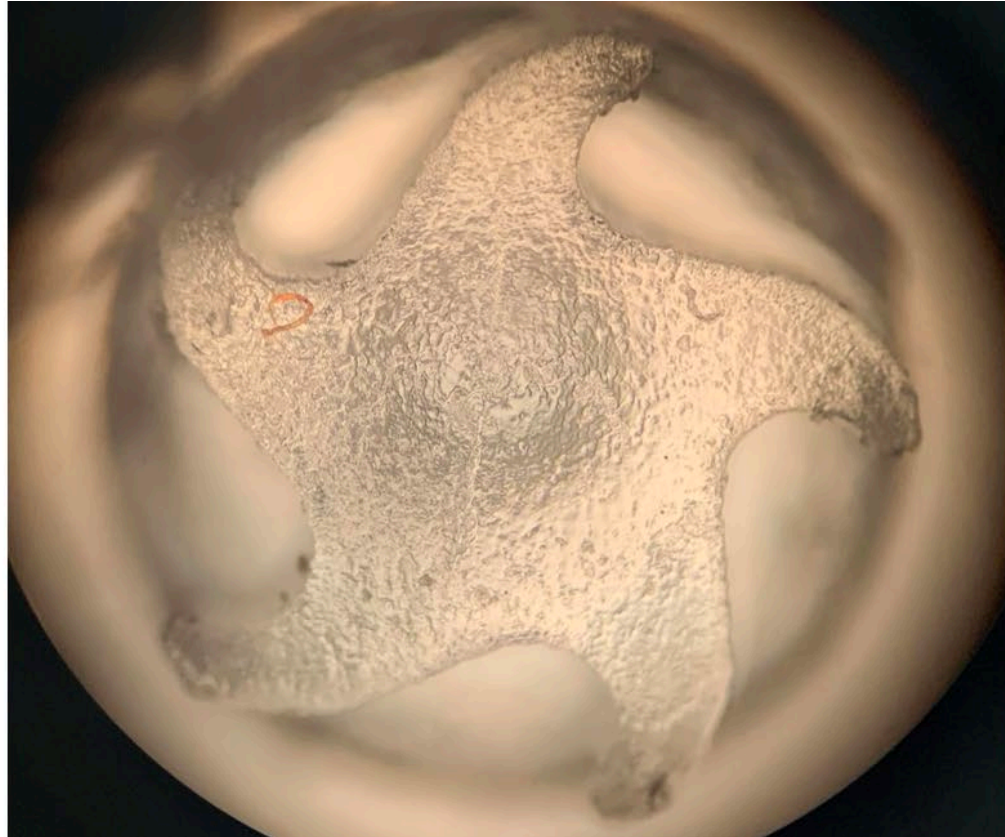
# Building Drive Caps in Your Own Lab!



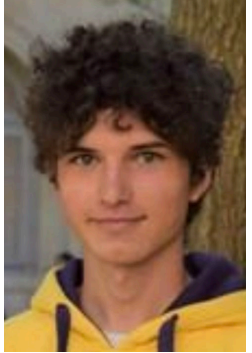
# Commercial and 3D-Printed 3.2 mm Drive Caps



Bruker 3.2 mm



3D-Printed 3.2 mm (Form 3+, Clear Resin)



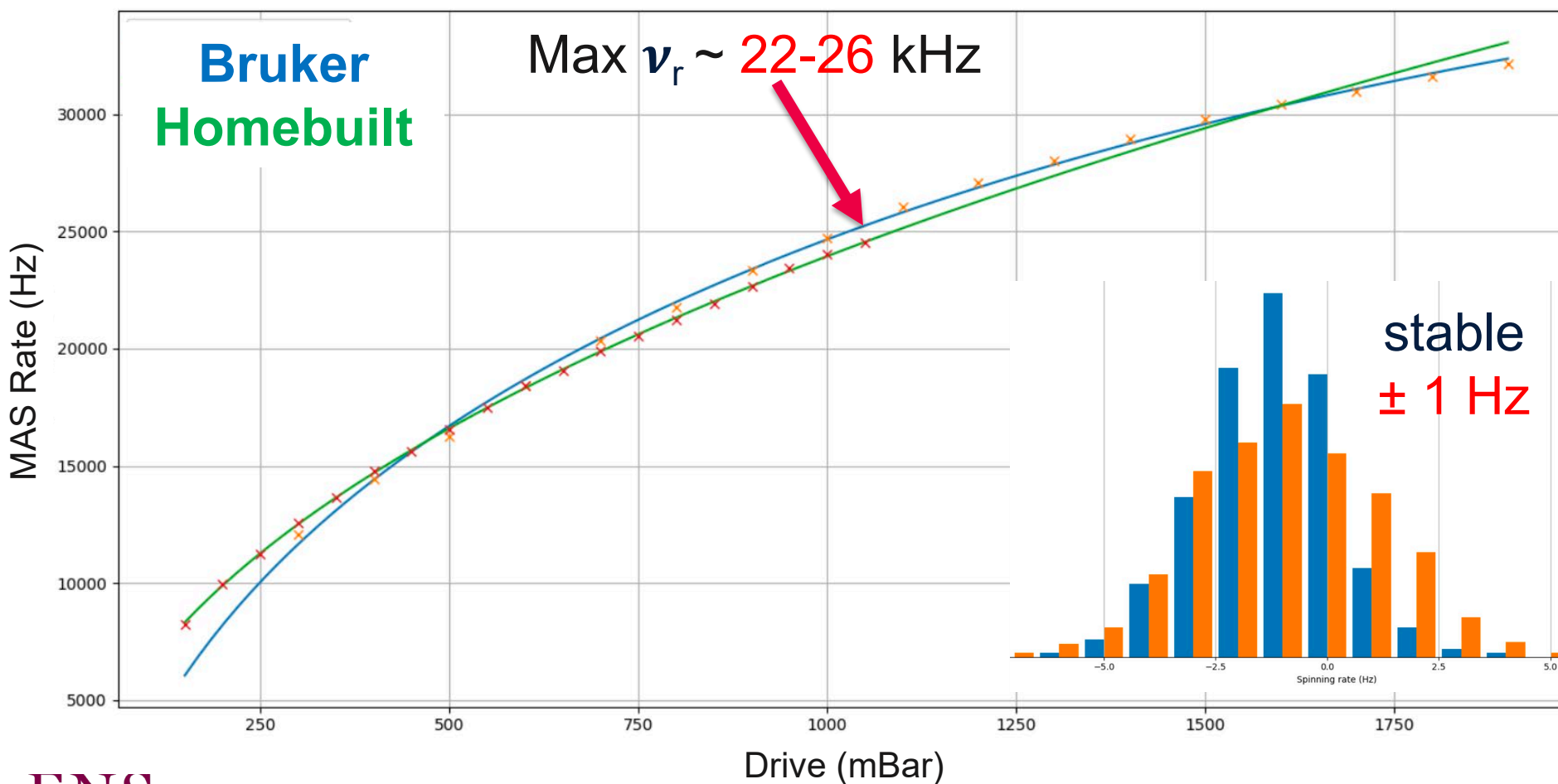
Cyriaque Amerein  
Utsab Banerjee

~ 1 week of  
undergrad's work

**> 90 %** success rate: spin **> 20 kHz** (similar as Bruker)



# MAS Performance of 2.5 mm Drive Caps



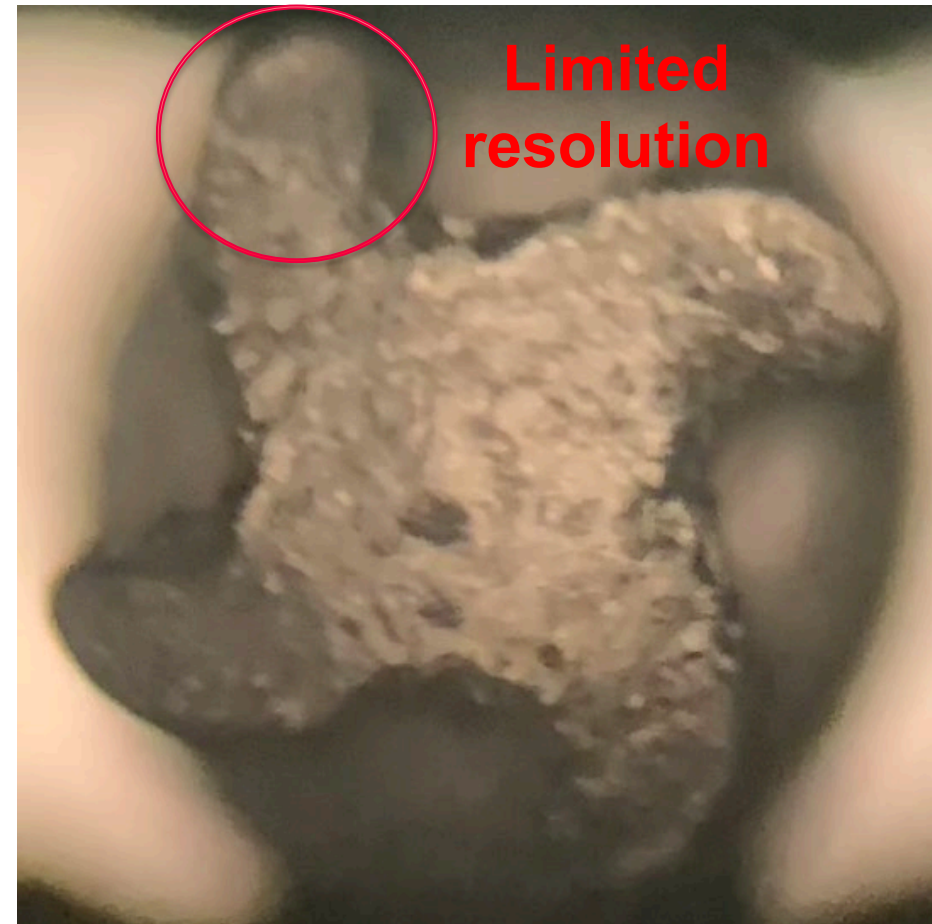
- Homebuilt: Most spin  $\sim 22-26$  kHz
- Bruker: 35 kHz

# Commercial and 3D-Printed 1.3 mm Drive Caps

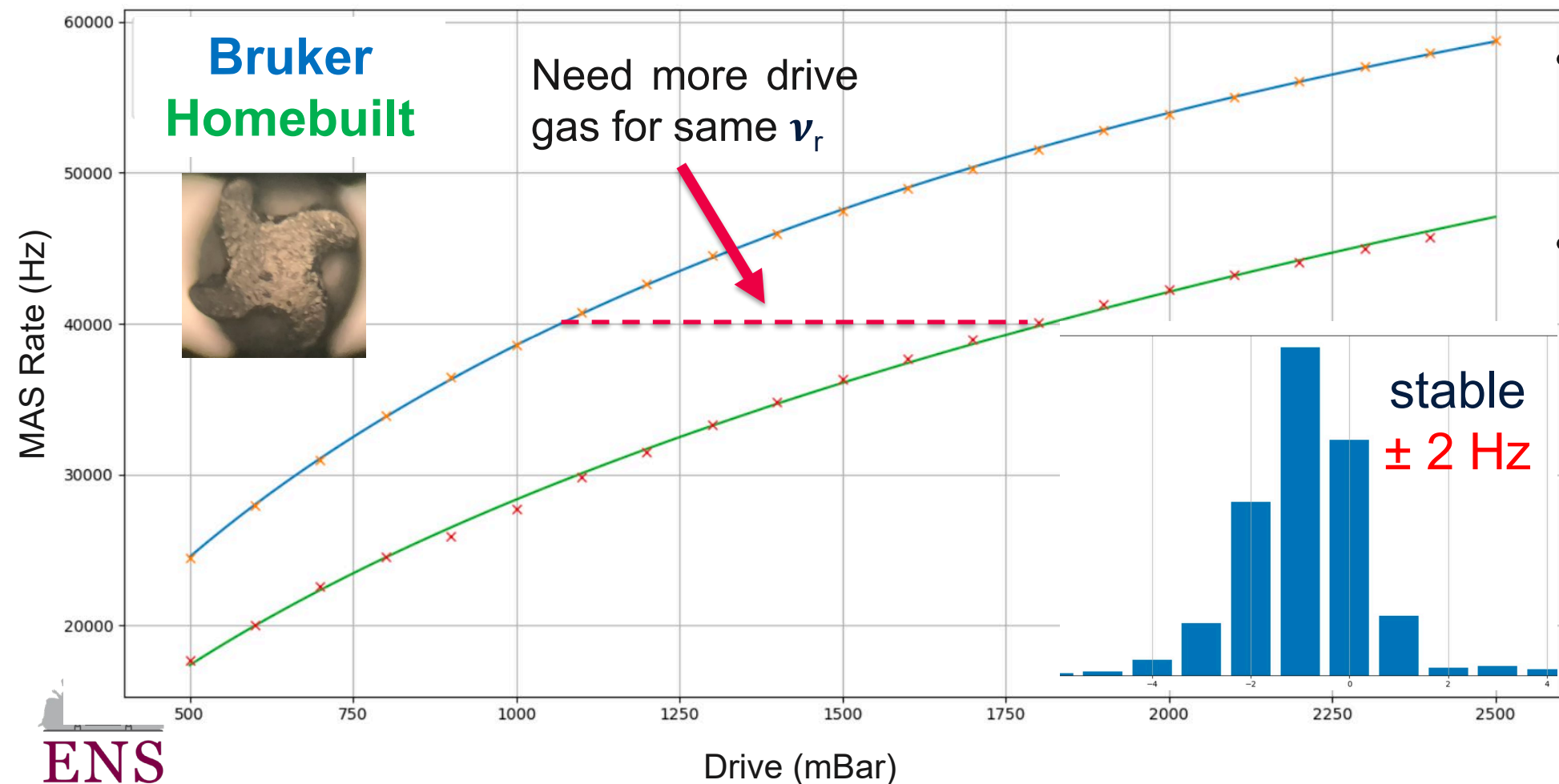
Bruker (Machined)



Desktop Printer (25  $\mu\text{m}$ )



# MAS Performance of 1.3 mm Drive Caps



- Homebuilt: > 85 % spin ~ 45 kHz

- Bruker: 67 kHz

Practical for the fragile 1.3 mm drive cap

# Commercial and 3D-Printed 1.3 mm Drive Caps

Bruker (Machined)



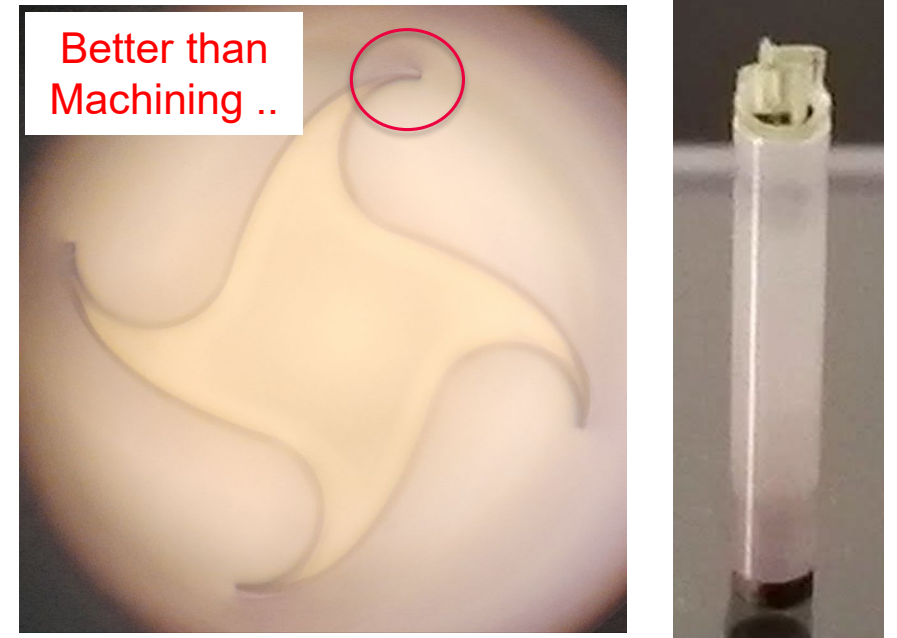
240 USD/pc (\$\$\$\$\$)  
~ 1 week  
~ 67 kHz

Desktop Printer (25  $\mu\text{m}$ )



~0.01 USD/pc (\$)  
~ few hours  
~ 45 kHz (> 85 %)

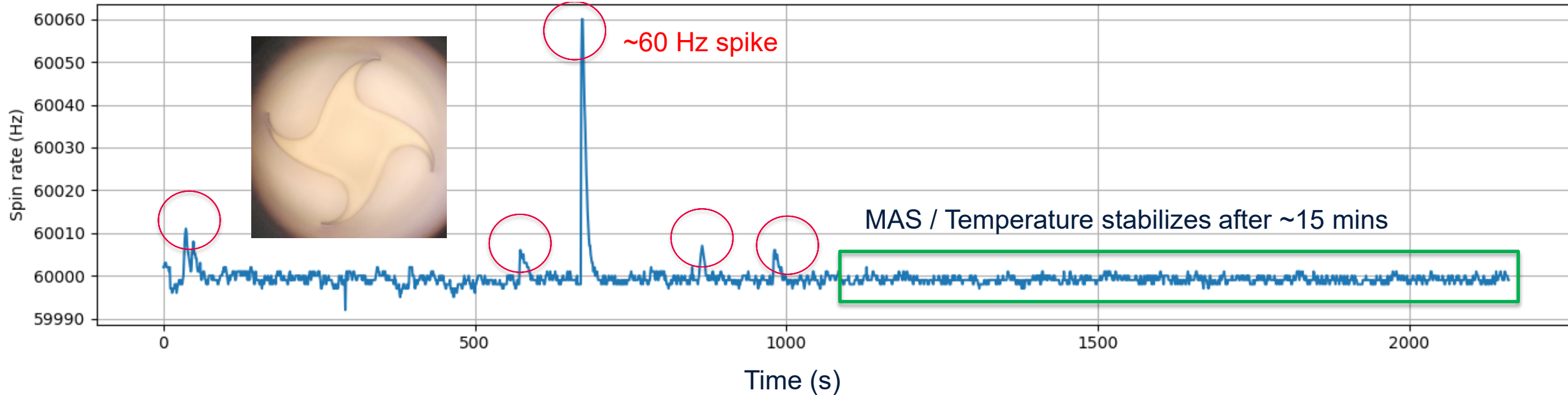
Industrial (2  $\mu\text{m}$ , BMF, P $\mu$ SL)



20~80 USD/pc (\$\$\$)  
~ 1 week  
Tested till 60 kHz (like Bruker)

# Industrial 3D-Printed 1.3 mm Drive Cap (2 $\mu\text{m}$ )

Spinning Stability of 3D-Printed 1.3 mm Cap (no cooling / VT gas)

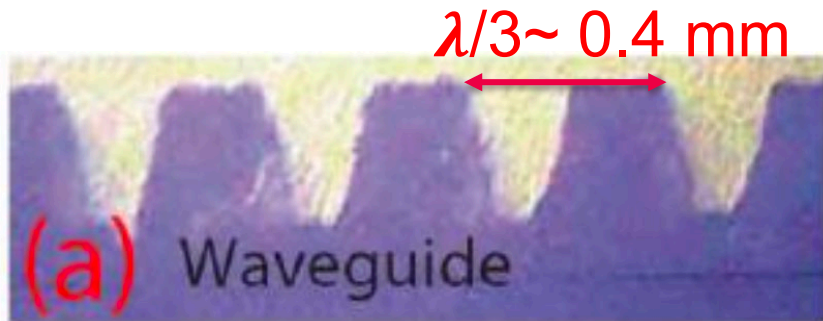


MAS frequency  $\nu_r = 60 \text{ kHz} \pm 2 \text{ Hz}$  (30 mins)

# 3D-Printed + Electroless Plating MW Waveguide

1 m normal waveguide (steel) loses  $75\% P_{mw}$

**Corrugation** minimizes ohmic losses till  $1\%$



Himmler et. al, preprint mr-2022-15 (2022)  
Woskov et. al, IEEE, 53, 1863 (2005)



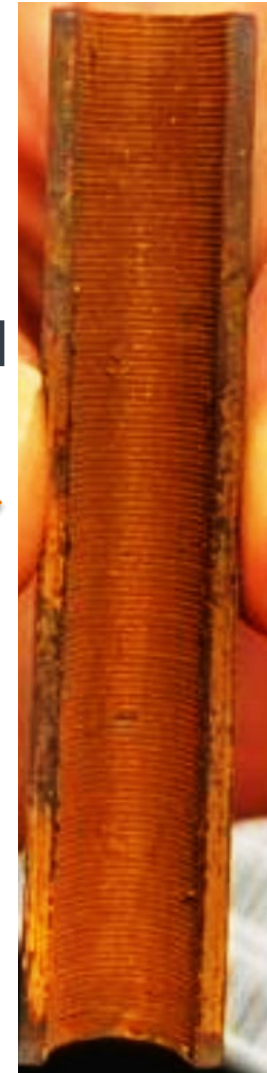
3D-Printed  
(Plastic)

Cu + Gold  
Plated



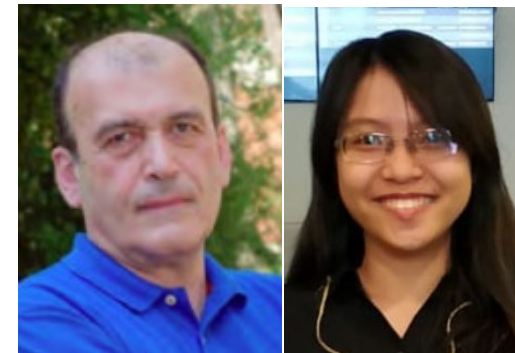
$\sim 2\ \mu\text{m}$

Skin depth @  
263 GHz  
 $= 0.13\ \mu\text{m}$



3D-Printed +  
Electroless Plated

Very Conductive !  
 $\sim 1\ \text{m}\Omega$

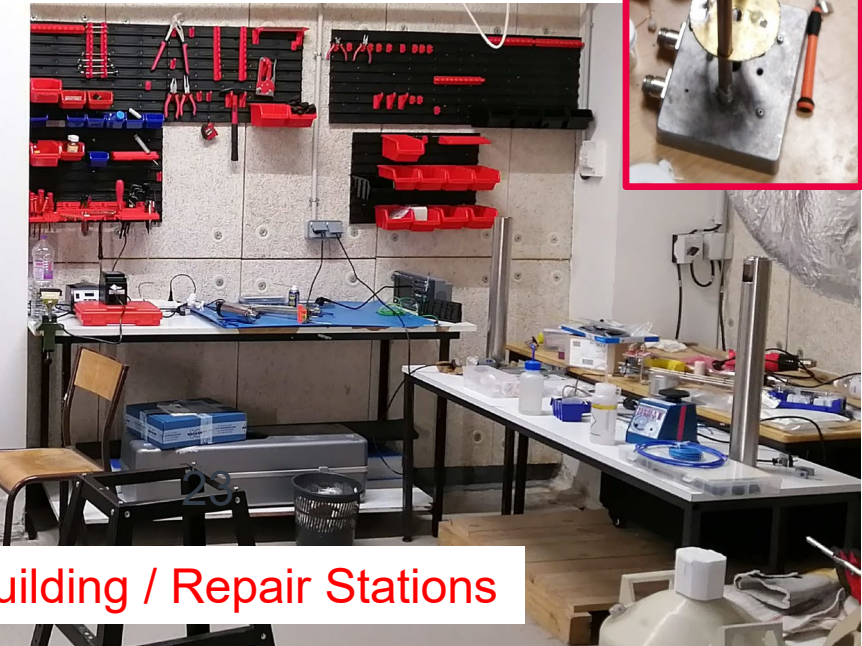
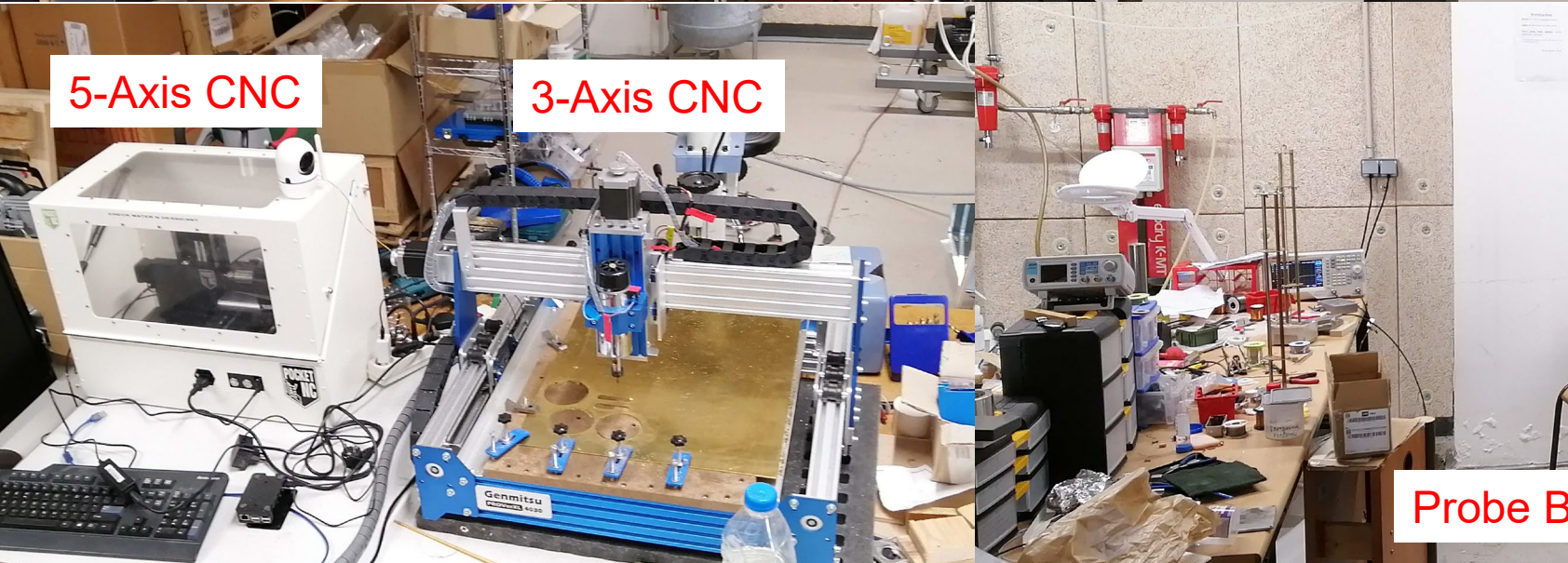
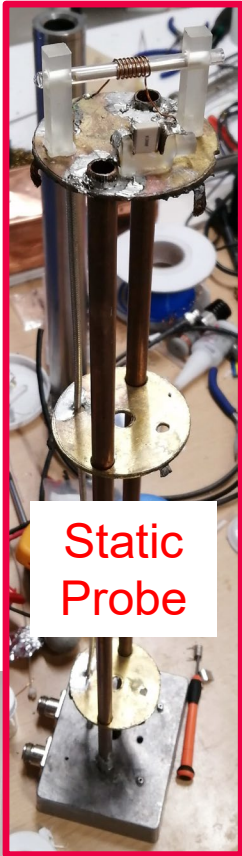


Nicolas Birlirakis  
Ngoc Diep Le

# Our Machining/Electrical Workshop (NMR Only)



- Accessories
- Oscilloscope
- Vector Network Analyzer
- Spectrum Analyzer
- 2 MHz LRC Meter
- Air Compressor
- 3D Printers
- Rotary tools



**Thank you for your attention !**



Zhenfeng Pang  
Utsab Banerjee  
Cyriaque Amerein  
Ngoc Diep Le  
Nicolas Birlirakis  
Mathieu Baudin

**Postdoc / PhD positions  
available !**

