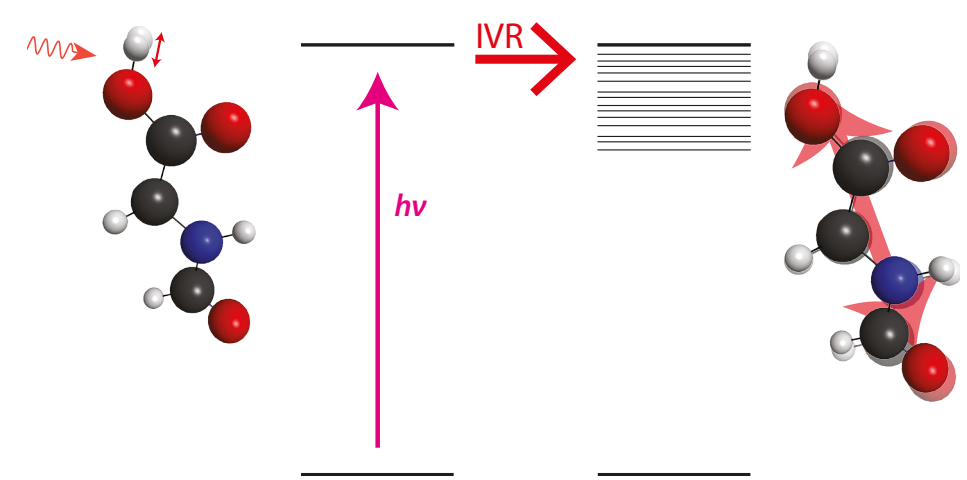
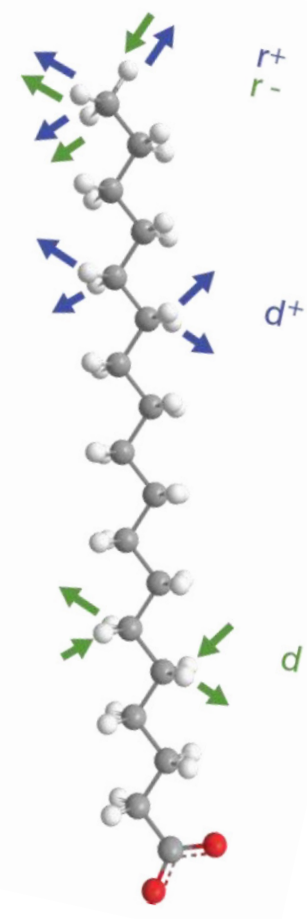


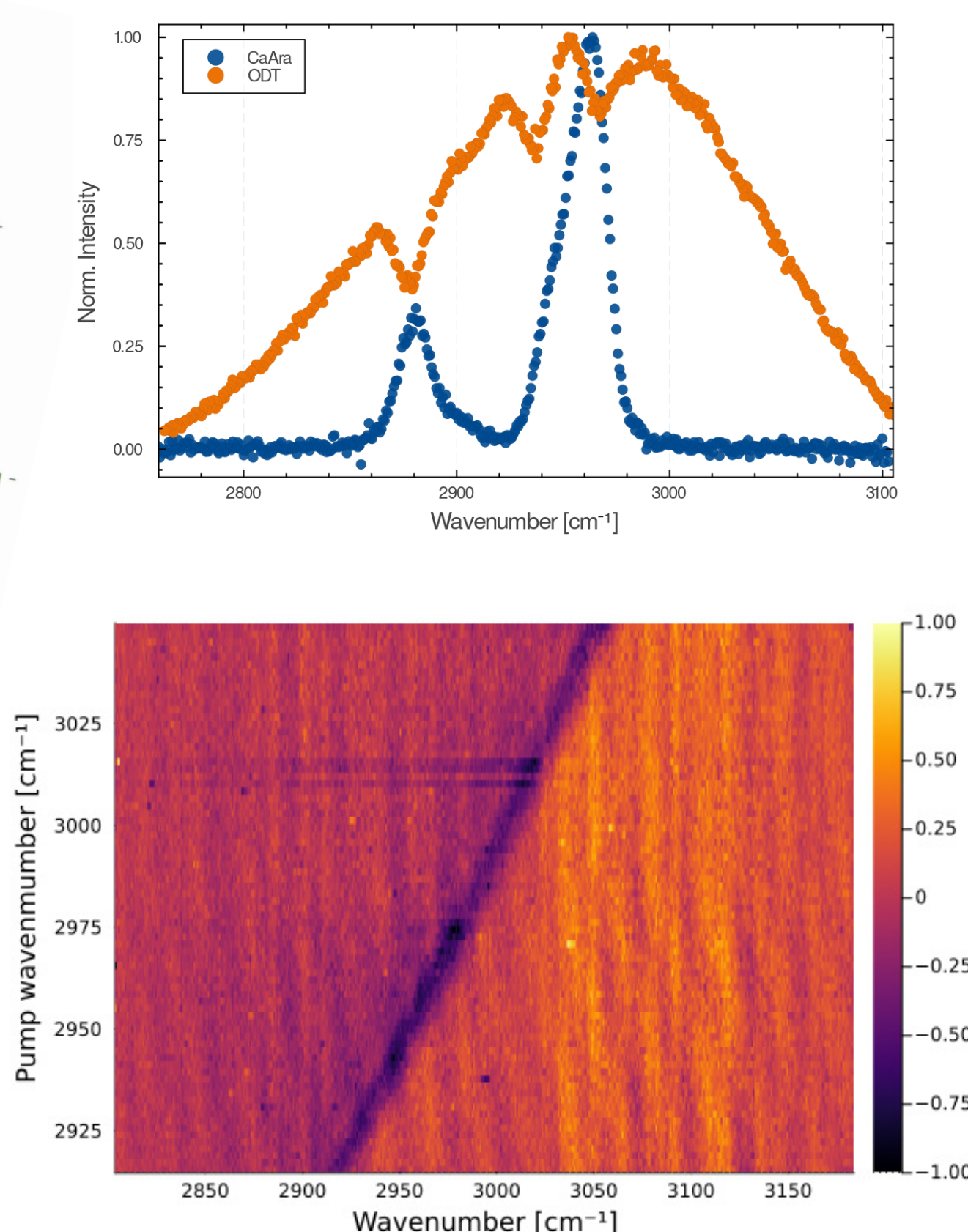
MOTIVATION

- Investigation of internal vibrational energy redistribution (IVR) of long alkyl chains on different substrates (e.g. glass vs. gold)



- The NR background is predominant on transition metal surfaces, since the d-electrons are easily excited by the upconversion pulse of SF photon

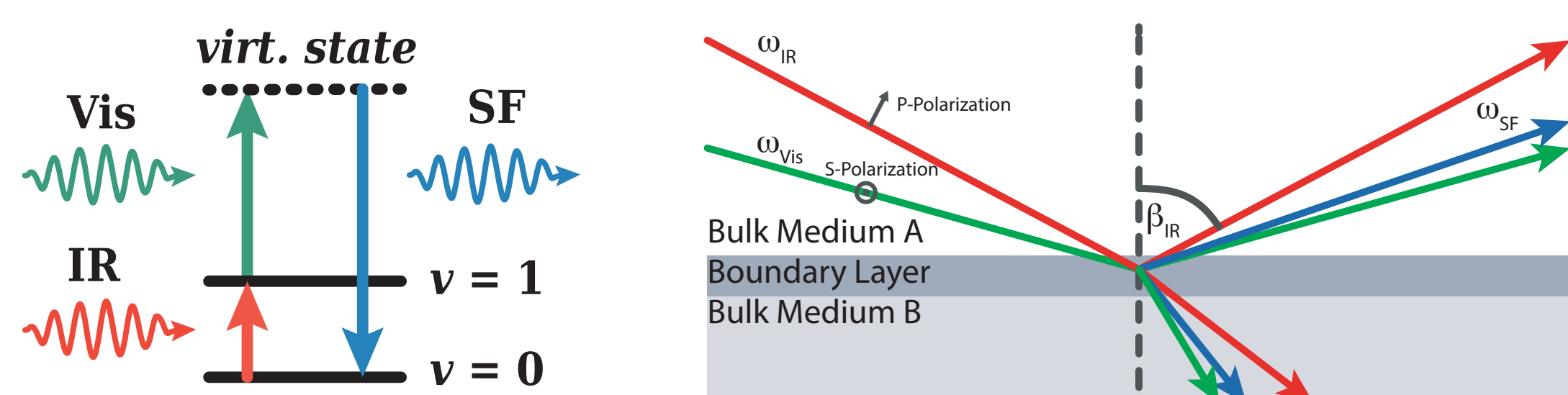
- NR signal hampers pump-probe experiments



THEORY

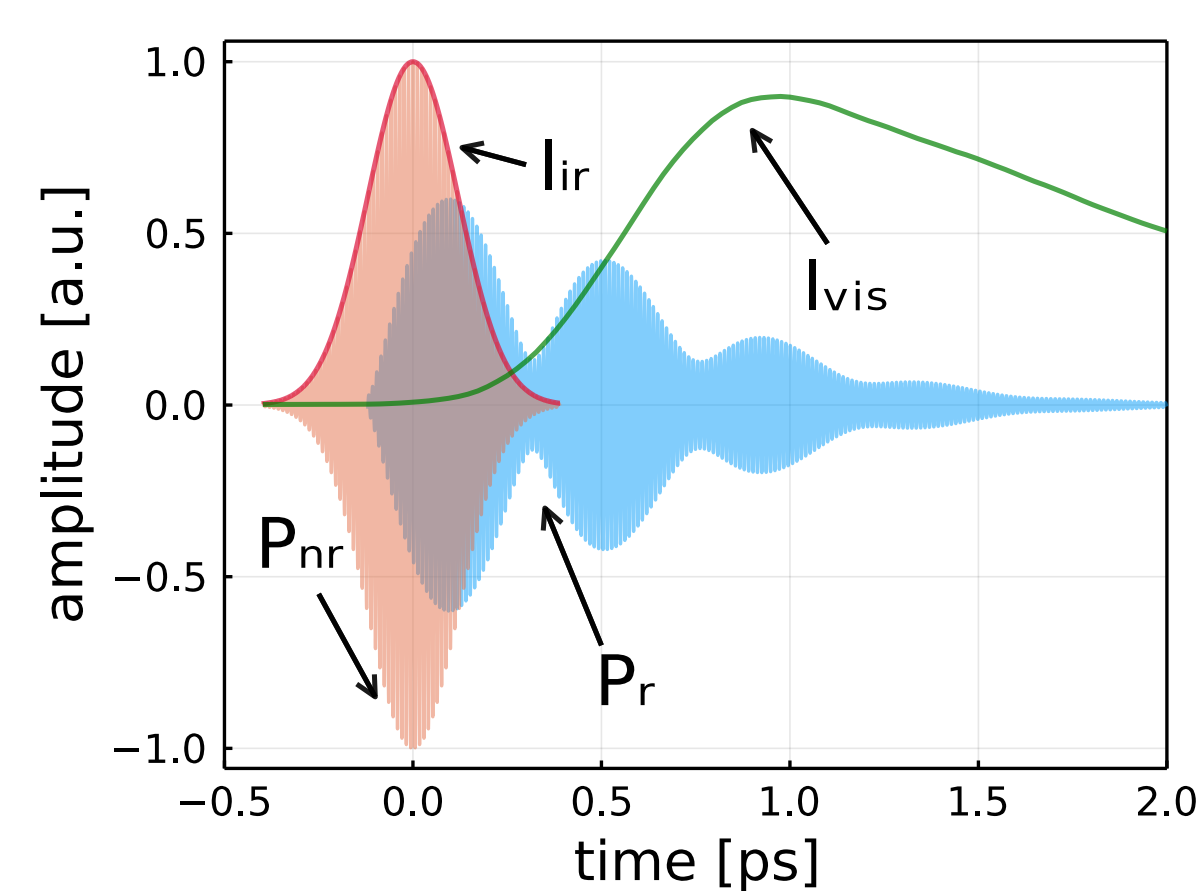
Sum-Frequency-Generation

- Induced second order polarization: $P \propto \chi^{(1)} \cdot E + \chi^{(2)} : E_1 E_2 + O(\chi^{(3)})$
- Interface selective (SF signal cancels in centro-symmetric media)



Non Resonant Suppression

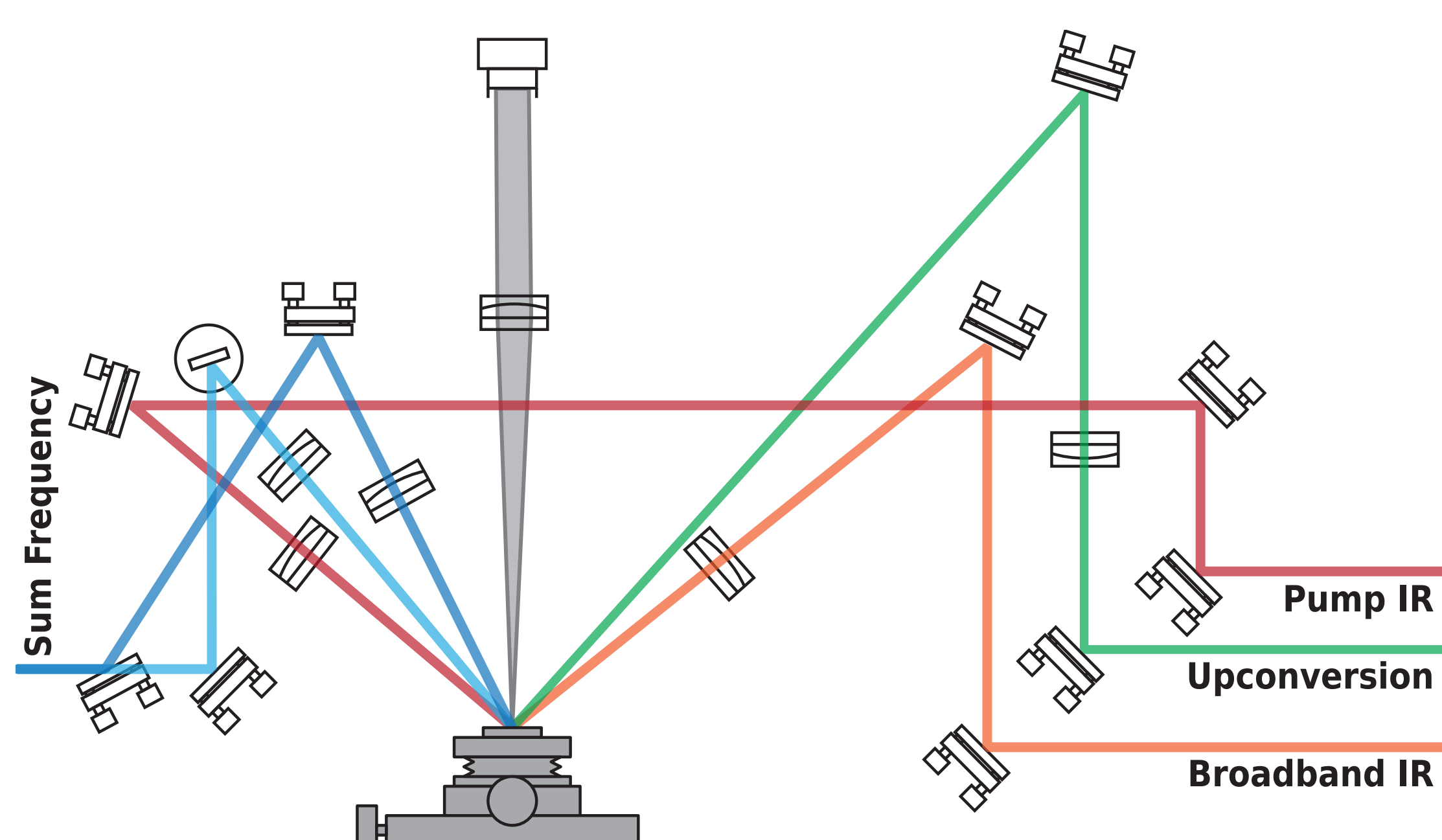
- Substrat polarization is non resonant and exhibits a time profile (P_{NR}) equal to the I_{IR}
- SFG of solely resonant signal is possible by delaying the I_{vis} with respect to I_{IR}
- Time asymmetric shape of I_{vis} is created by a Fabry-Pérot Etalon



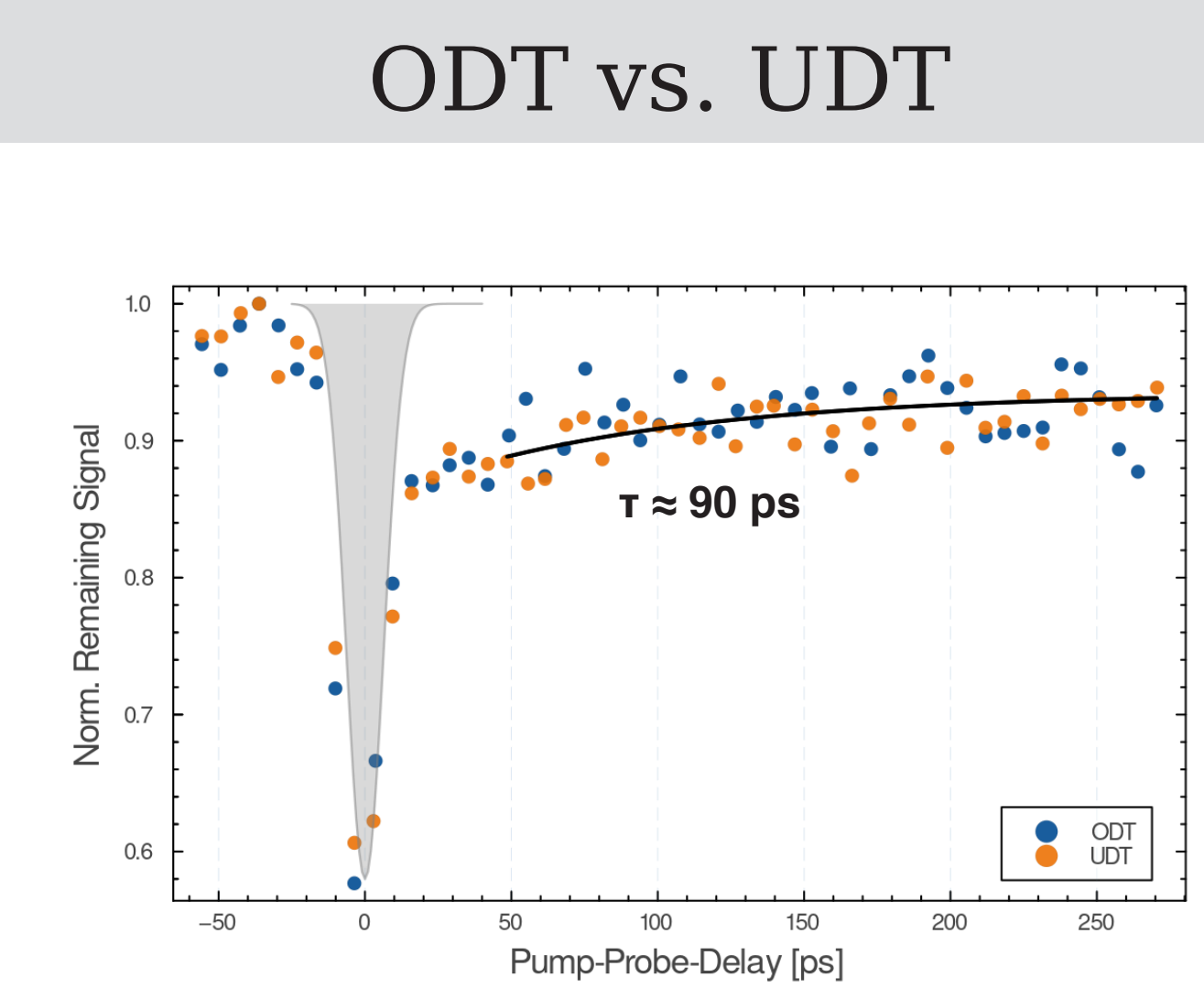
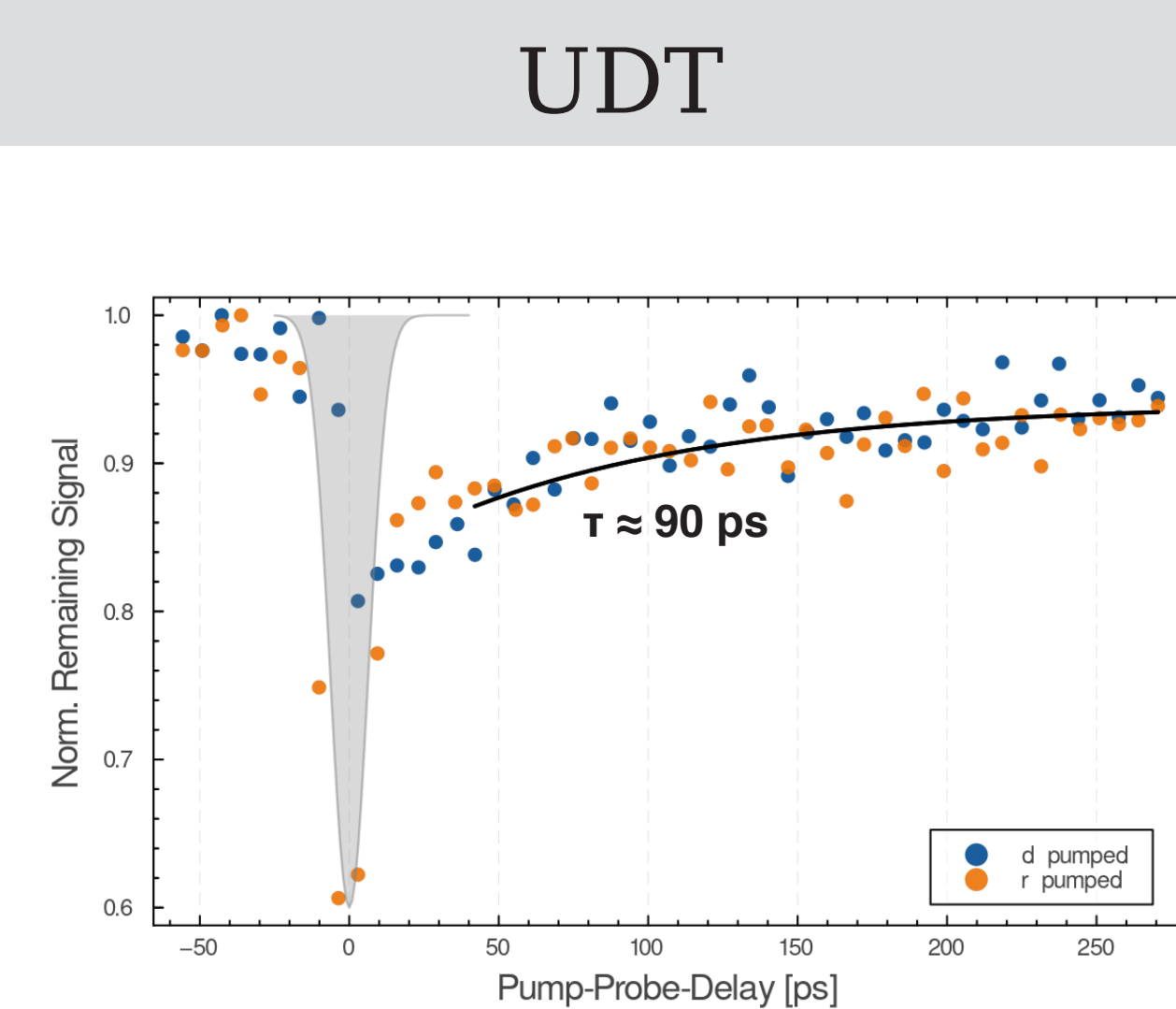
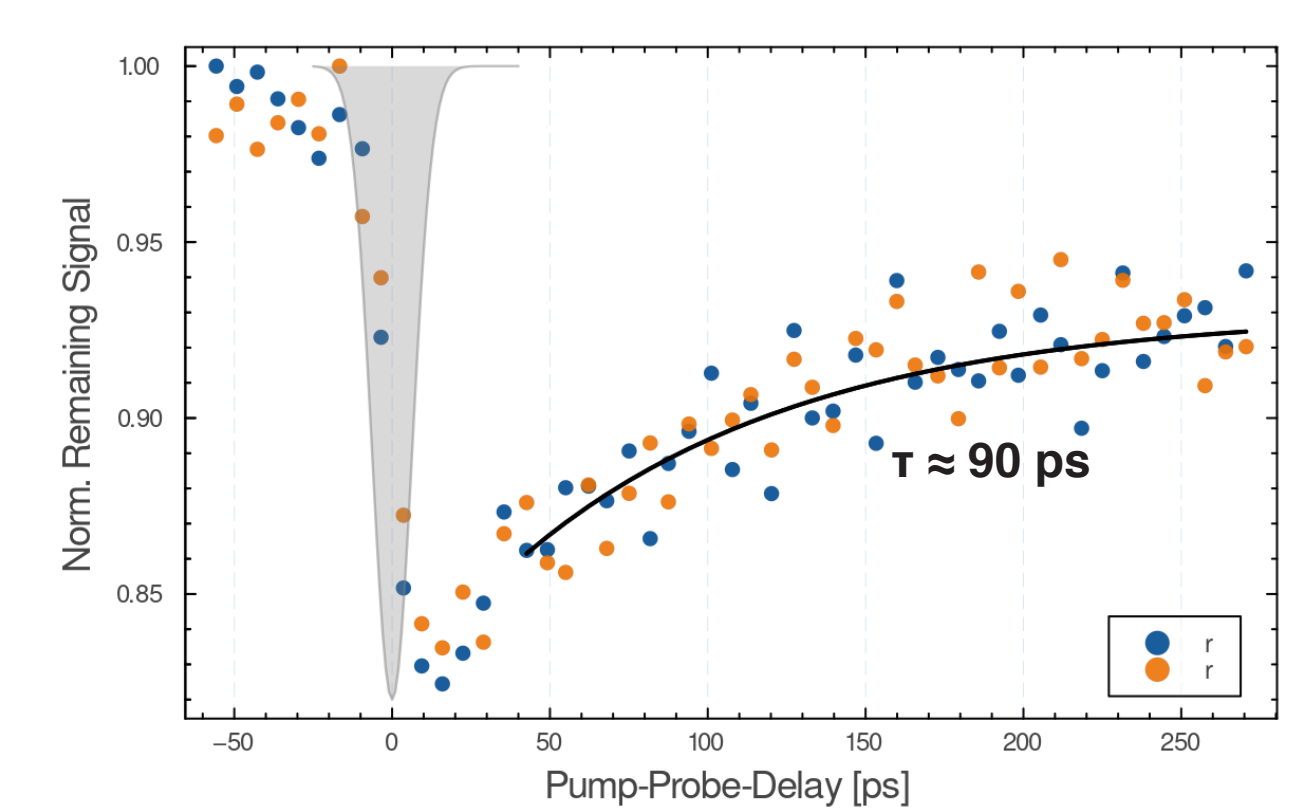
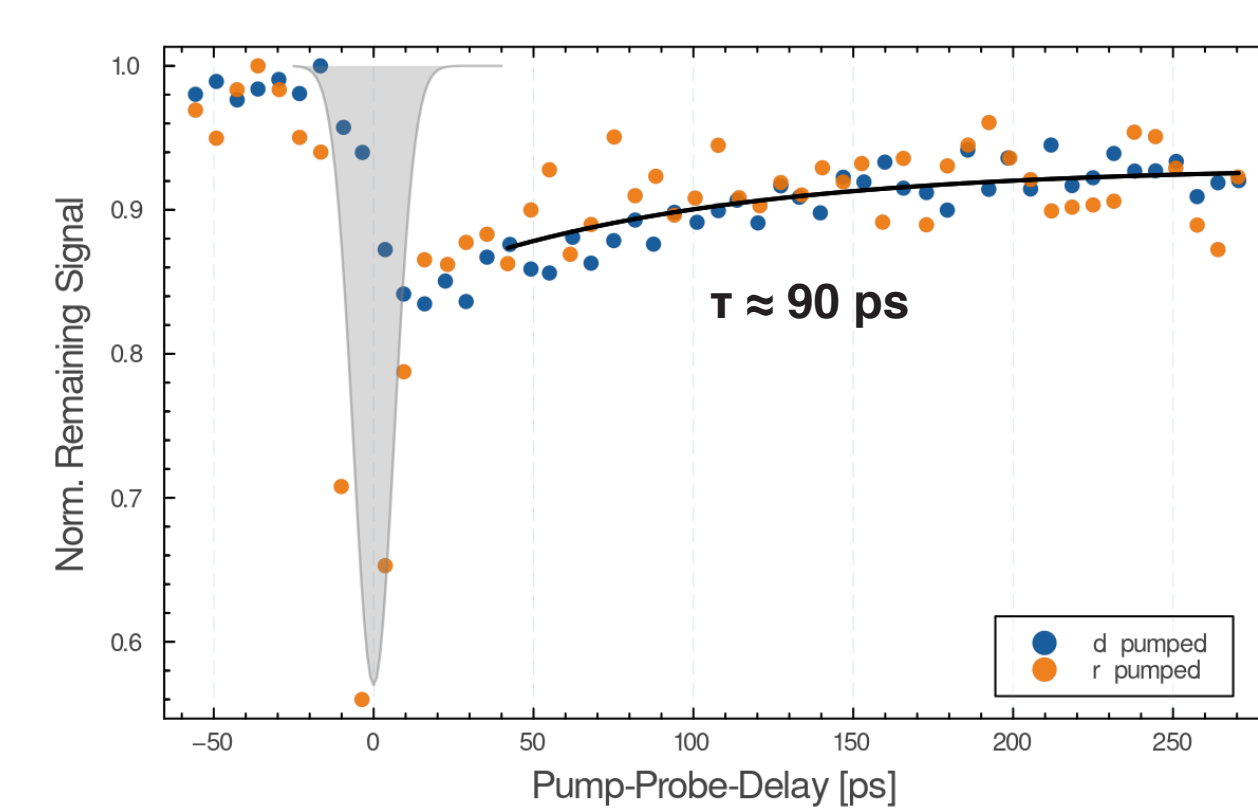
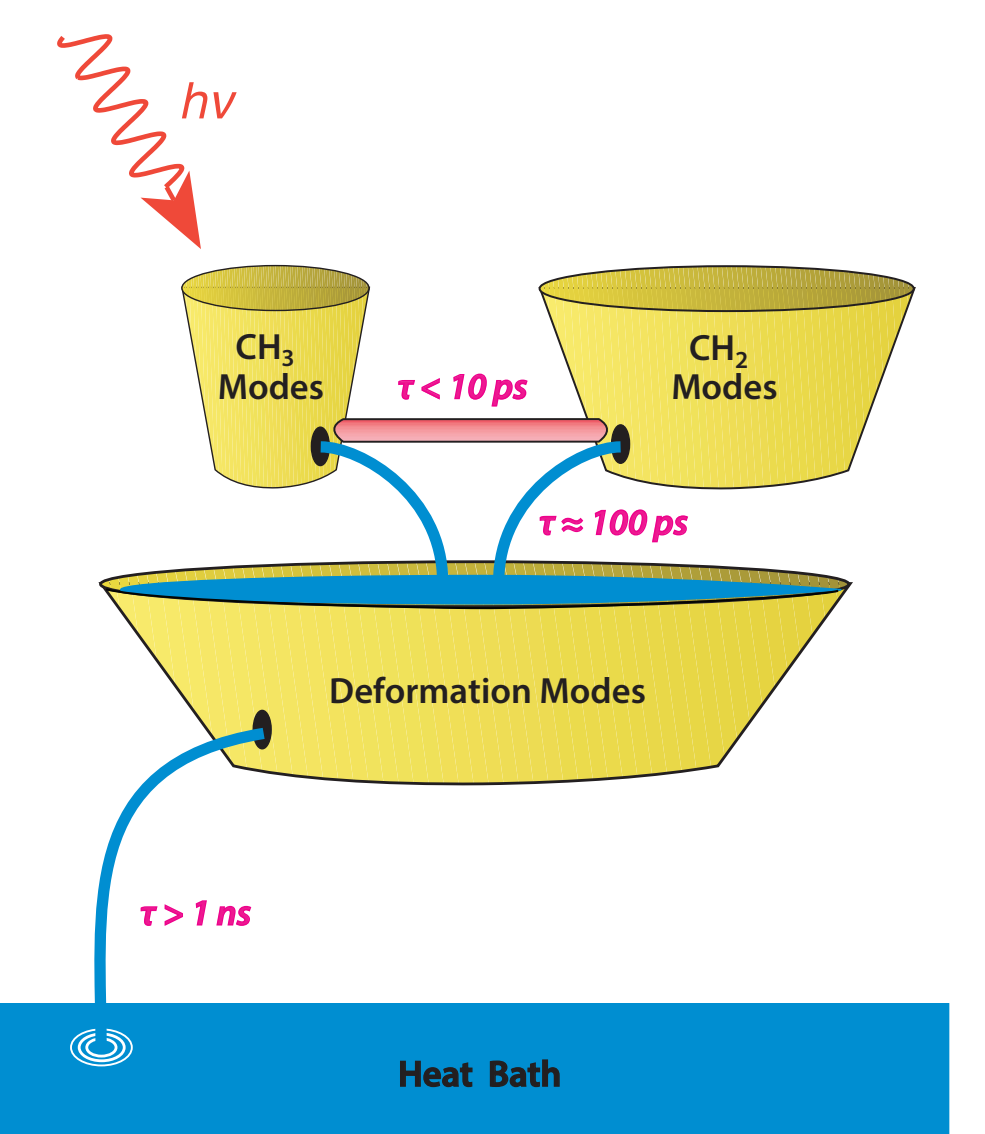
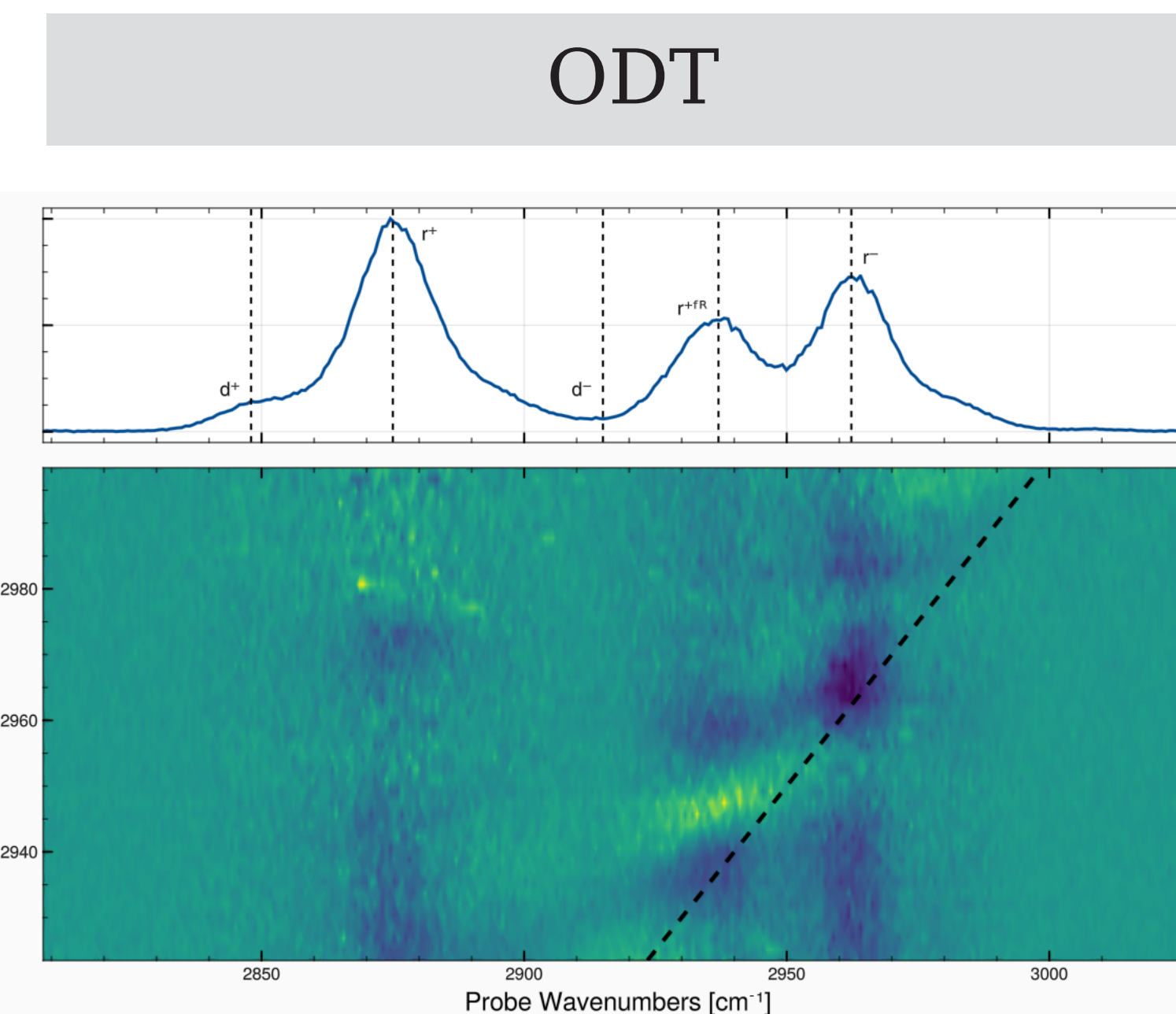
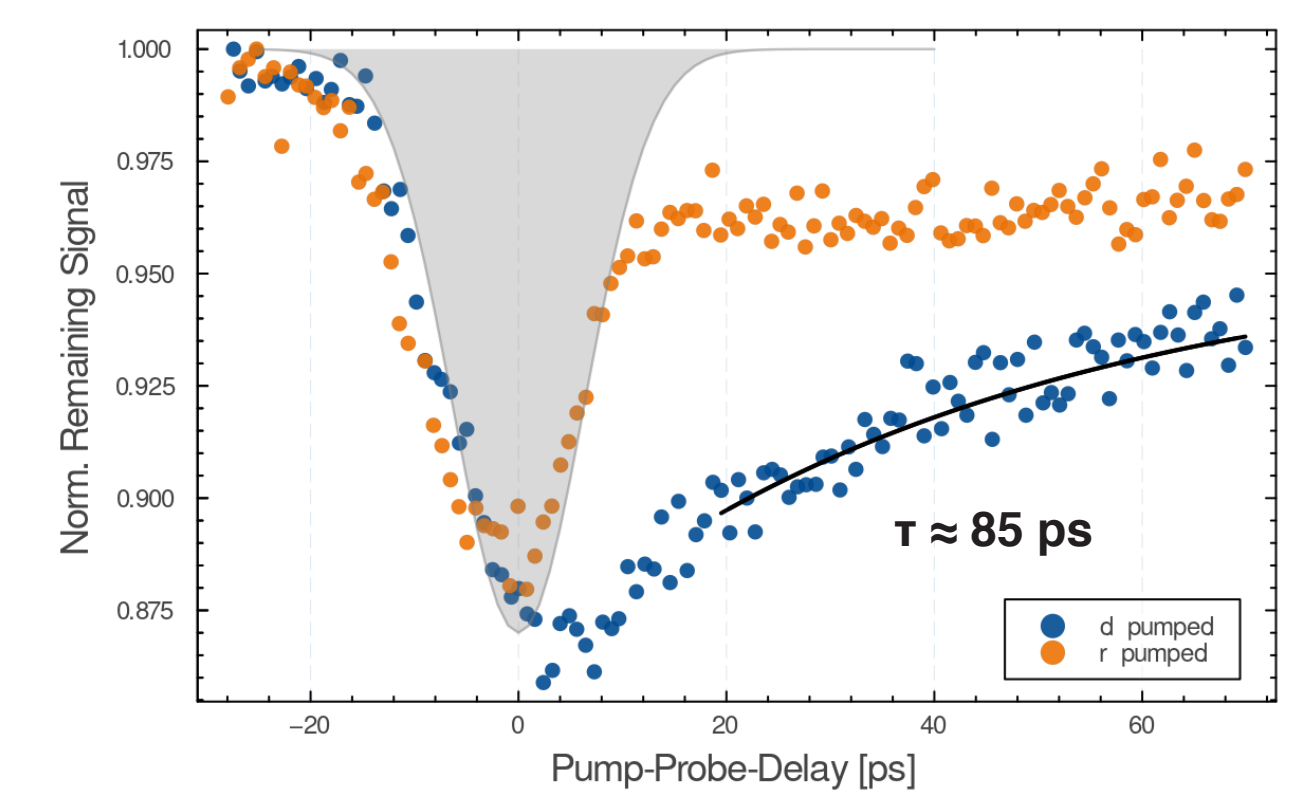
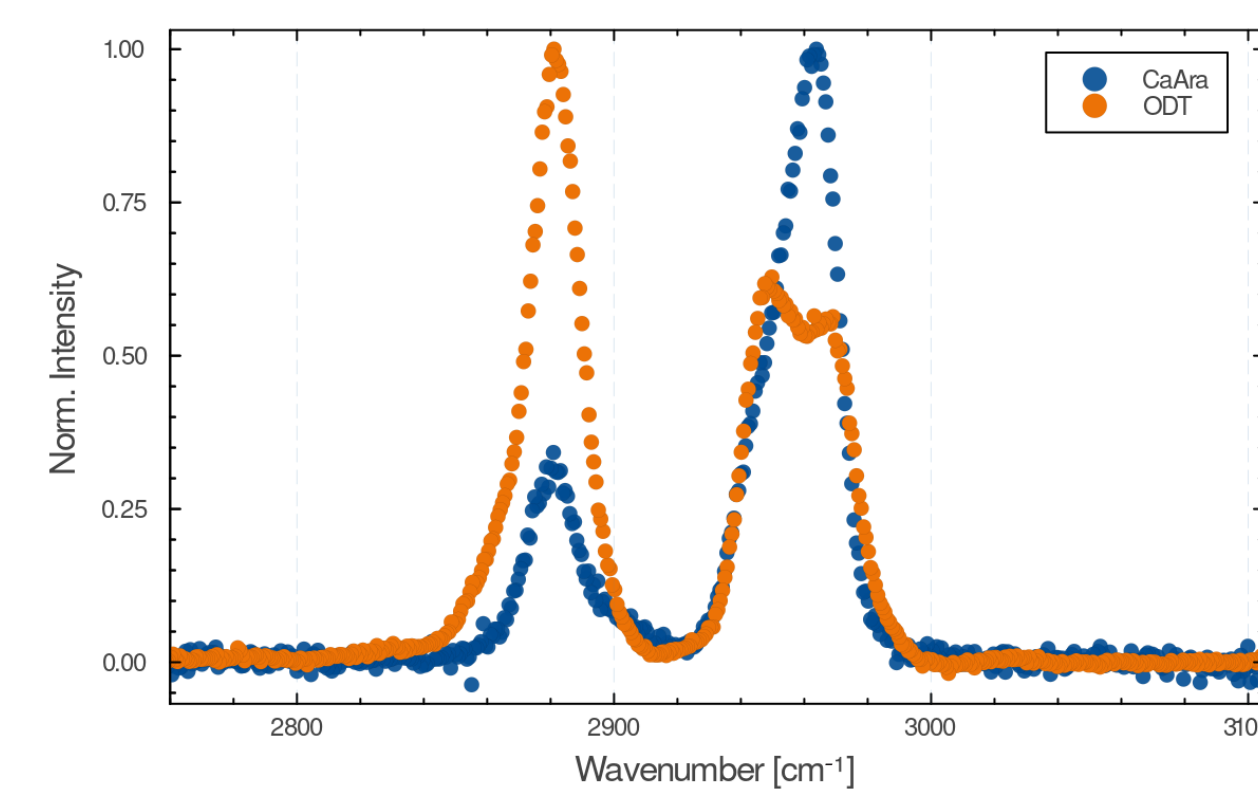
EXPERIMENTAL SETUP

Laser Specifications^[1]

- SHG / Fabry Pérot Etalon: 512 nm 2 kHz 3 mW 8.6 cm⁻¹ (no effect on spectral resolution wanted)
- fs-OPA (IR Probe / Light Conversion): 2 kHz 300 fs 200 cm⁻¹ 1.5 μm (100 mW) - 16 μm (6 mW)
- PG711 DFG (IR Pump / Ekspla): 1 kHz 20 ps 5 cm⁻¹ 1.3 μm (150 mW) - 3.4 μm (100 mW) 3.4 μm (100 mW) - 19.5 μm (0.2 μW)
- Pharos (Pump Laser / Light Conversion): 1024 nm 2 kHz 6 W 300 fs



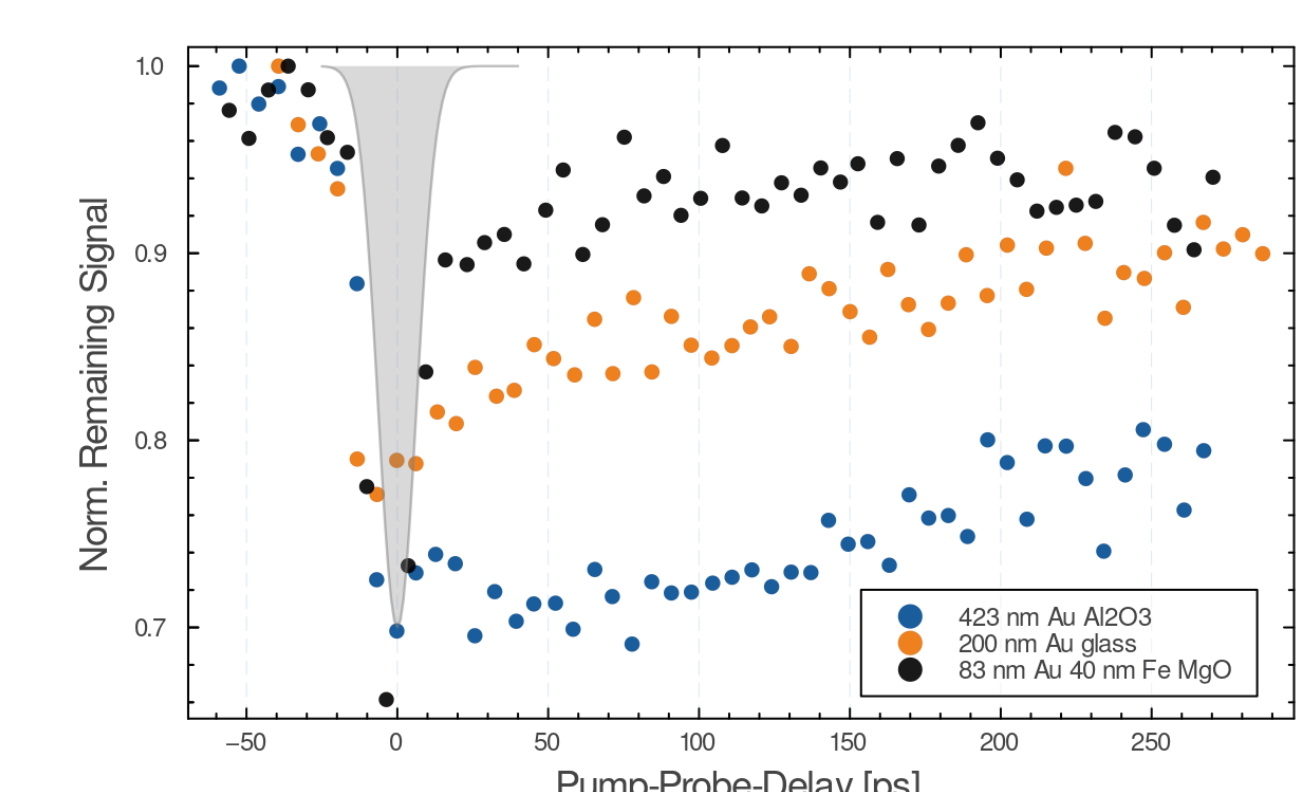
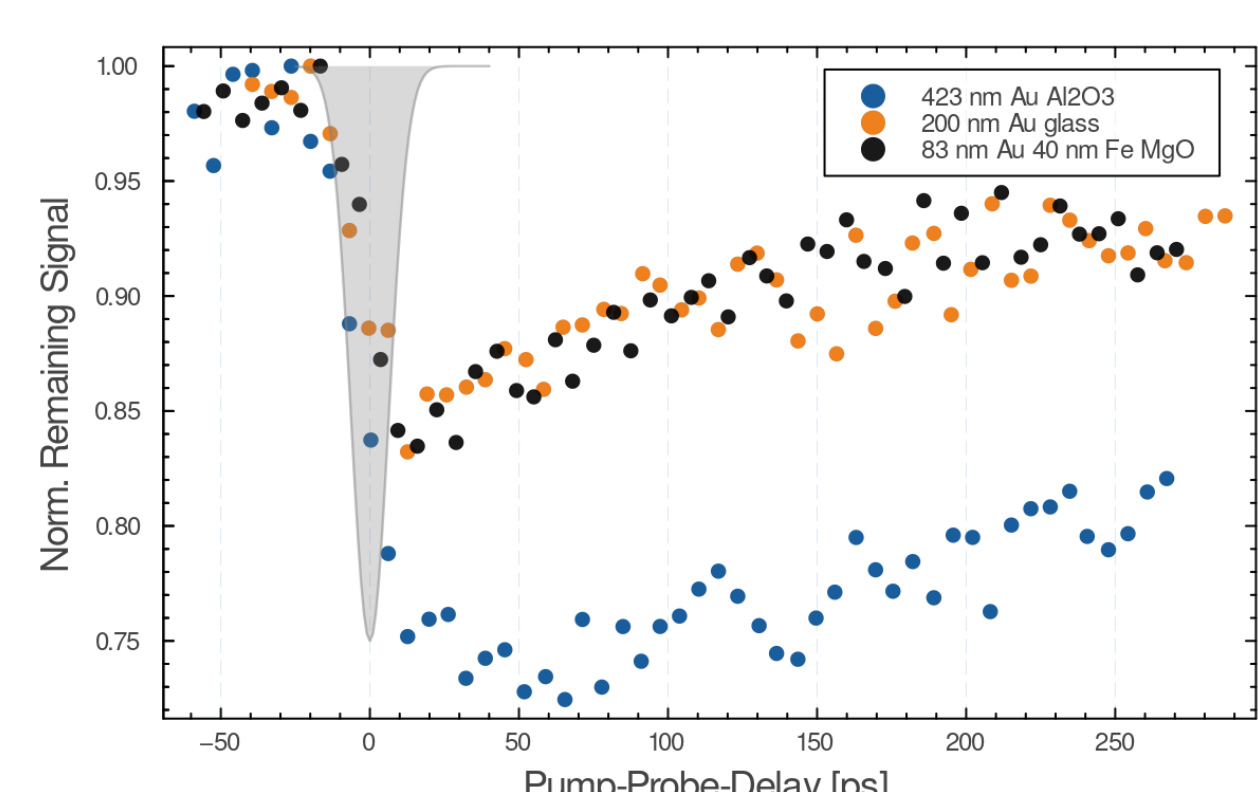
RESULTS



- Pumping r^- mode of ODT on Au: rapid bleach around time zero is more pronounced in comparison to Ca/Au on glass
- Similar time constants for energy redistribution from the CH-stretching to deformation modes for Ca/Au, ODT and UDT
- Signal increase in r_{fr} mode at time zero for ODT/UDT

OUTLOOK

- Influence of gold thickness on dynamics?
 - 83 nm Au + 40 nm Fe on MgO
 - 200 nm Au on glass
 - 423 nm Au on sapphire
- d^- pumped: c) exhibits very different dynamics in comparison to a) and b)
- r^- pumped: all three substrates result in different dynamics



[1] Lackner, M.; Hille, M.; Hasselbrink, E. Vibrational Energy Redistribution between CH Stretching Modes in Alkyl Chain Monolayers Revealed by Time-Resolved Two-Color Pump-Probe Sum Frequency Spectroscopy. *J Phys Chem Lett* 2019, 11 (1), 108–112.
[2] Ye, S., Sato, Y., & Uosaki, K. (1997). Redox-induced orientation change of a self-assembled monolayer of 11-ferrocenyl-1-undecanethiol on a gold electrode studied by in situ FT-IRRAS. *Langmuir*, 13(12), 3157–3161