Two-dimensional coherent spectroscopy of doped Helium nanodroplets

Frank Stienkemeier

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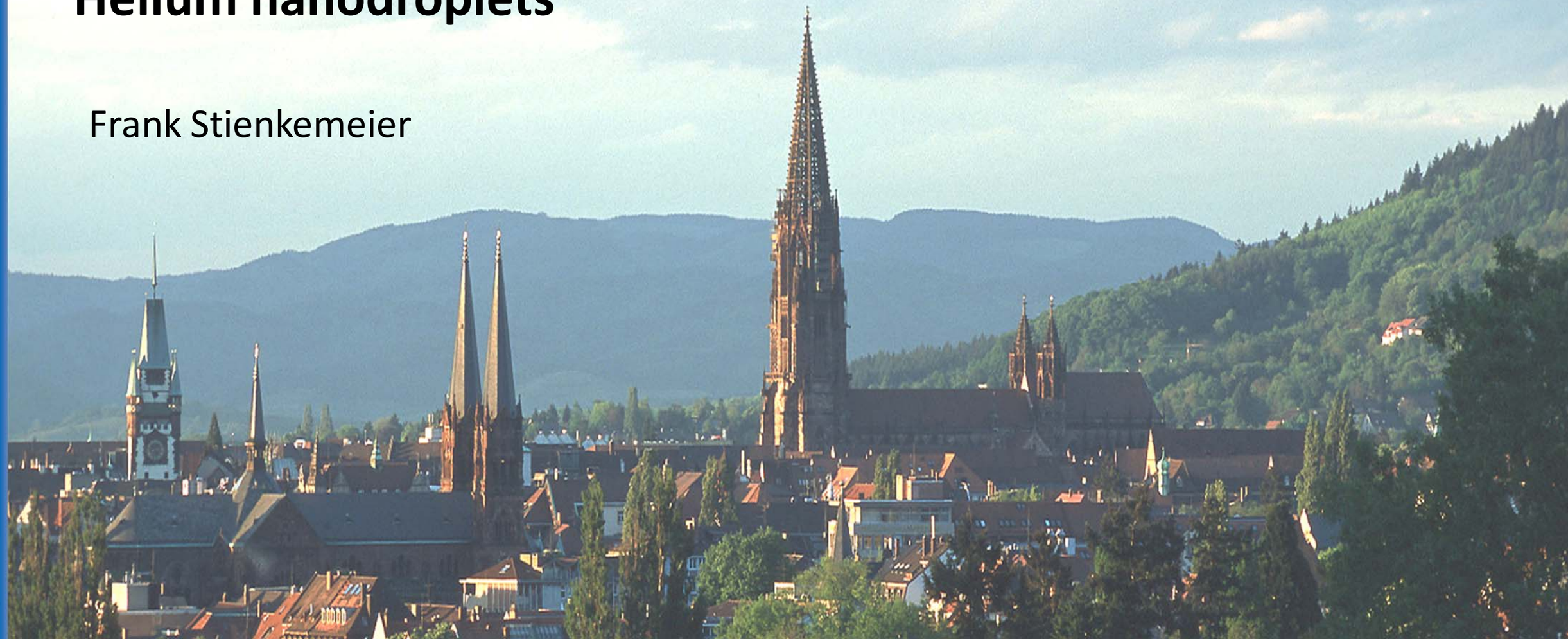
University of Freiburg



Outline

- Introduction
  - Femtosecond experiments
  - Coherent multidimensional spectroscopy
- 2d-coherent spectroscopy of doped helium nanodroplets
  - Wave packet dynamics of Rb dimers
  - Dynamics of dopant molecules with the helium environment
- Conclusion

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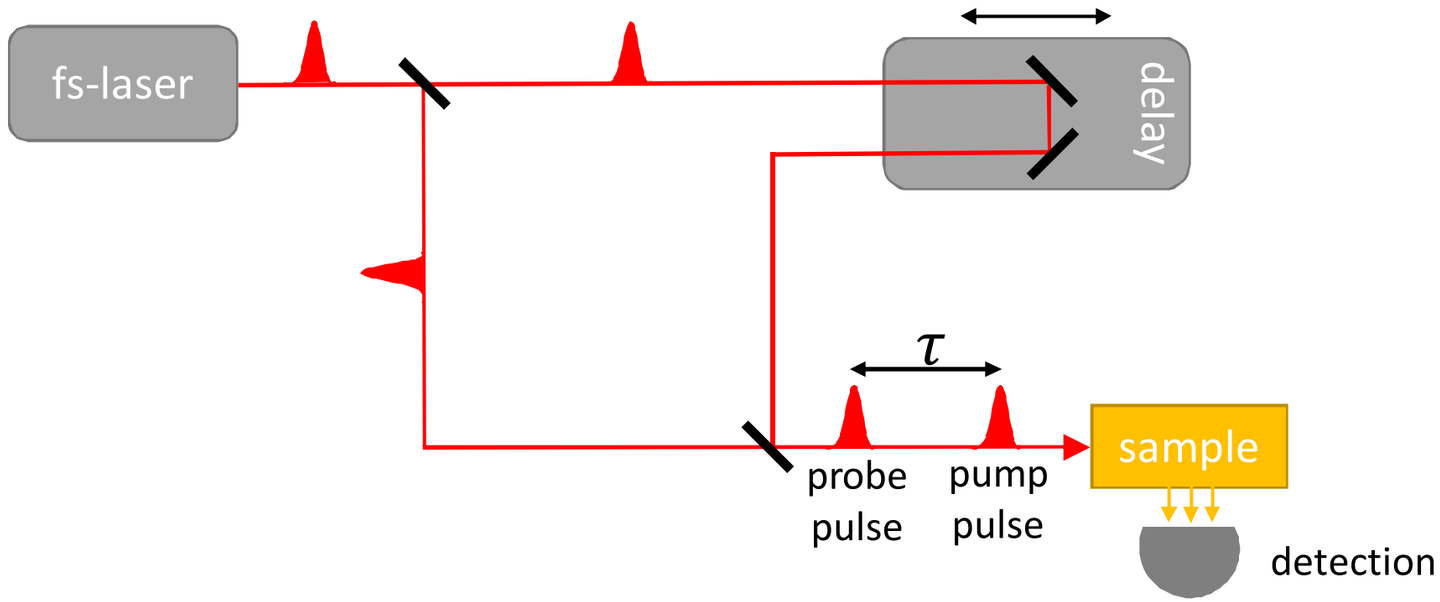
Femtosecond methods



a) **Time-dependance of an action signal**

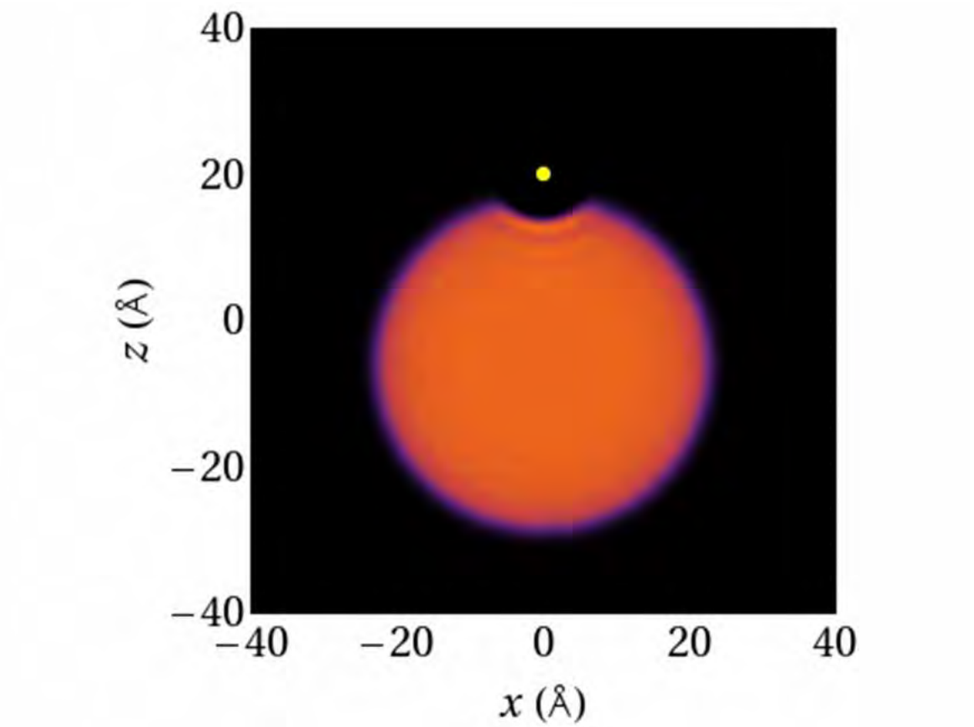
b) Wave packet dynamics (Tannor-Kosloff-Rice)

c) Wave packet interferometry (Brumer-Shapiro)

d) Multidimensional coherent spectroscopy

Simulations: M. Barranco et al. (Uni Barcelona)

Rb*

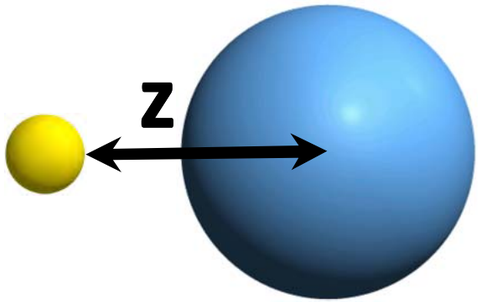


Rb: equal electron density surface

5s 

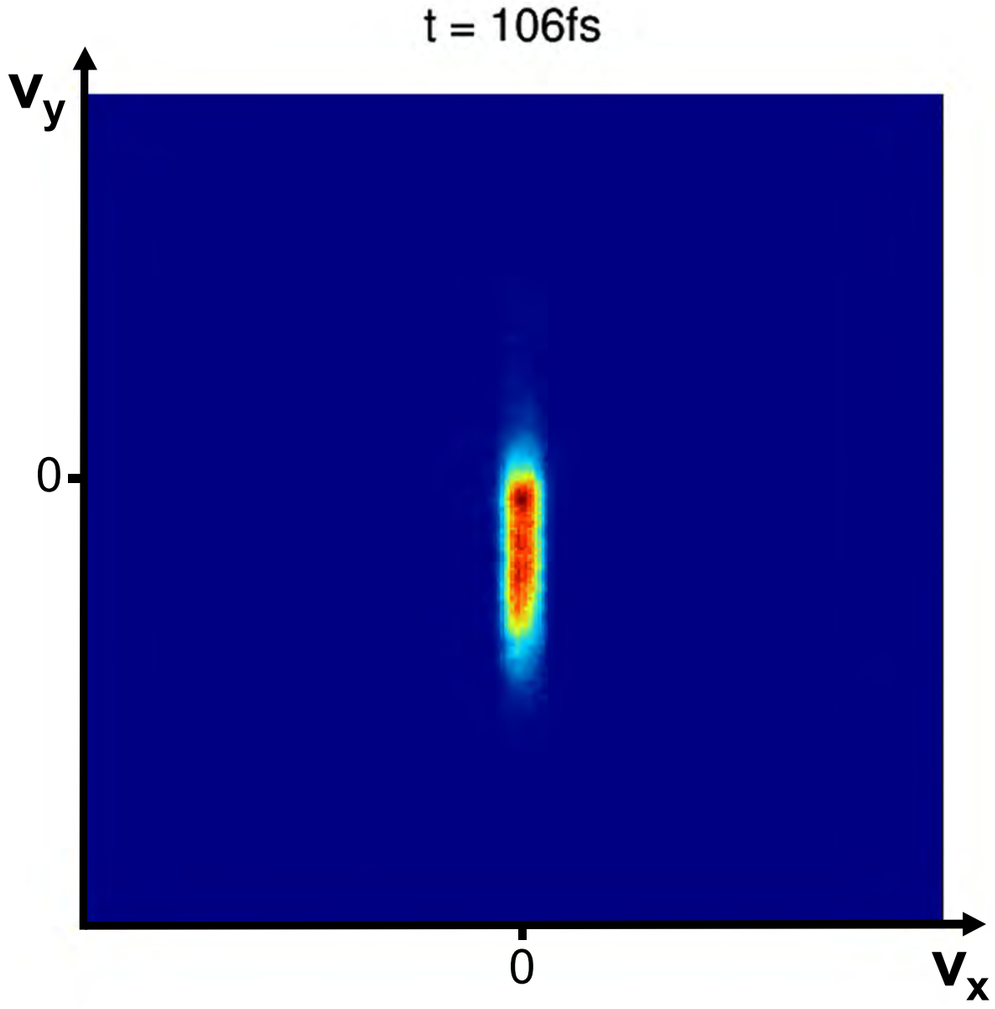
5p 

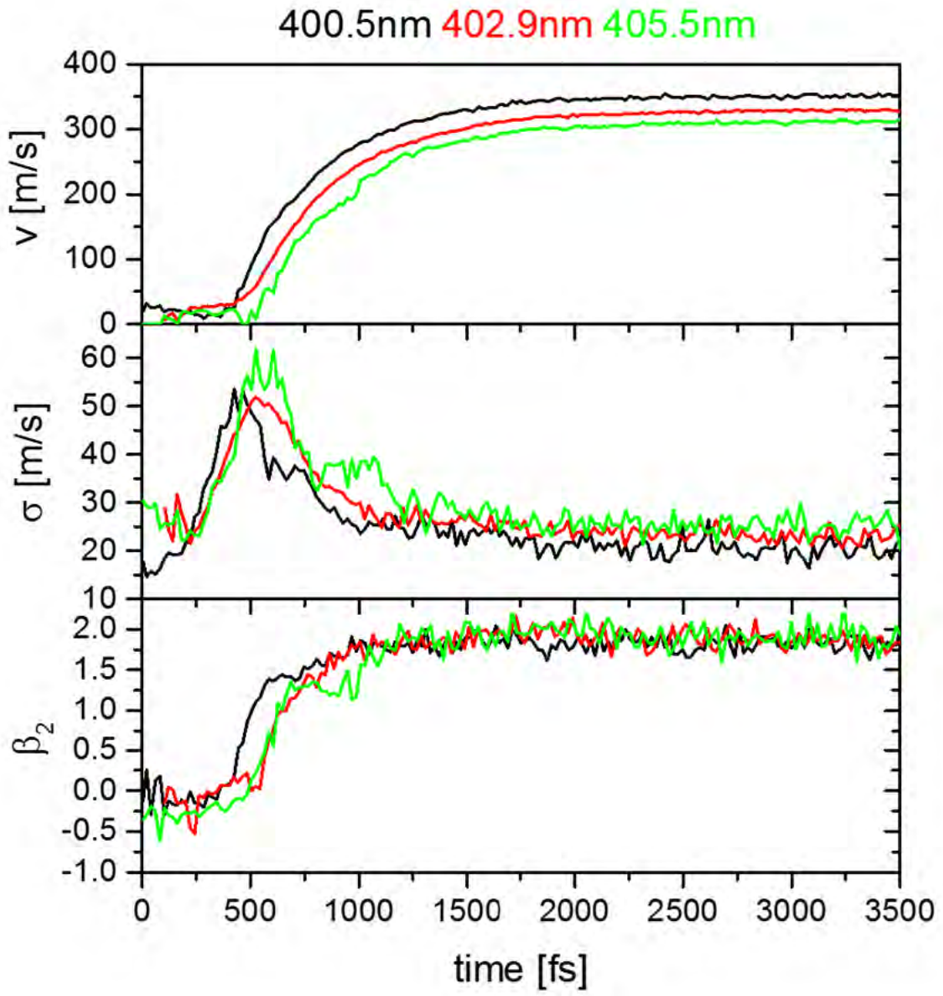
Rb He_N



J. v. Vangerow et al., J. Phys. Chem. A **118**, 6604 (2014)

Pump probe Rb^+ Velocity Map Imaging





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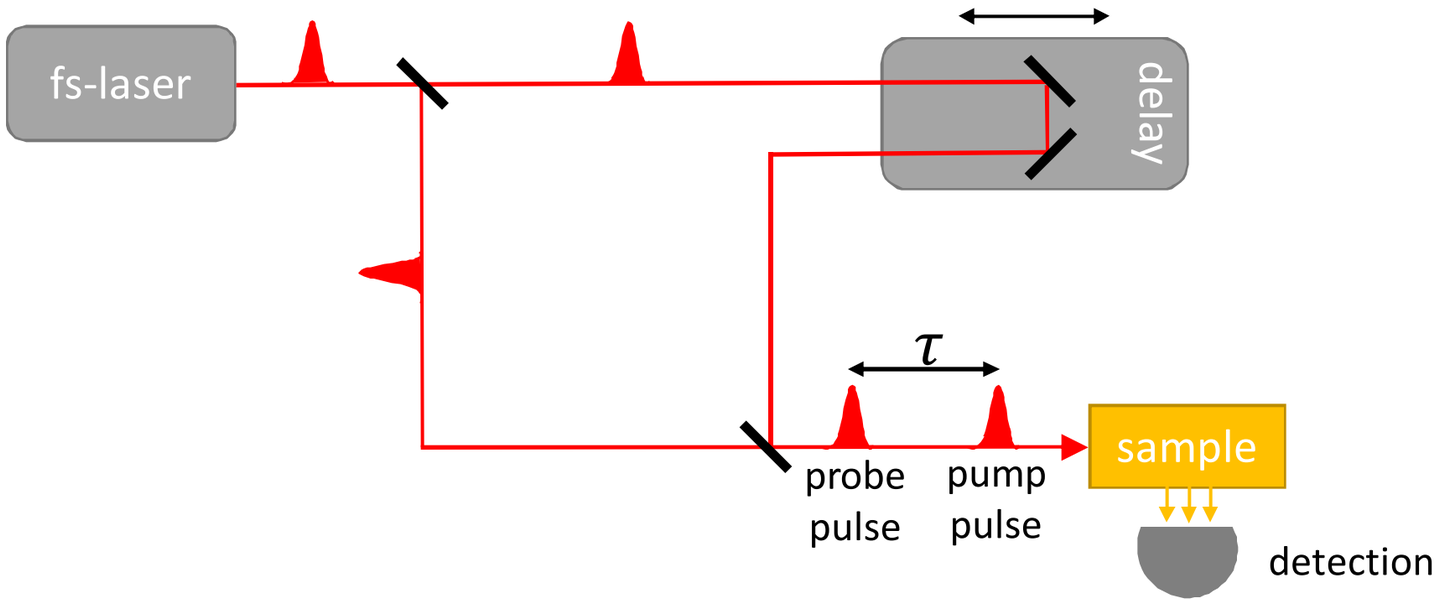
Femtosecond methods



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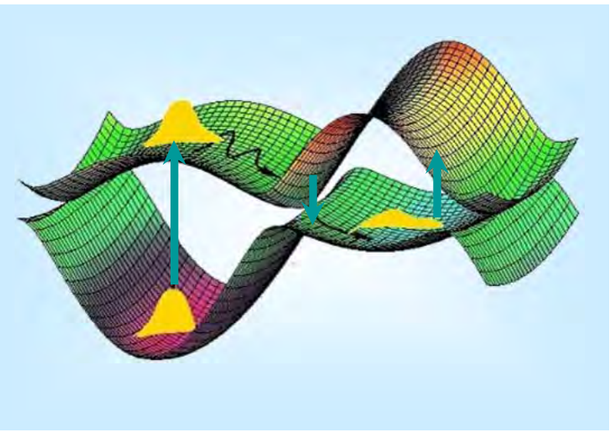
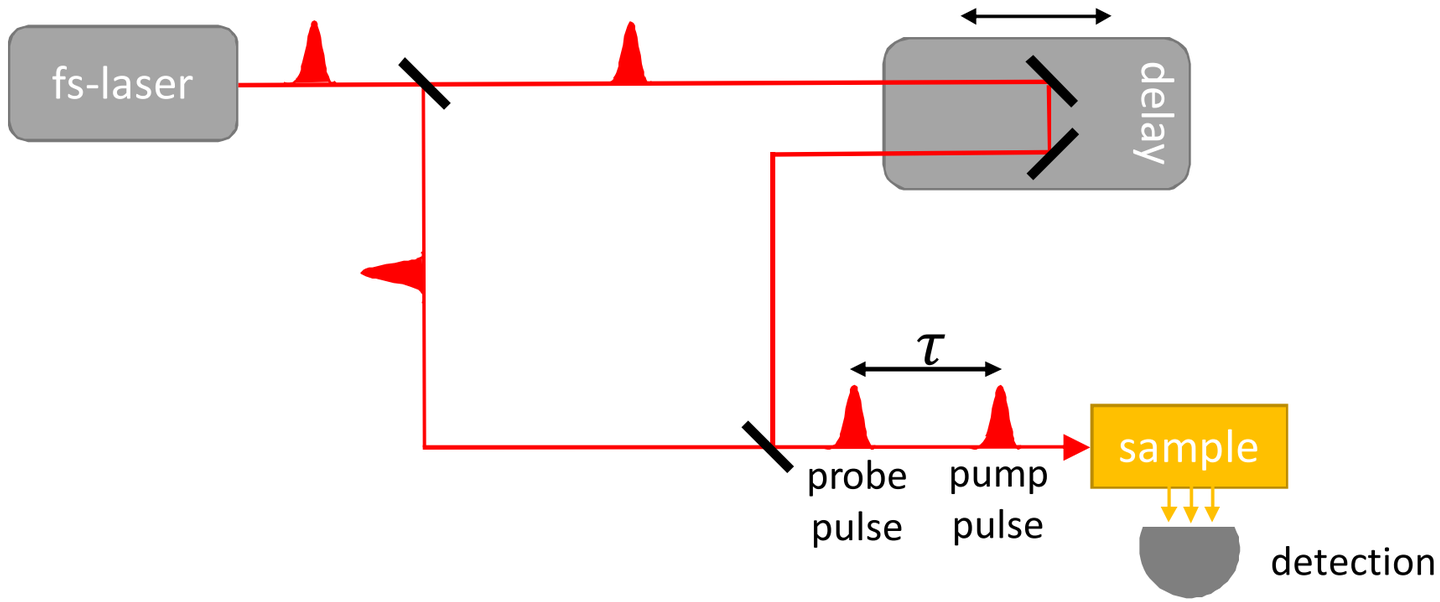


Femtosecond methods



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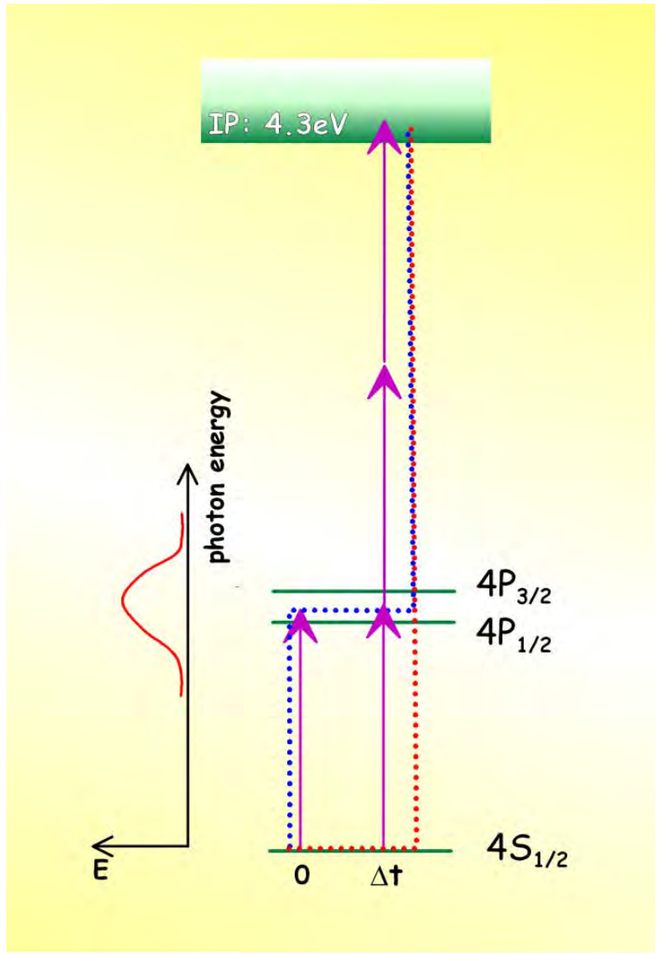
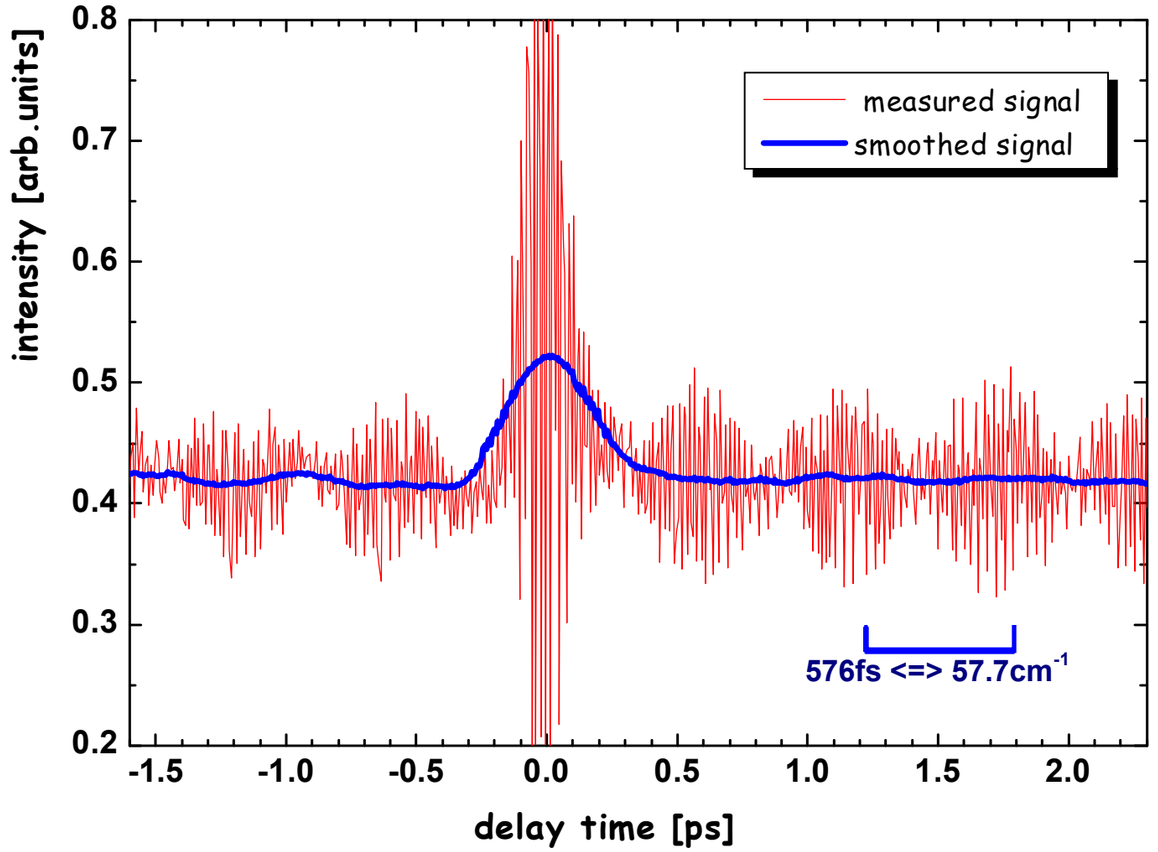
Quantum interferences of K atoms – **nJ** pulse energies

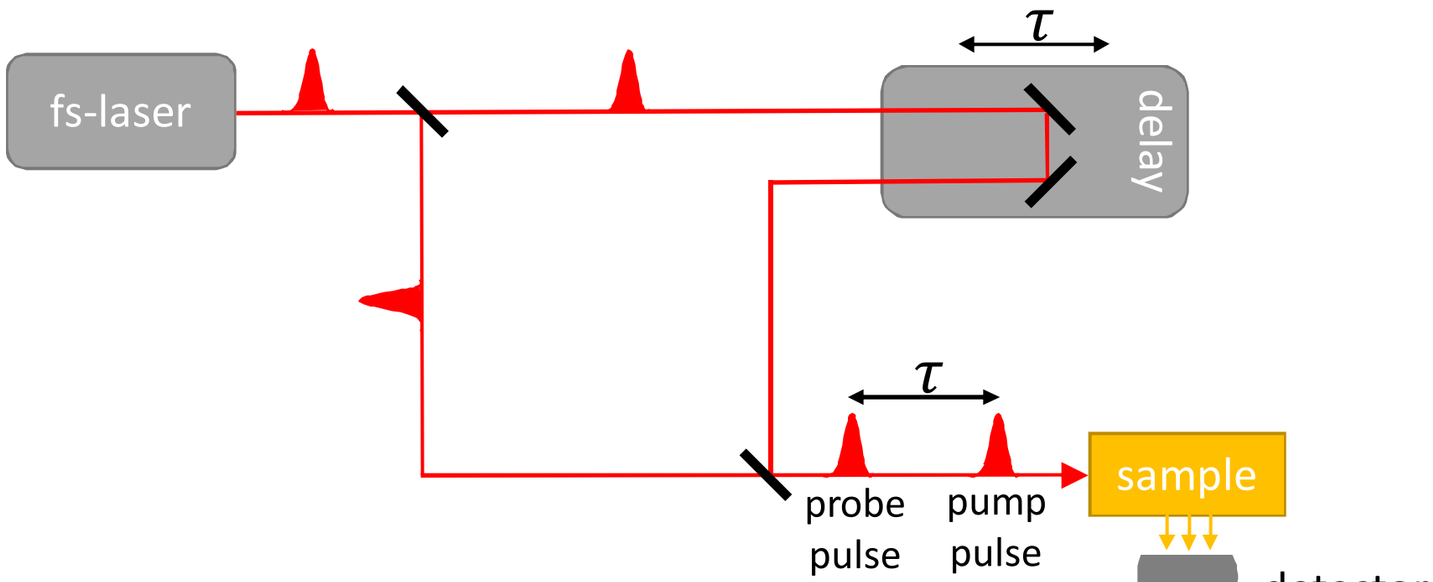
Multi-Path Interference



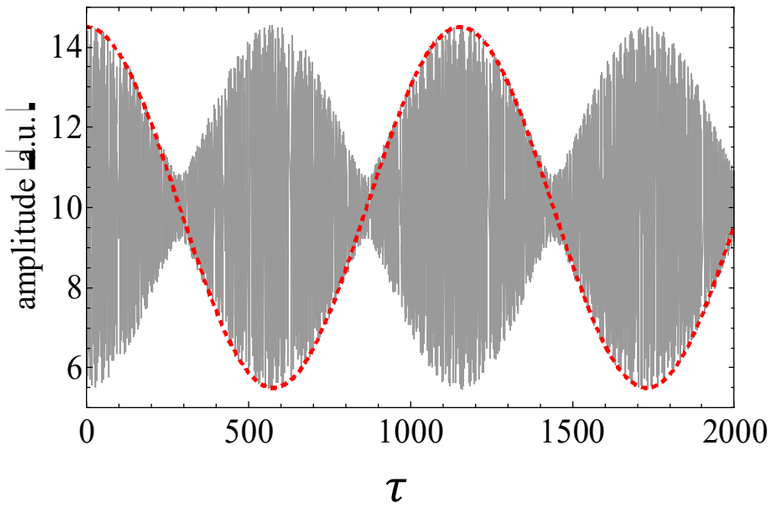


ΔE_{so}= 57.72 cm^{-1}

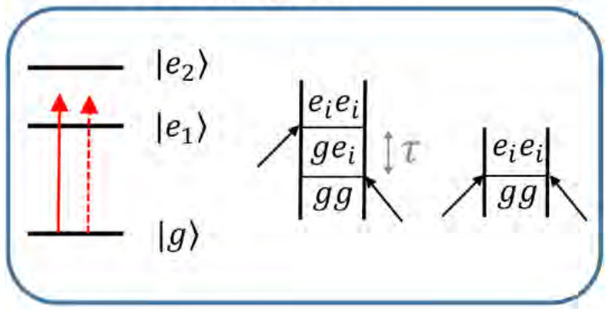
Conventional pump-probe



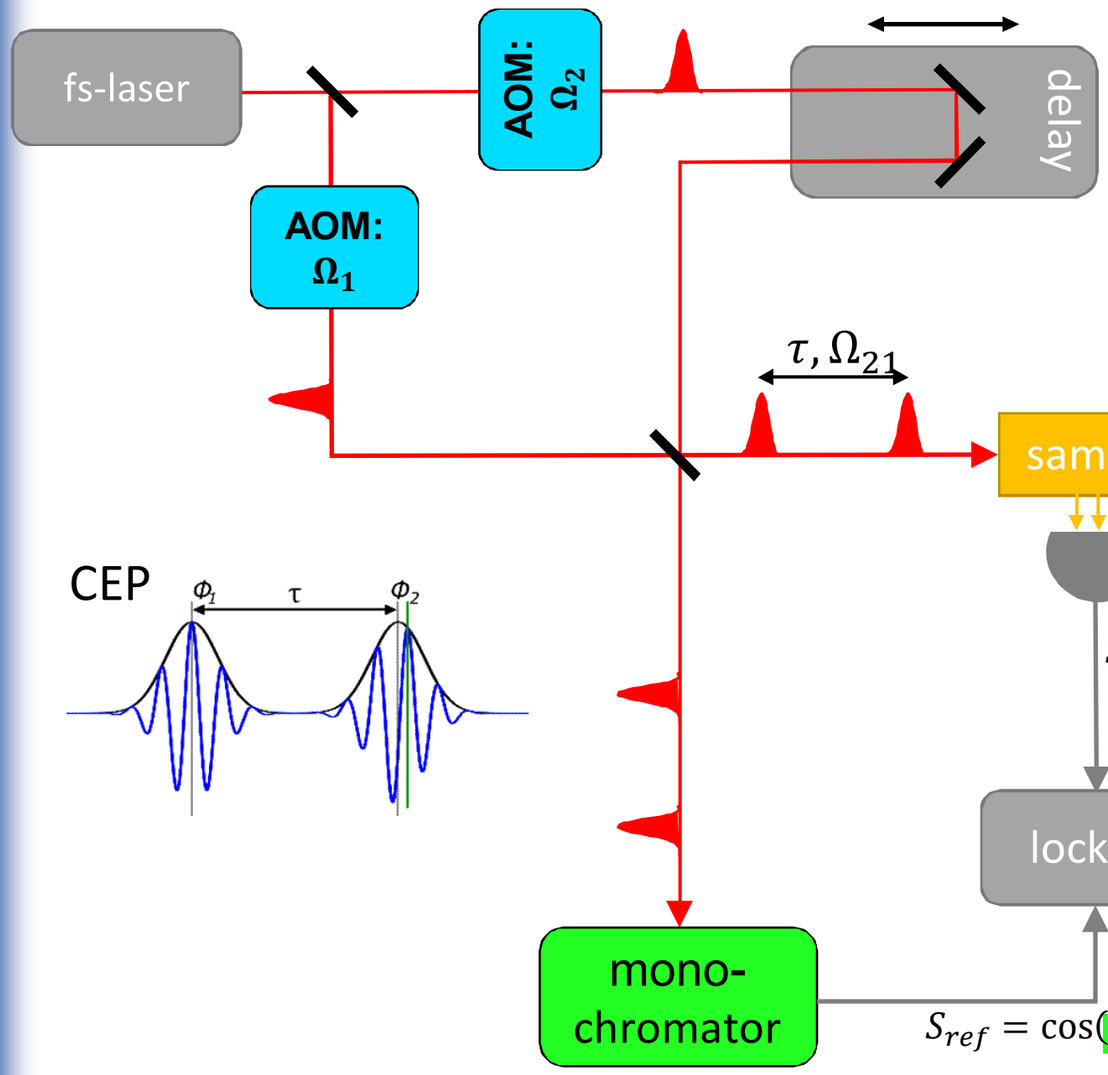
$$S \propto c + \sum a_i \cos(\omega_{e_i g}\tau)$$



Three-level system:



Phase-modulated pump-probe technique

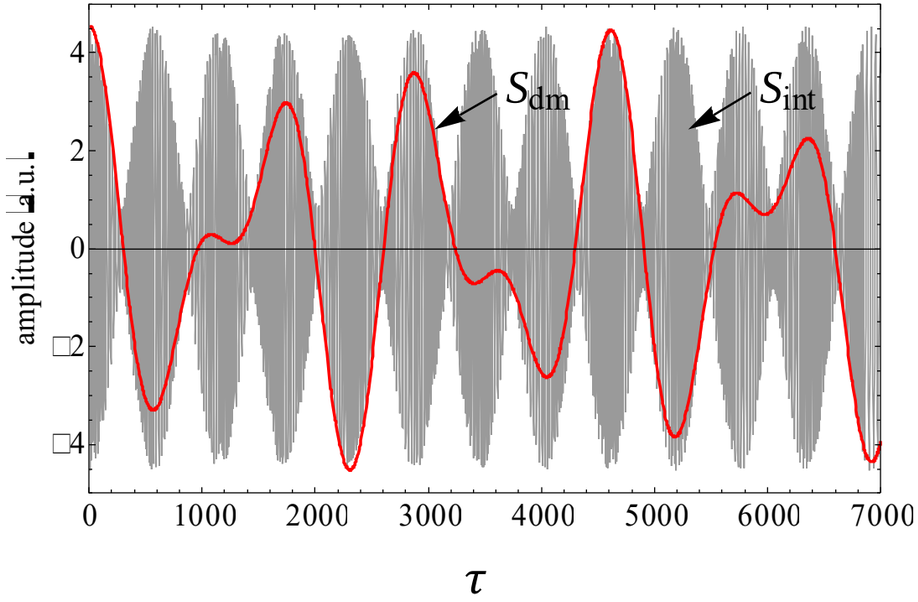


CEP

$$S \propto c + \sum a_i \cos(\omega_{e_i g}\tau + \Omega_{21} t)$$

$$S_{dm} \propto \sum a_i \cos\left((\omega_{e_i g} - \omega_M)\tau\right)$$

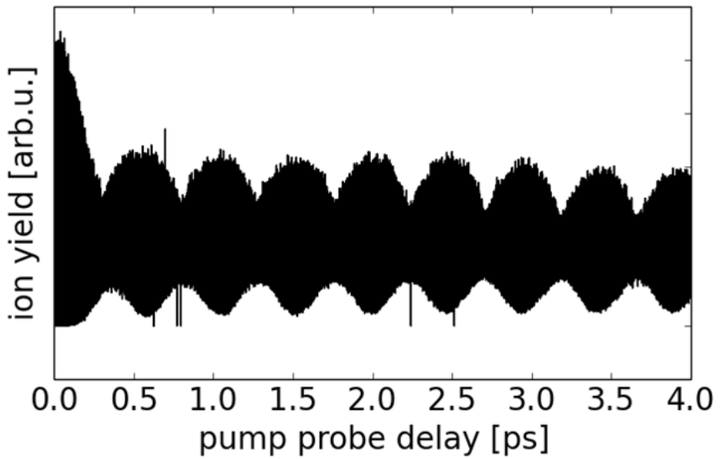
$$S_{ref} = \cos(\omega_M \tau + \Omega_{21} t)$$

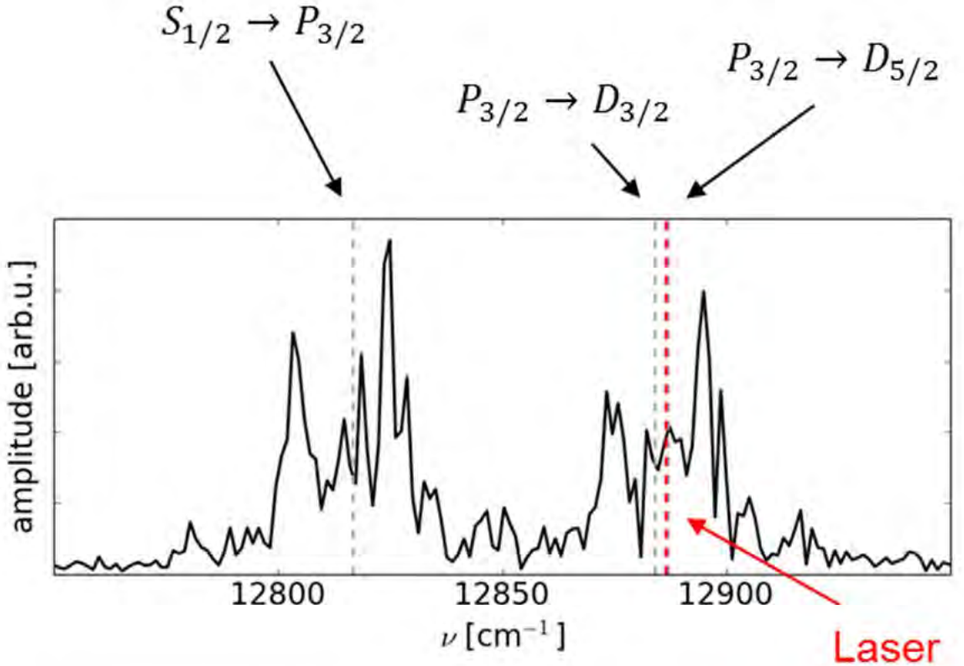


P.F. Tekavec, T.R. Dyke, A.H. Marcus, J. Chem. Phys. **125**,194303 (2006)
L. Bruder, M. Mudrich, F. Stienkemeier, Phys. Chem. Chem. Phys. **17**, 23877 (2015)

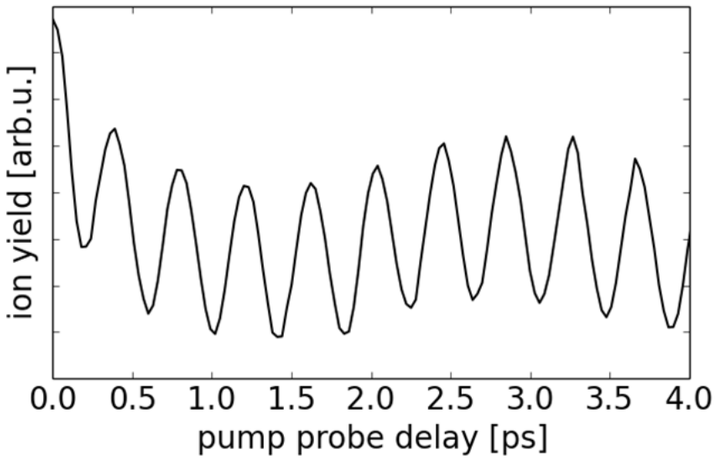
Comparison of phase modulation technique to conventional WPI

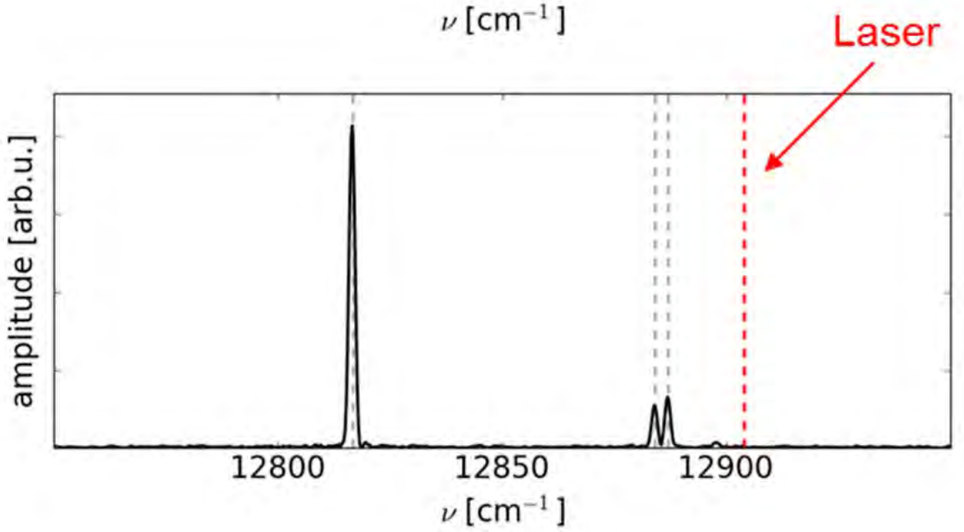
Conventional pump-probe:





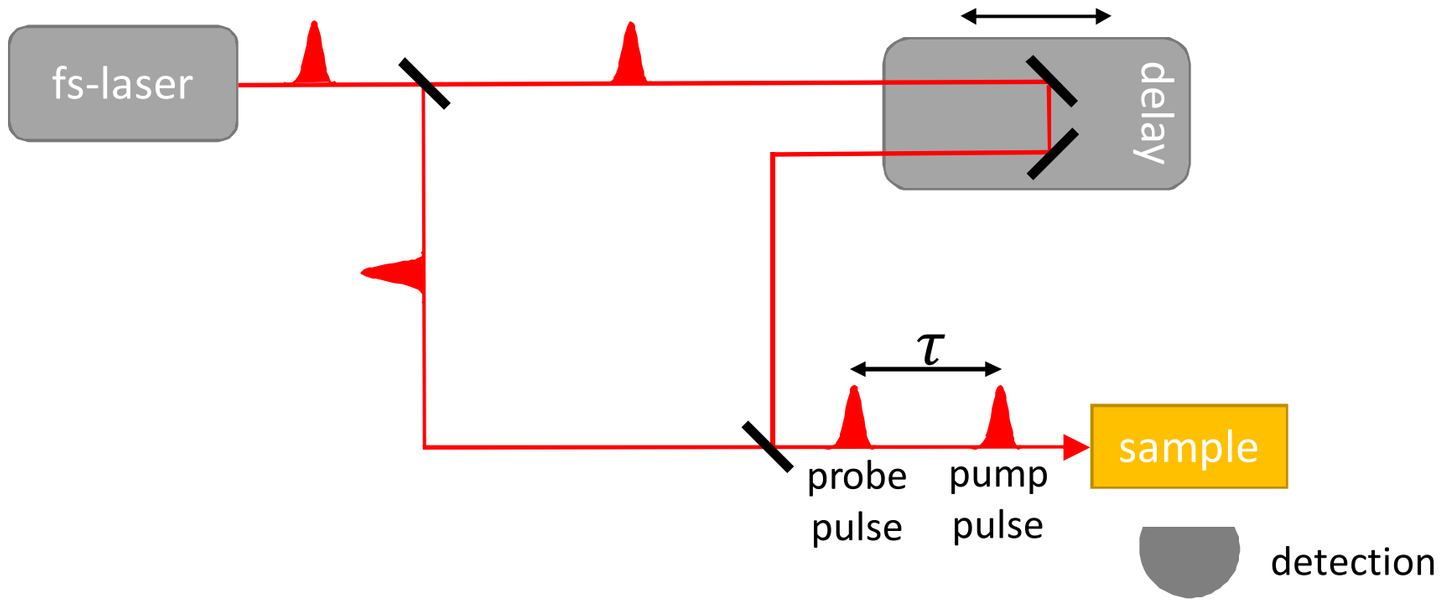
Phase-modulated pump-probe:





L. Bruder, M. Mudrich, F. Stienkemeier, Phys. Chem. Chem. Phys. **17**, 23877 (2015)

Femtosecond methods



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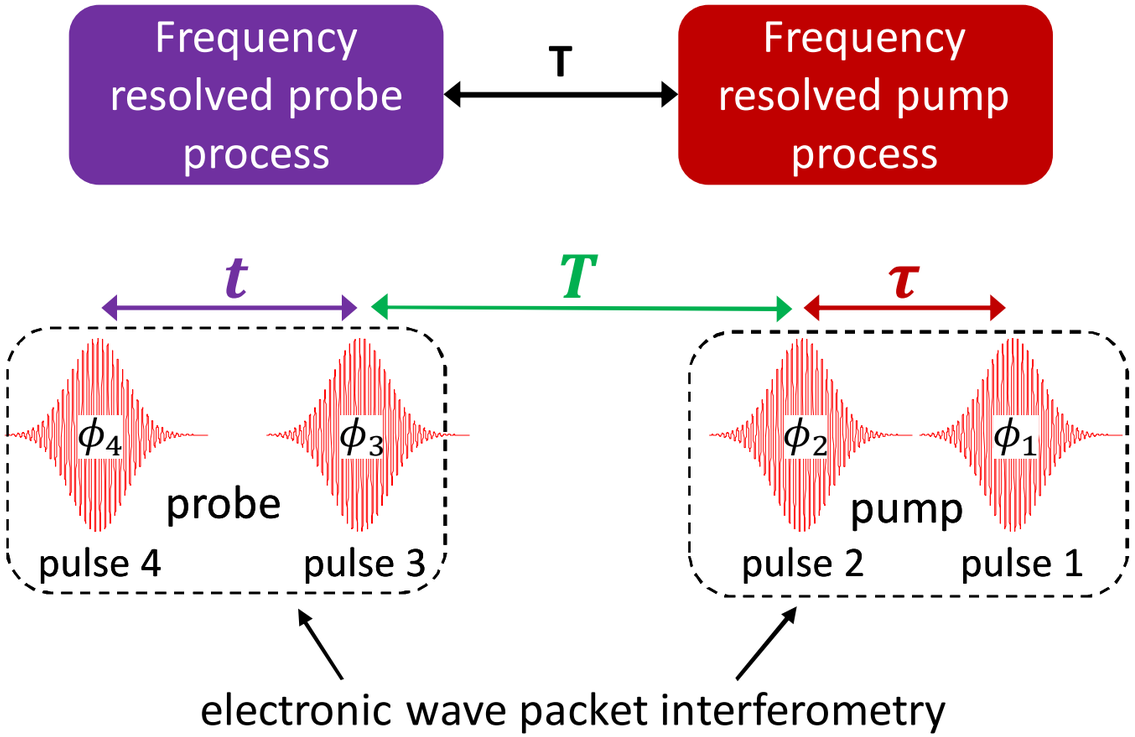
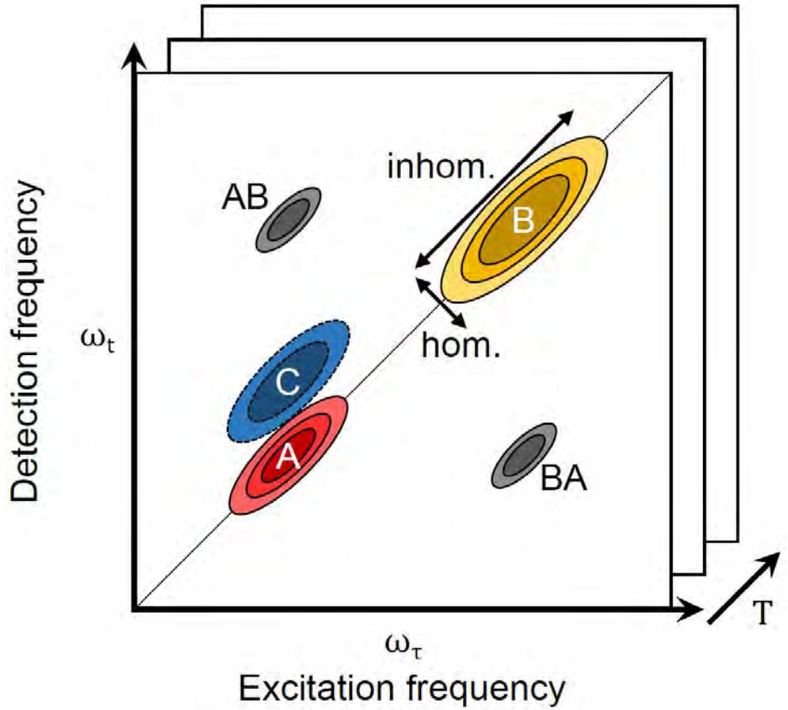
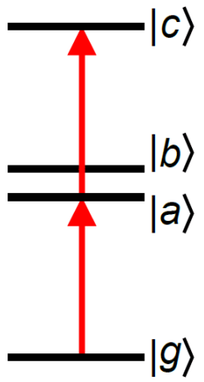
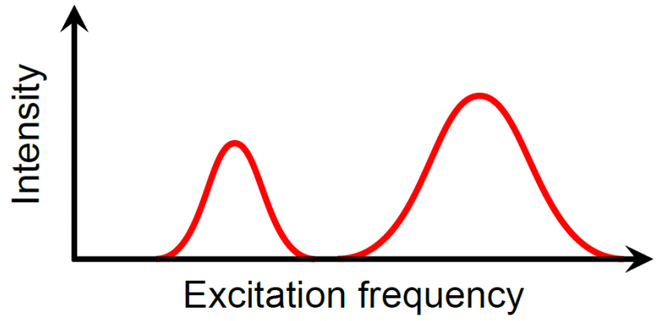
2-dimensional spectroscopy





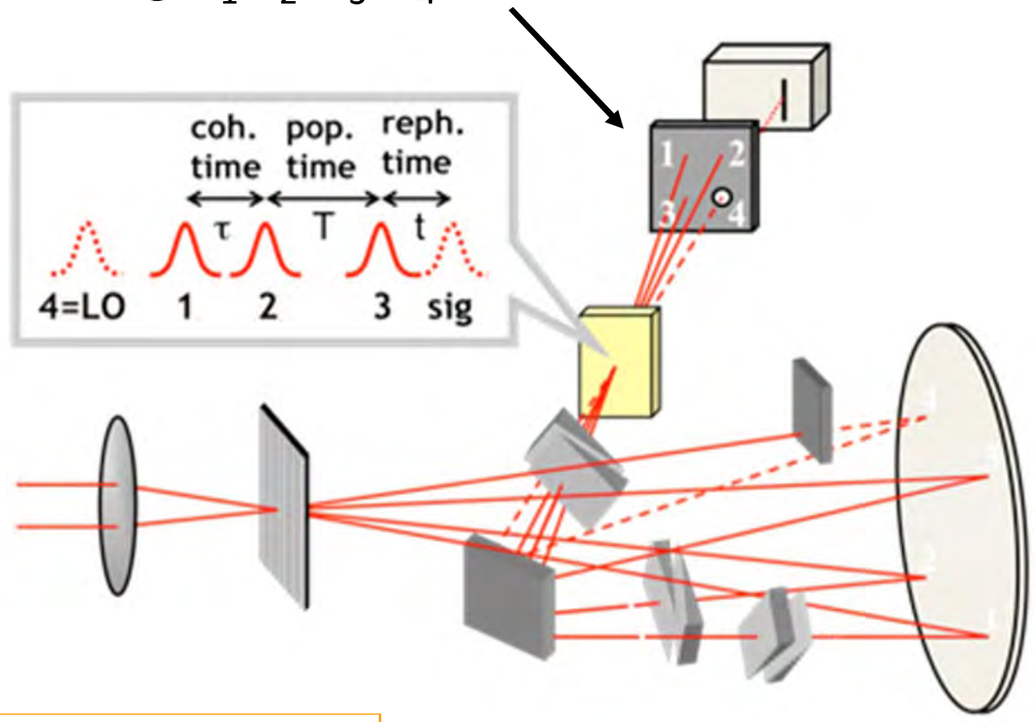


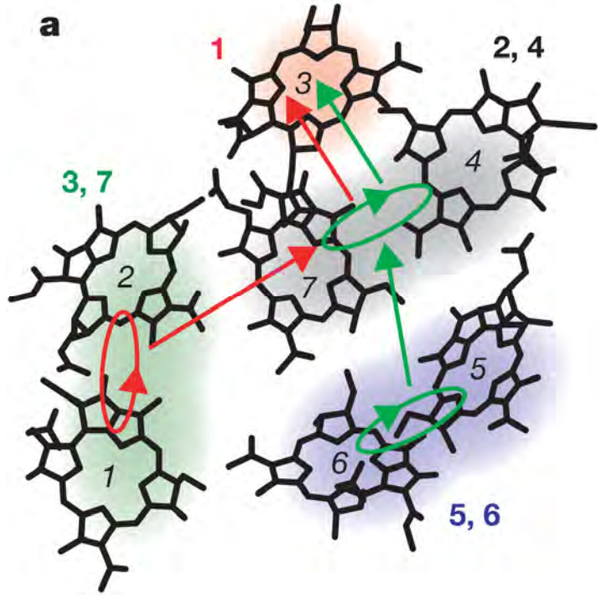


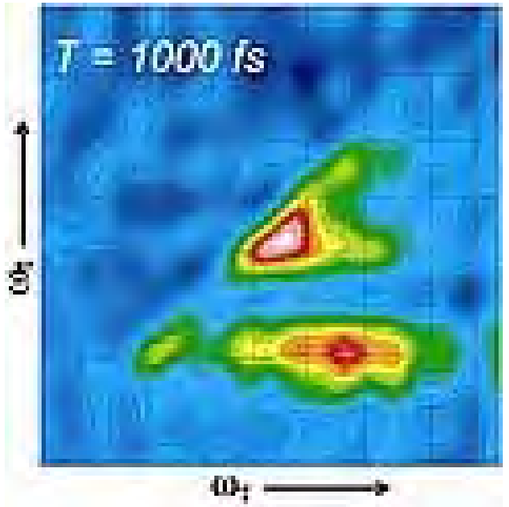
2D spectroscopy – FMO complex, light harvesting

Four-wave mixing

Mask defining **phase matching** conditions
e.g. $k_1-k_2+k_3=k_4$



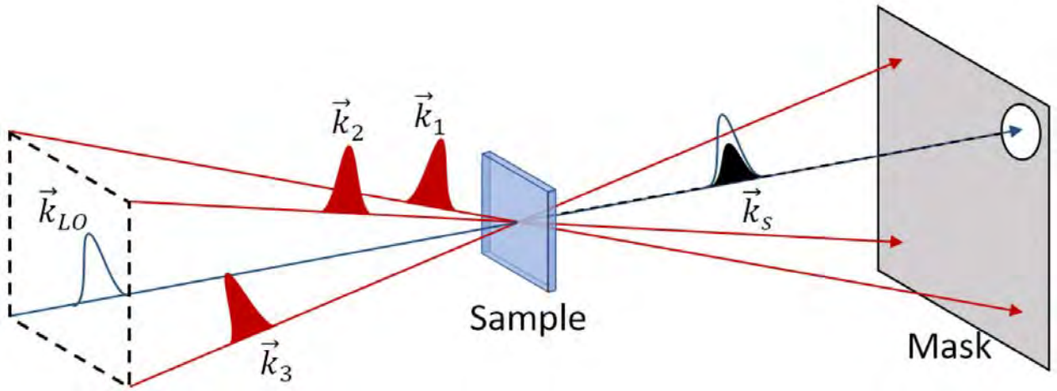




Web page Flemming group, Berkeley

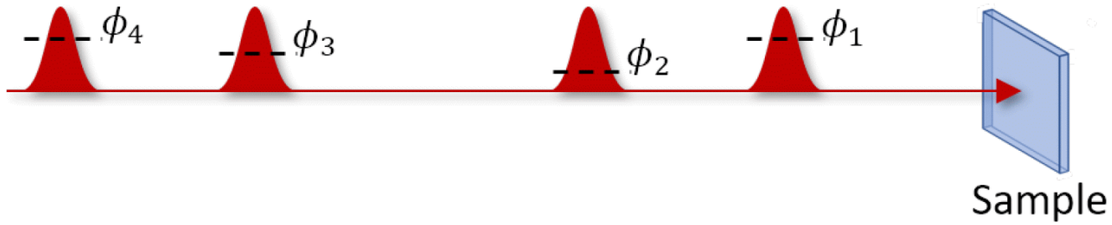
Robin M. Hochstrasser PNAS **04**,14190 (2007)
T. Brixner, et al. Nature **434**, 625 (2005)

2-D spectroscopy at dillute samples: Phase matching – Phase cycling



Four-wave mixing:

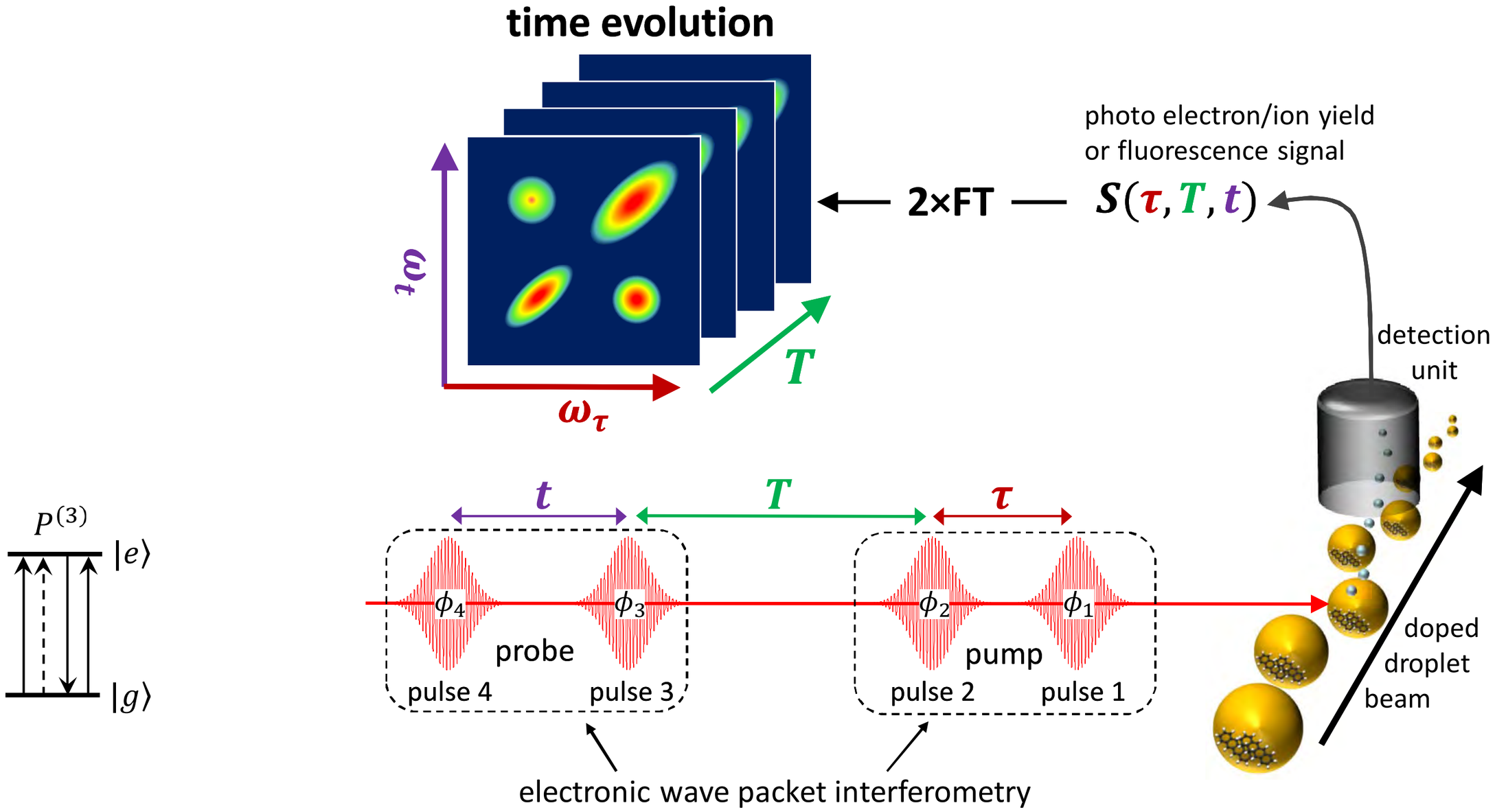
- Advanced geometry of the optical setup
- Macroscopic ensemble effect, no option for small particle numbers
- Low sensitivity, photon detection



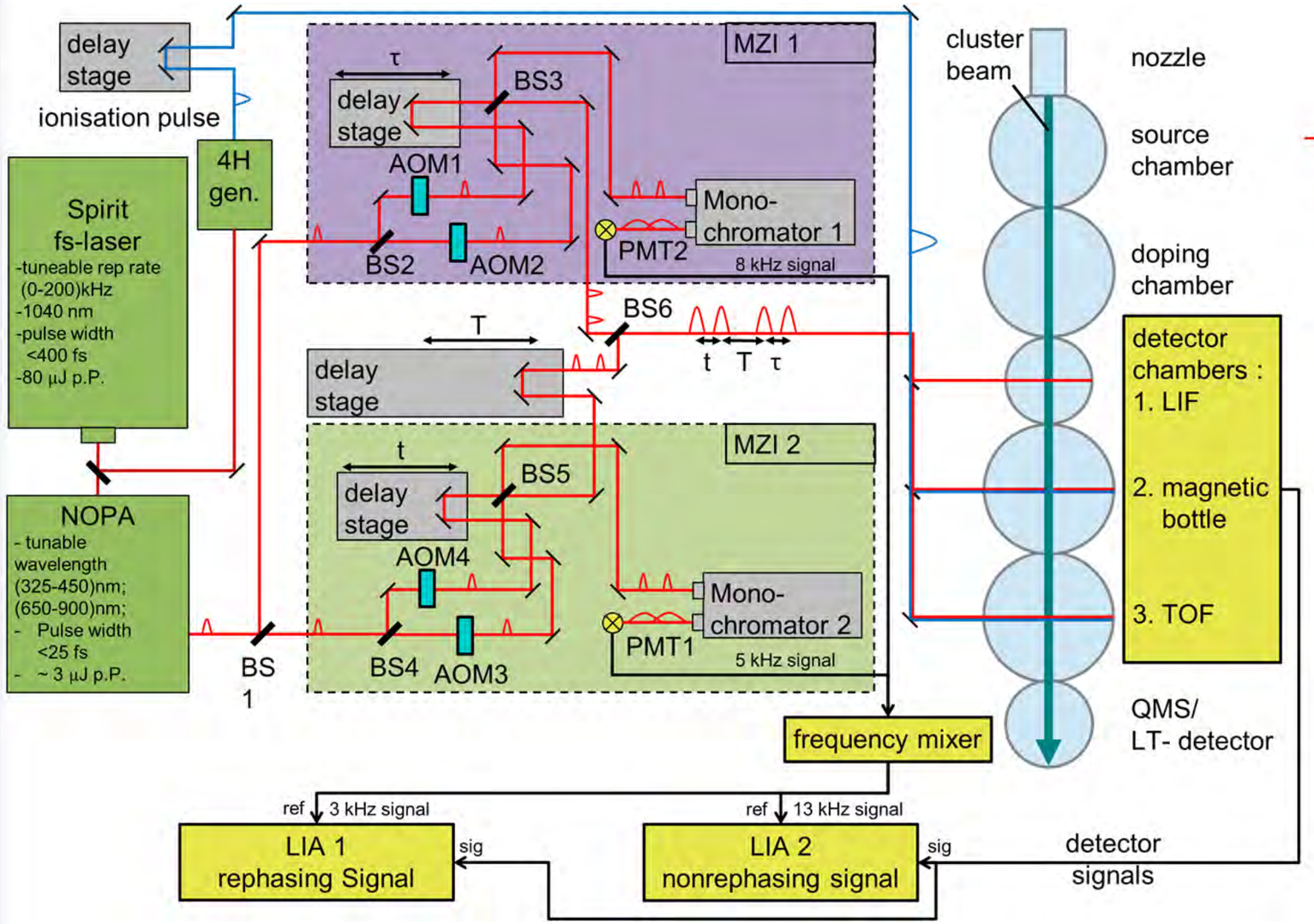
Phase cycling:

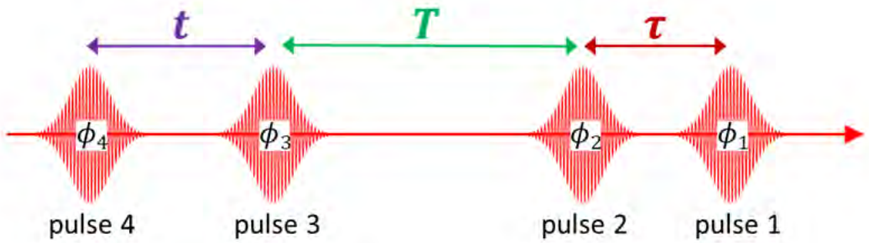
- Detection of population states (charged particles, photons, absorption, …)
- High sensitivity and phase stability
- Collinear optical pulse sequence (still advanced optical setup)

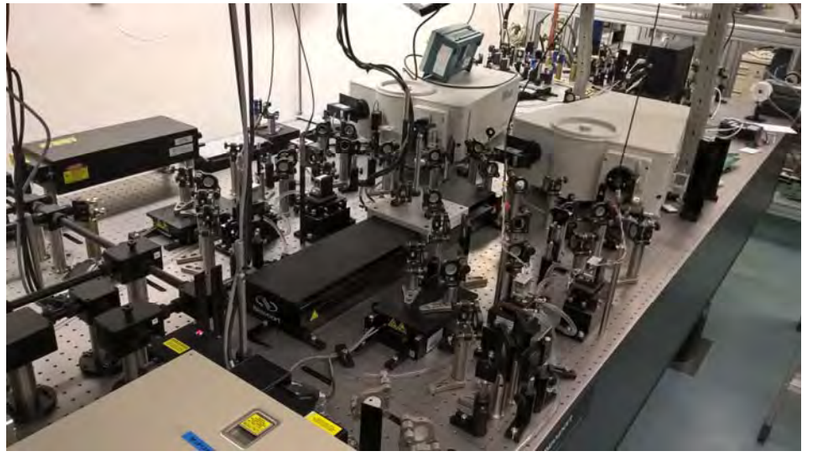
Phase-modulated 2D electronic spectroscopy



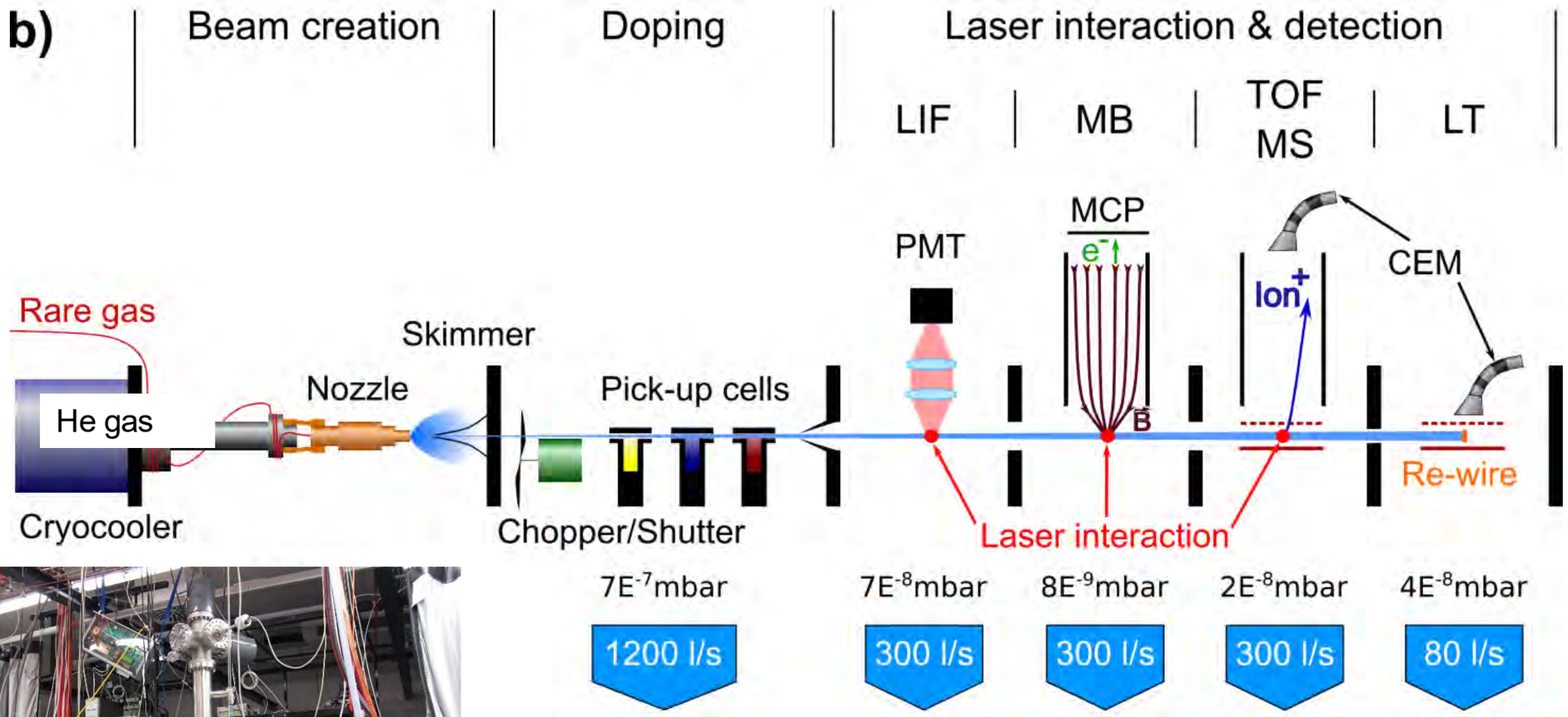
Optical setup

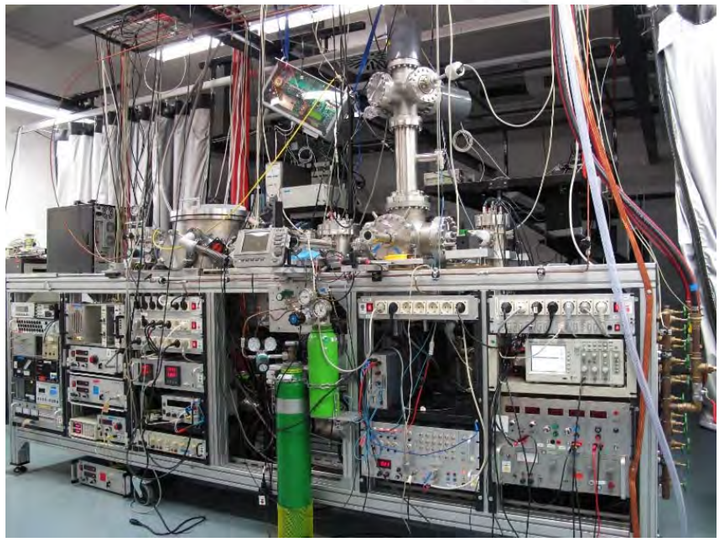






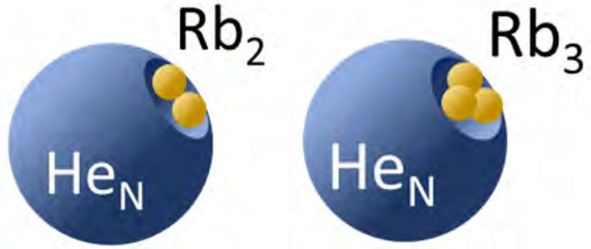
Droplet beam apparatus



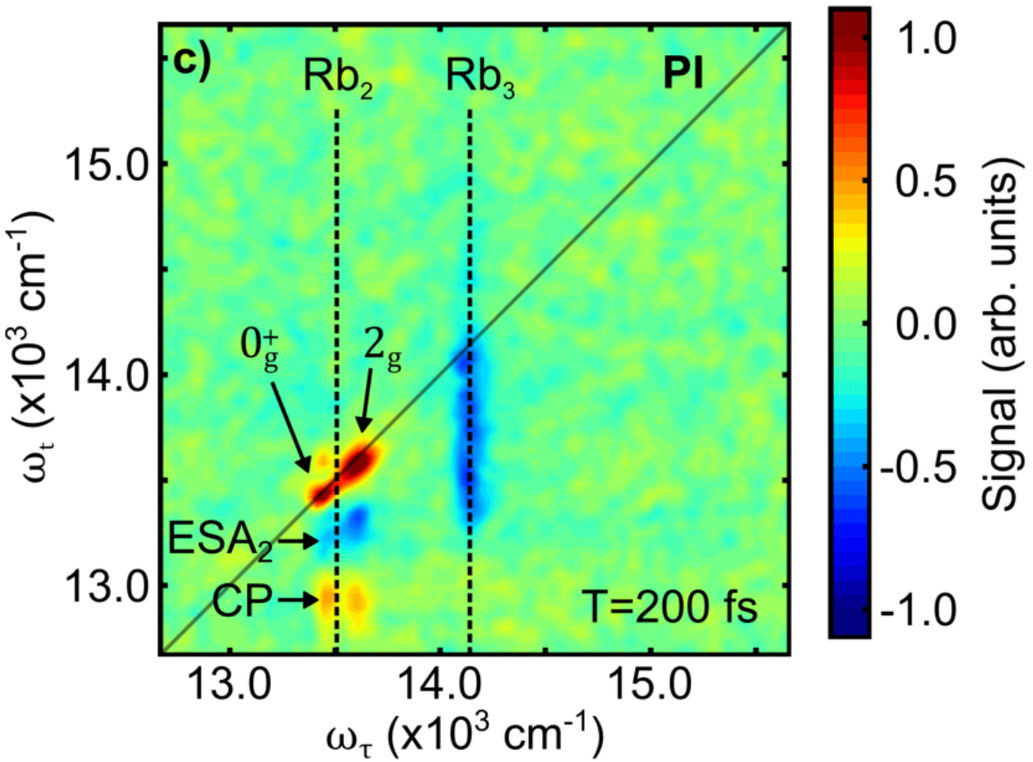


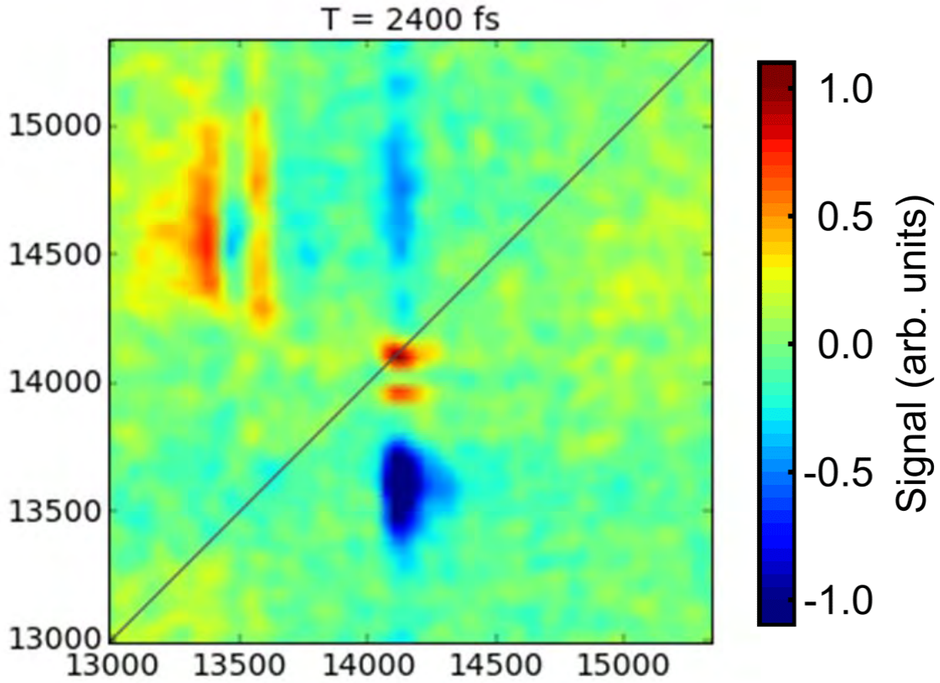
2-dimensional electronic spectroscopy at molecular beam targets

weakly-bound high-spin molecules



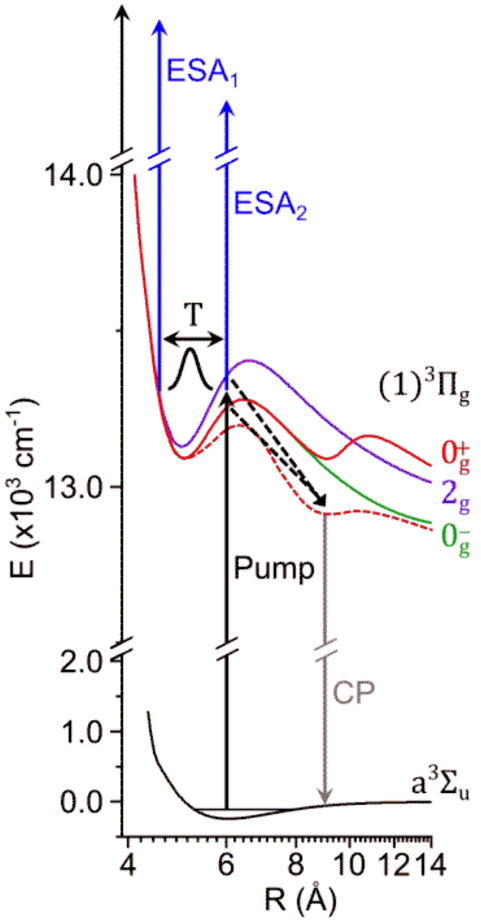
Photoionization, target density: 10^7 cm^{-1}

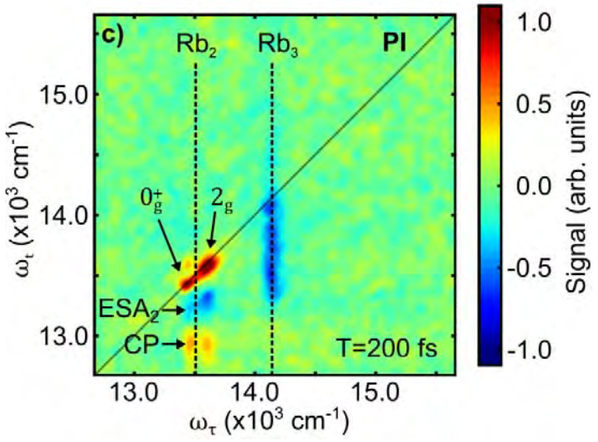




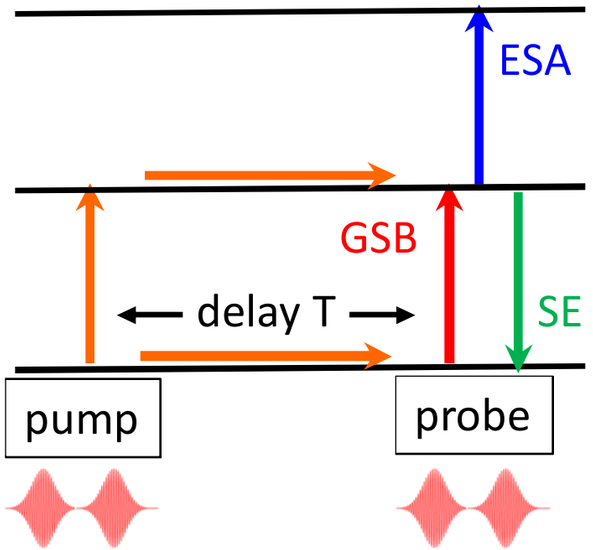
L. Bruder, U. Bangert, M. Binz, D. Uhl, R. Vexiau, N. Bouloufa-Maafa, O. Dulieu, F. Stienkemeier, Nat. Comm. **9**, 4823 (2018)

2-dimensional electronic spectroscopy at molecular beam targets

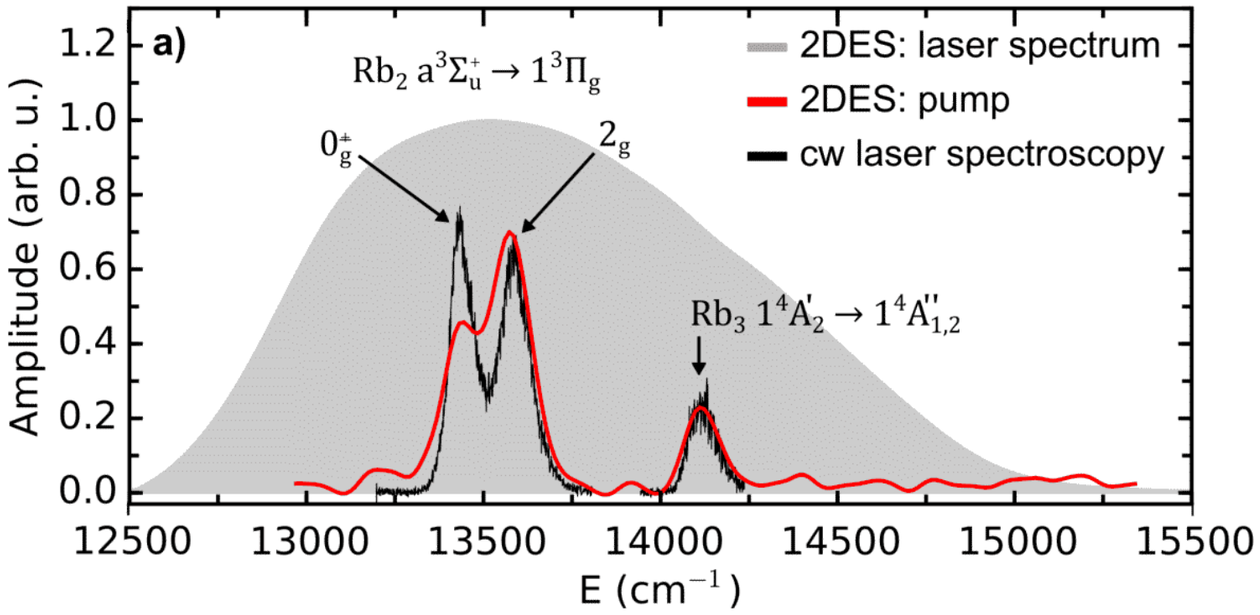




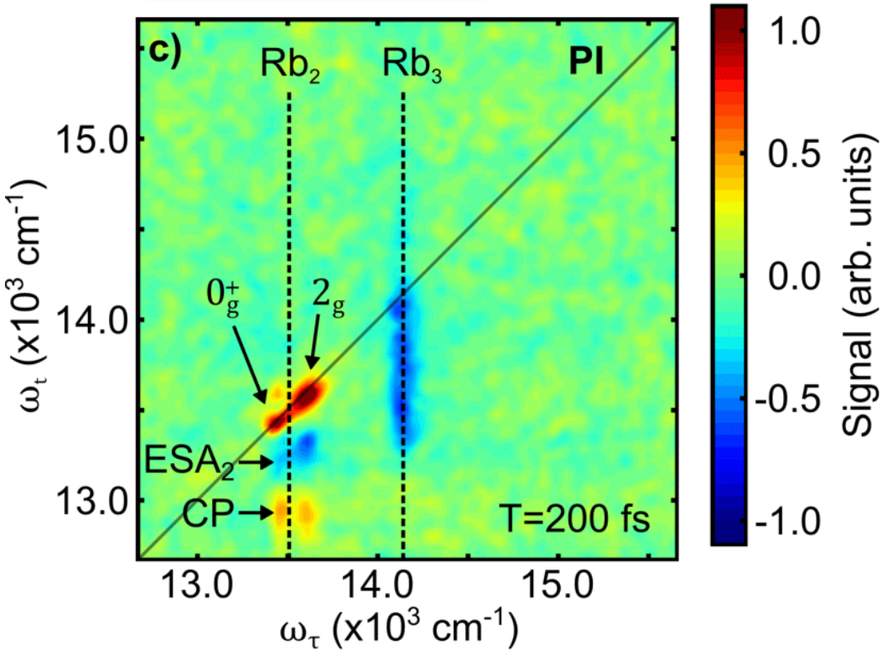
SE	Stimulated emission
ESA	Excited state absorption
GSB	Ground state bleach
CP	Cross peak



Comparison with fluorescence **absorption** spectra

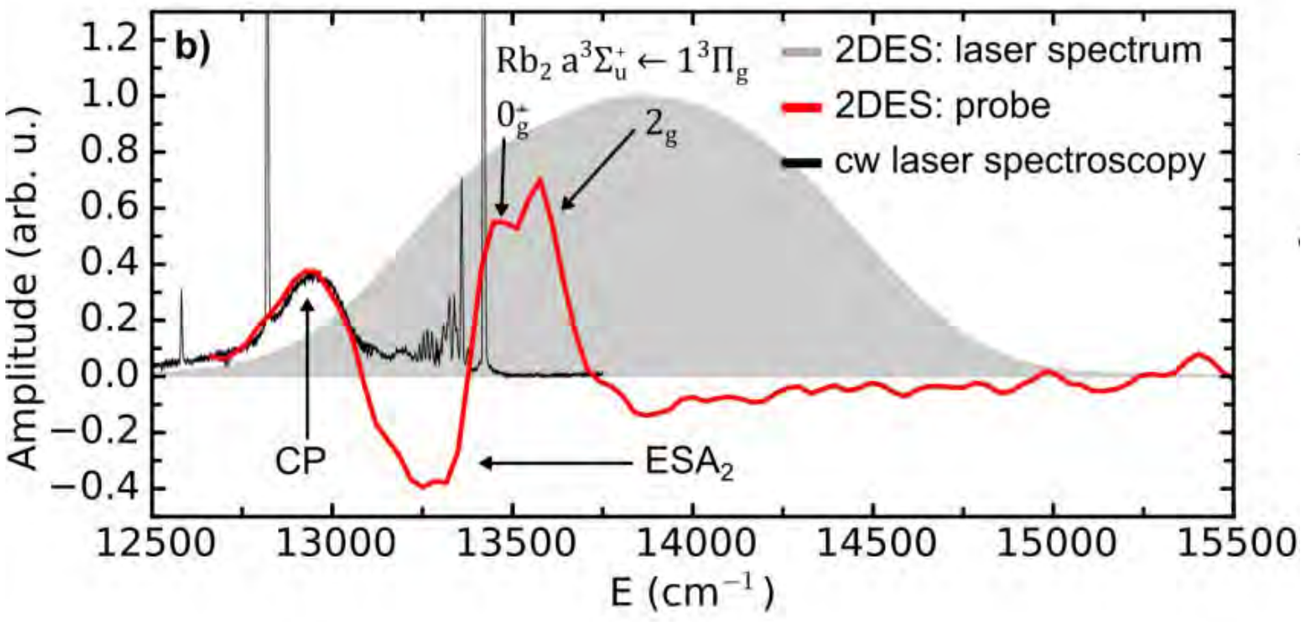


Photoionization

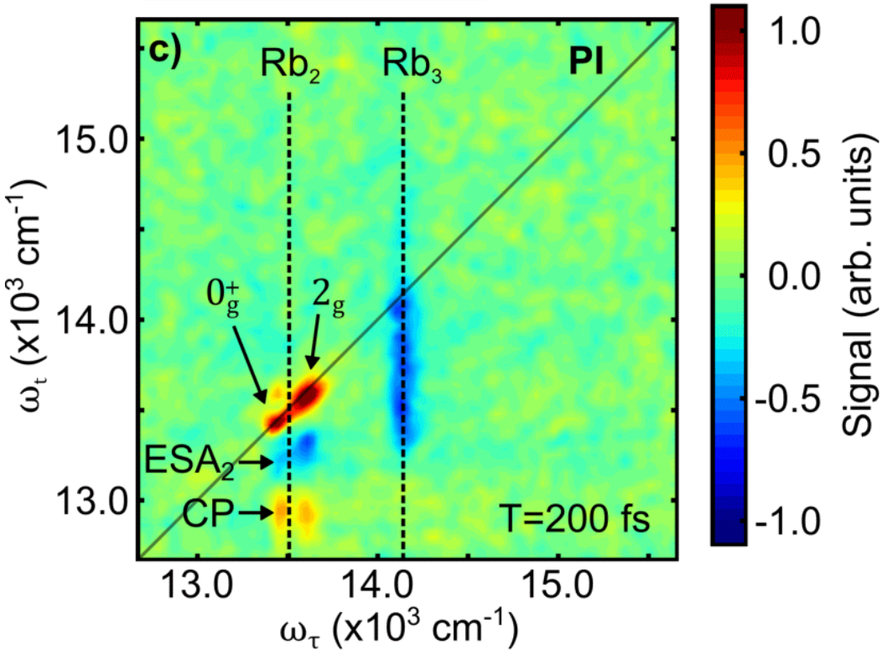


Bruder et al., Nat. Comm. **9**, 4823 (2018)
Allard et al., J. Phys. B: At. Mol. Opt. Phys. **39**, 1169 (2006)
Nagl et al., Phys. Rev. Lett. **100**, (2008)

Comparison with fluorescence **emission** spectra



Photoionization



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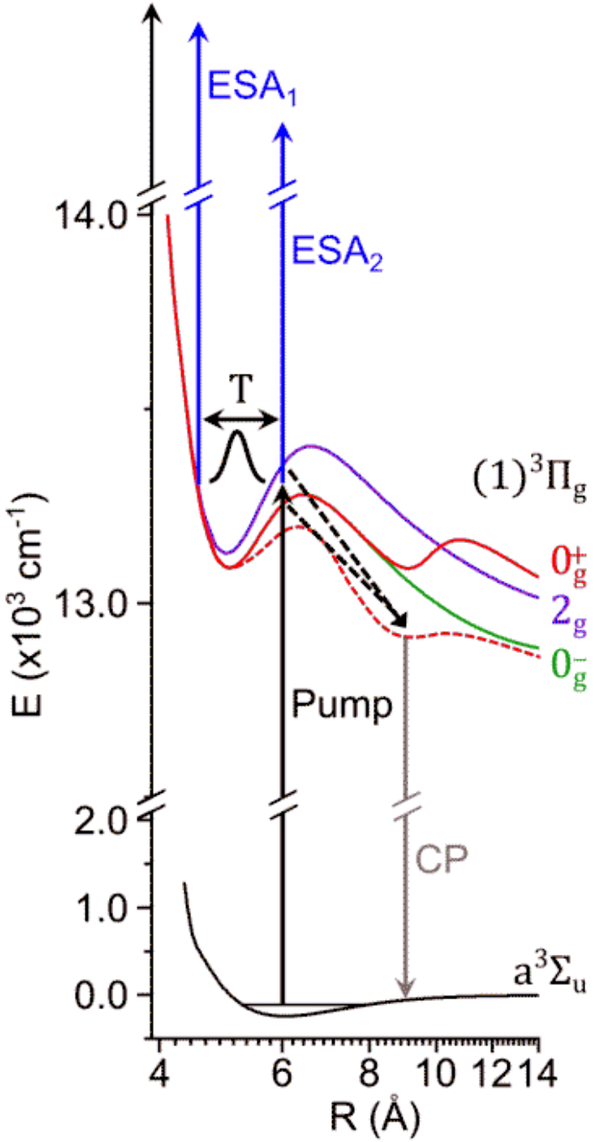
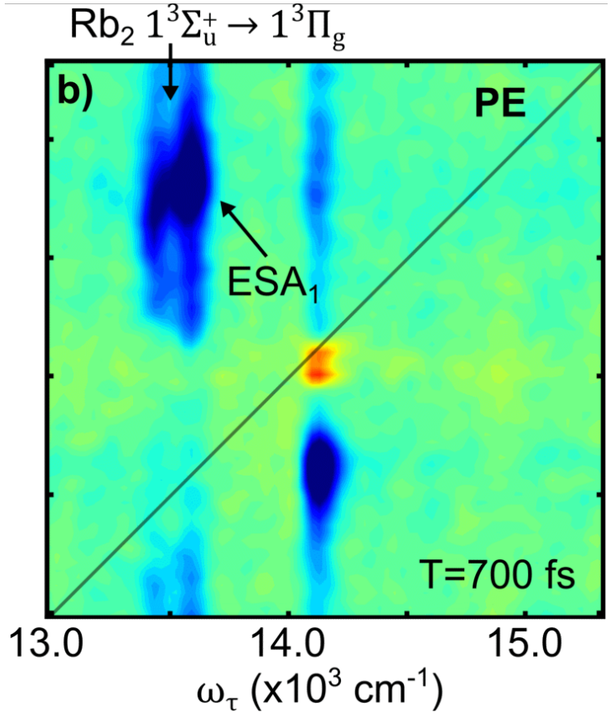
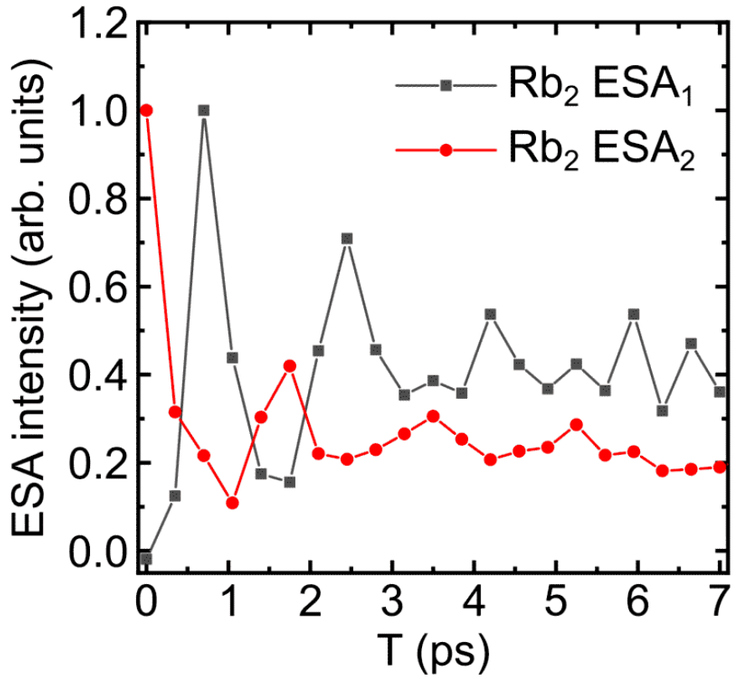
Comparison with fluorescence **emission** spectra



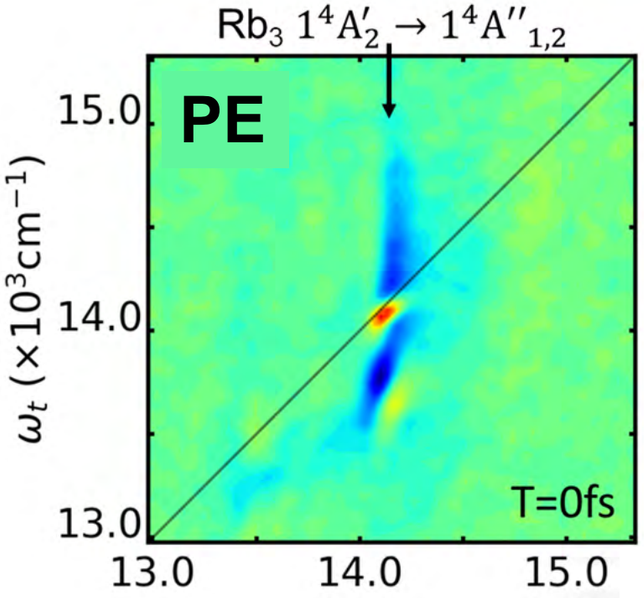
Photoelectrons

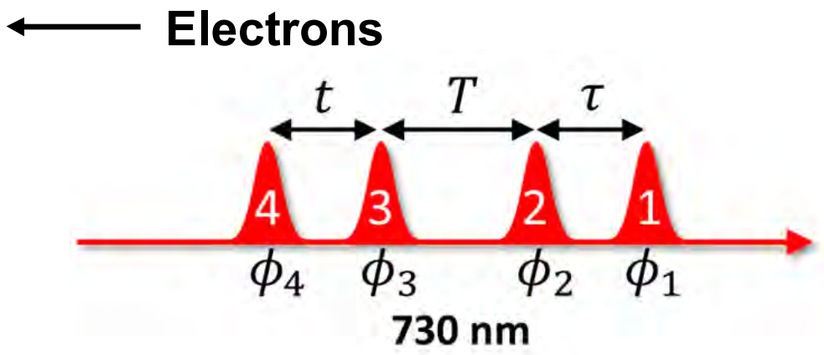


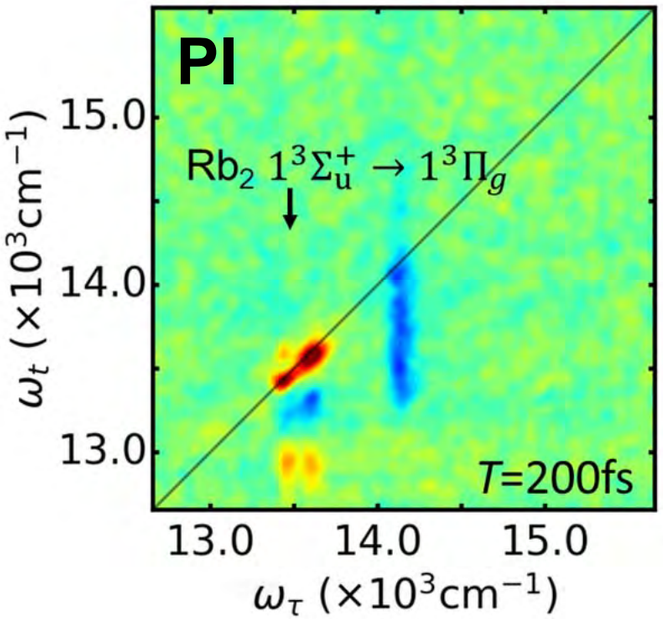


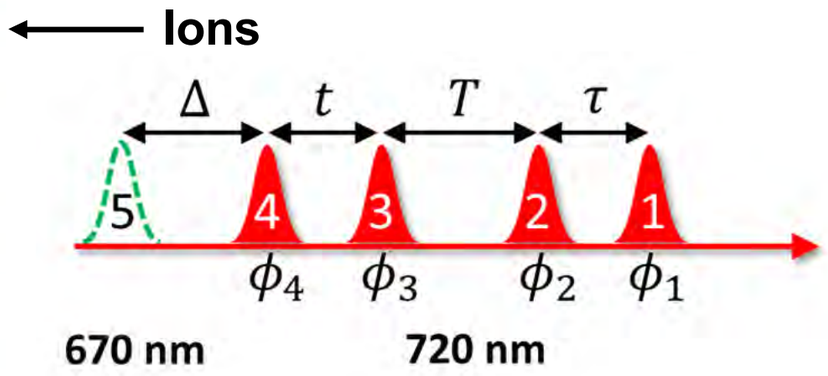
L. Bruder, U. Bangert, M. Binz, D. Uhl, R. Vexiau, N. Bouloufa-Maafa, O. Dulieu, F. Stienkemeier, Nat. Comm. **9**, 4823 (2018)

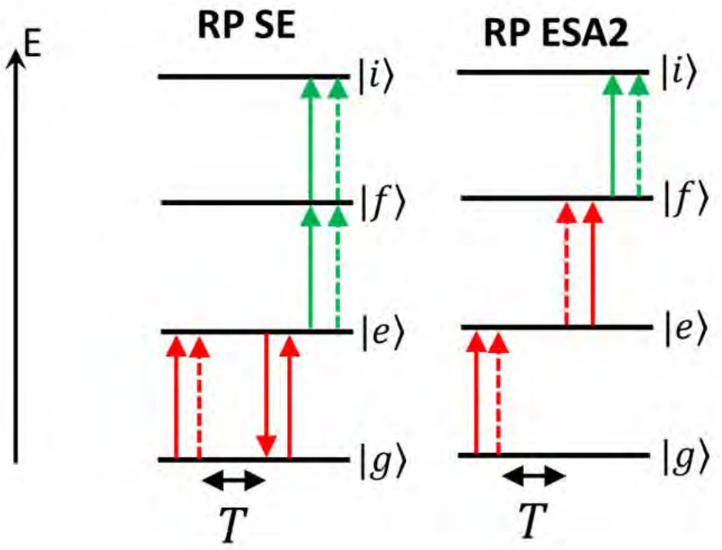
Detection of ions and electrons





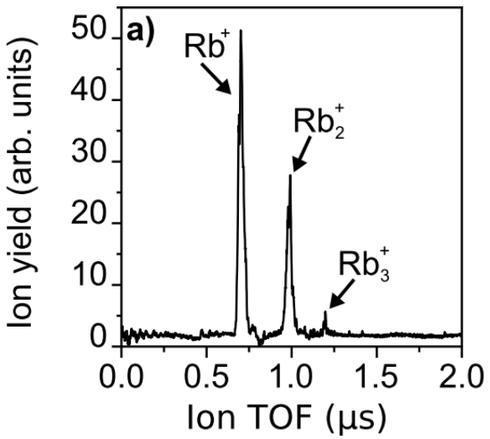






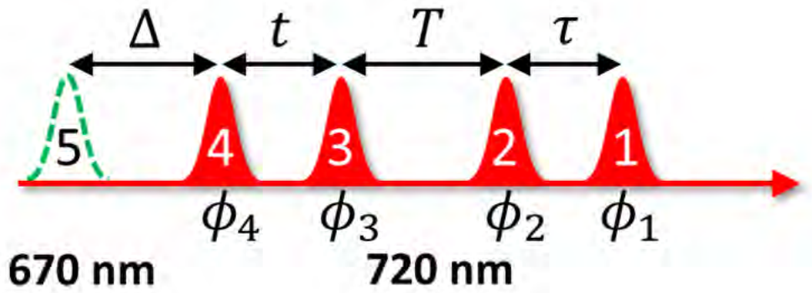
Mass-resolved detection

TOF trace



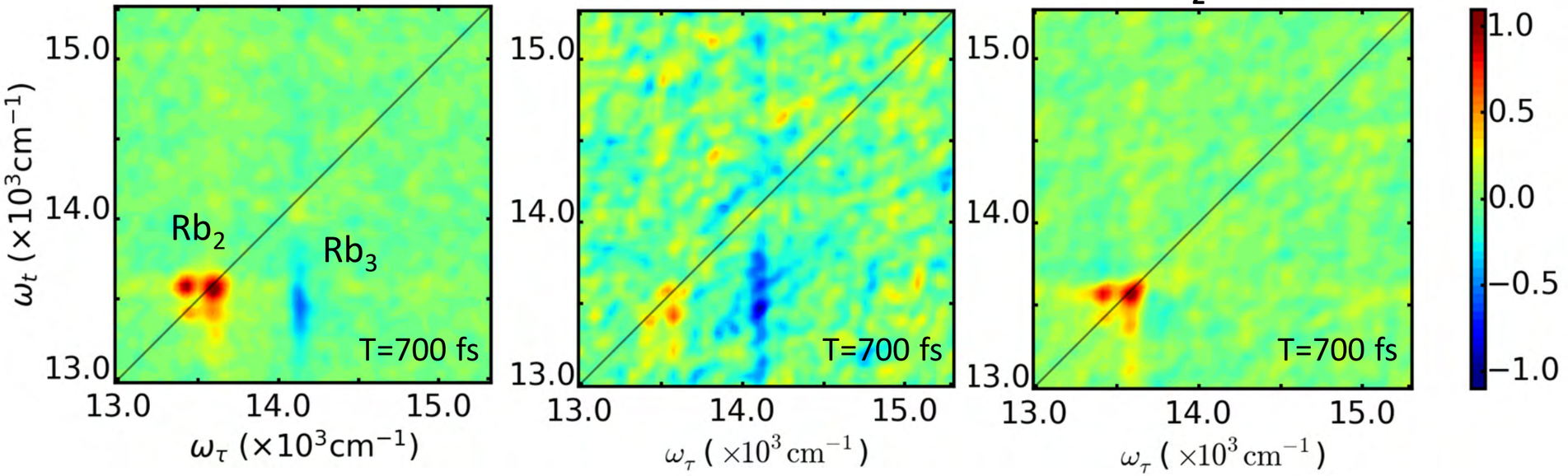
Ion time-of-flight (TOF)
gated with boxcar integrator

Pulse scheme

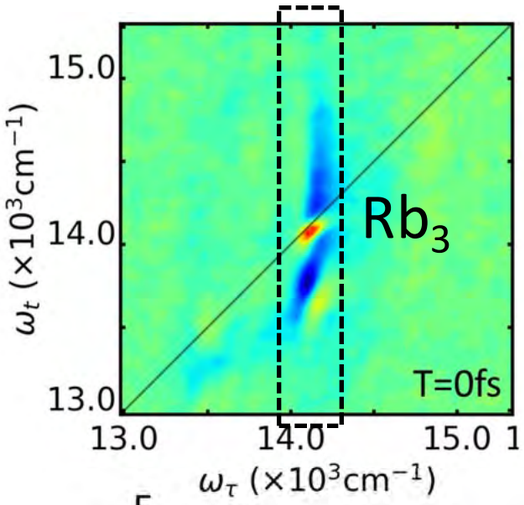


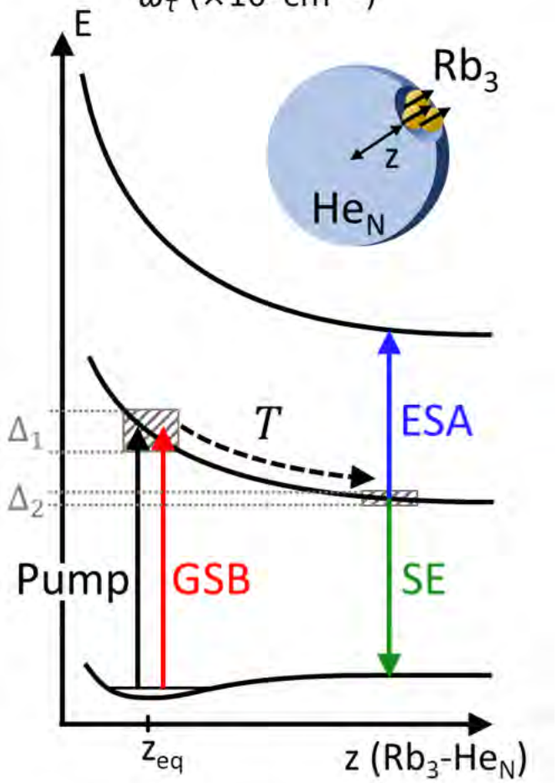
Mass resolution → additional information (e.g. dissociation channels)

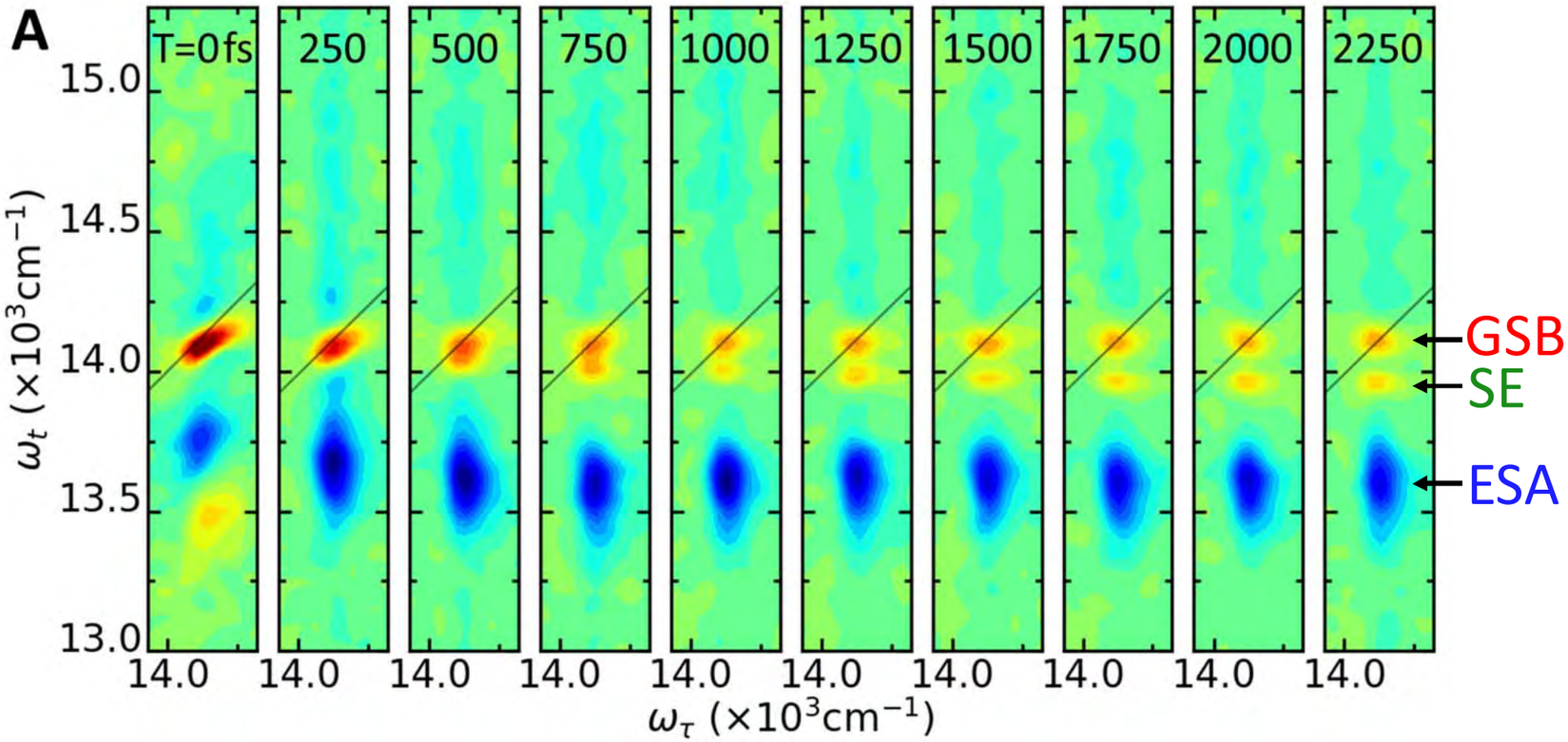
Integral ion yield | **Rb^+ mass** | **Rb_2^+ mass**



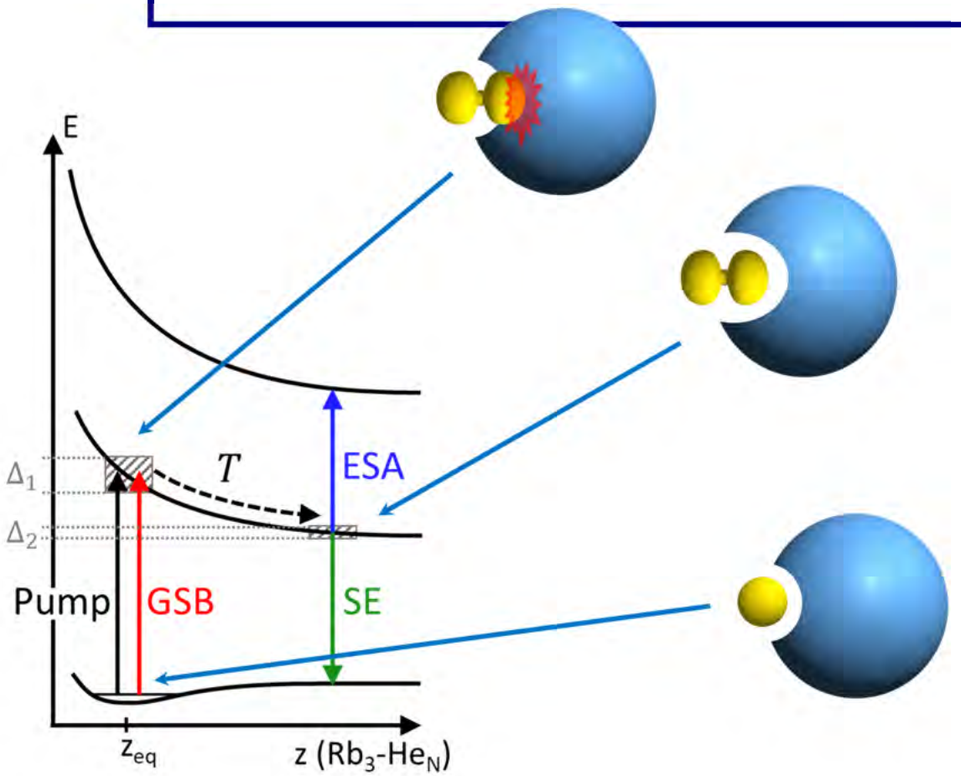
Molecule – matrix interaction

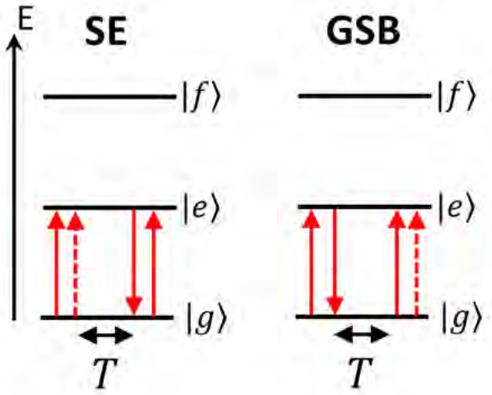


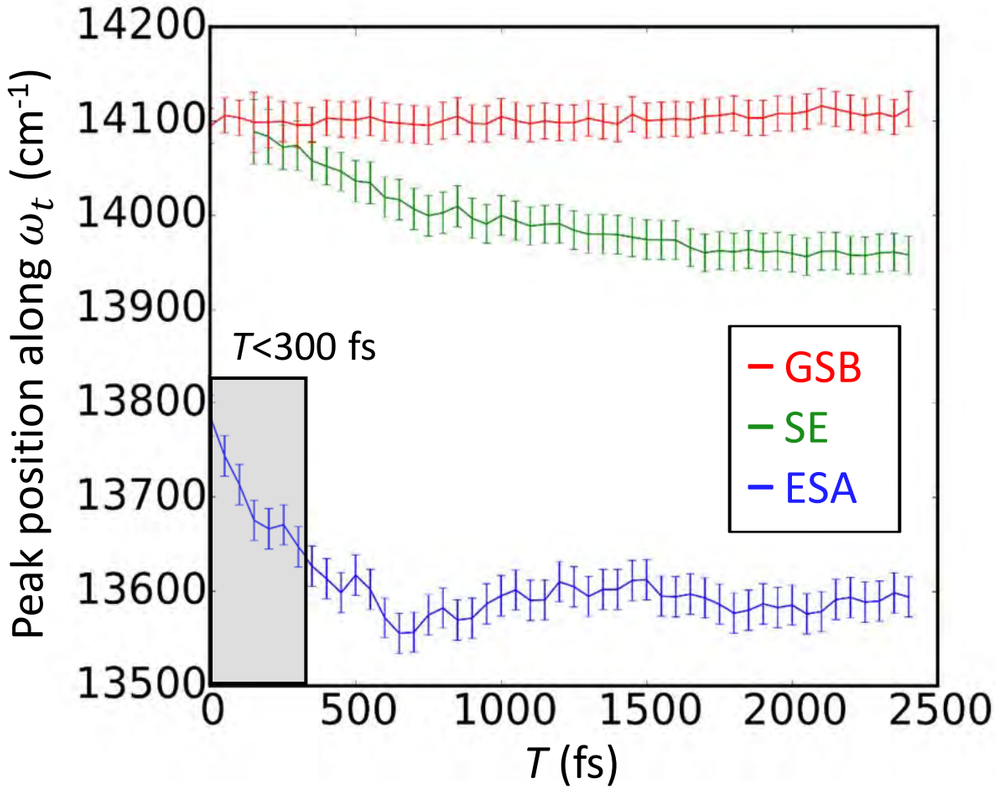


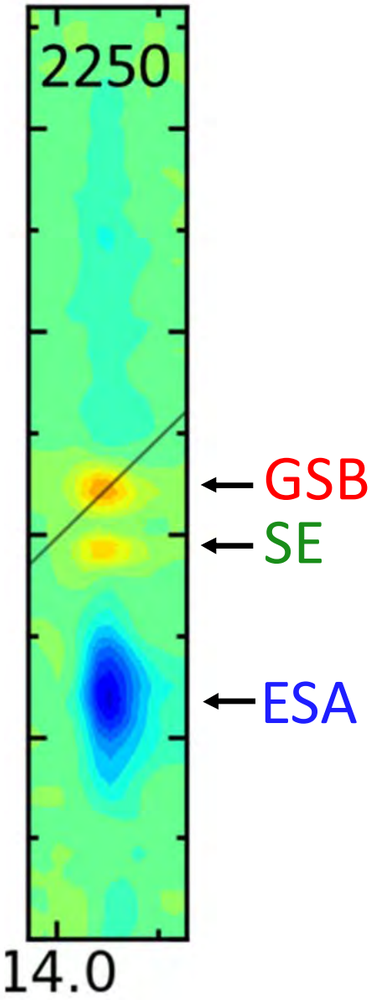


Molecule – matrix interaction









Conclusions

- 2-dimensional electronic spectroscopy of molecular beams at target densities of **$10^7 cm^{-3}$**
  - → Unprecedented spectro-temporal resolution
  - → “Complete” information on energies and the dynamics
- Rb_2: Dynamics of wave packet propagation and relaxation into lower states
- Rb_3: Dynamics of interaction with the helium surface

Outlook

→ Application to organic excitation and **charge transfer complexes** to unravel complex dynamics

→ Phase modulation enables efficient and selective detection of **higher order processes**

- **Many-body effects** of interacting ensembles
- HHG light sources: coherent multidimensional schemes are possible without direct **XUV pulse manipulation**

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More details on phase-modulated coherent spectroscopy

See Posters:

Ulrich Bangert
Two-dimensional electronic spectroscopy of Rb_3 in helium nanodroplet isolation

Daniel Uhl
Photoelectron two-dimensional coherent spectroscopy

Marcel Binz
Peak shape modulations in two-dimensional electronic spectroscopy caused by intense laser pulses

Friedemann Landmesser
Two-dimensional electronic spectroscopy of isolated, cold molecular nanosystems

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L. Bruder, et al., Phys. Chem. Chem. Phys. **21**, 2276 (2019)

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