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Title: Frontiers in chemical physics

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Intended for: Panel discussion at my interview at the Center for Combustion Research
at Sandia

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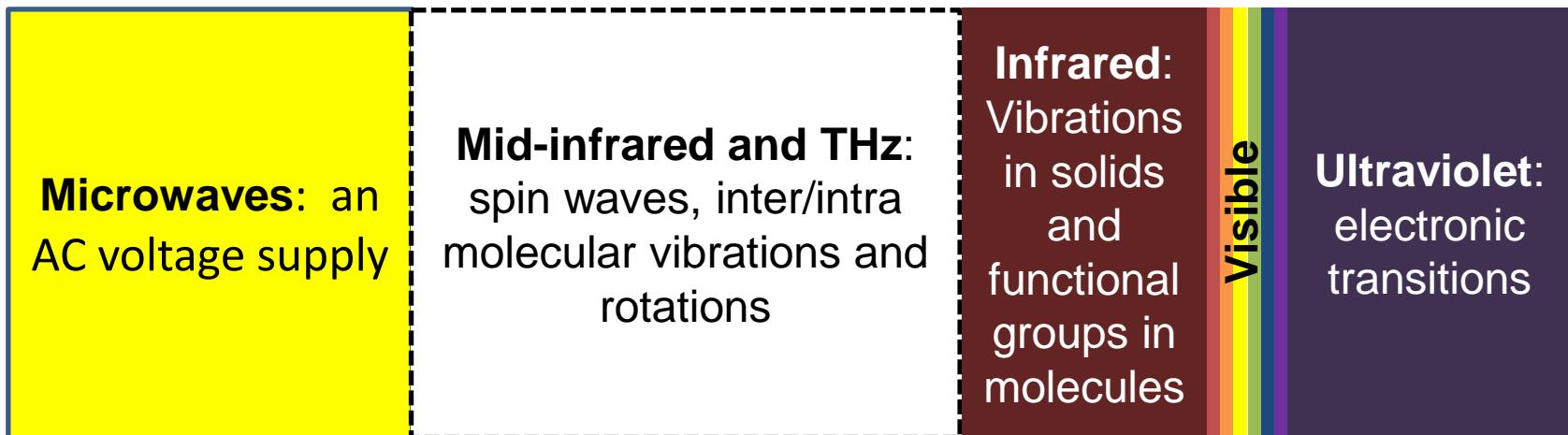
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Time resolving chemistry with ultrashort pulses in the 0.1-40 THz spectral range

Electronics: field induced effects

Electronics and Optics!

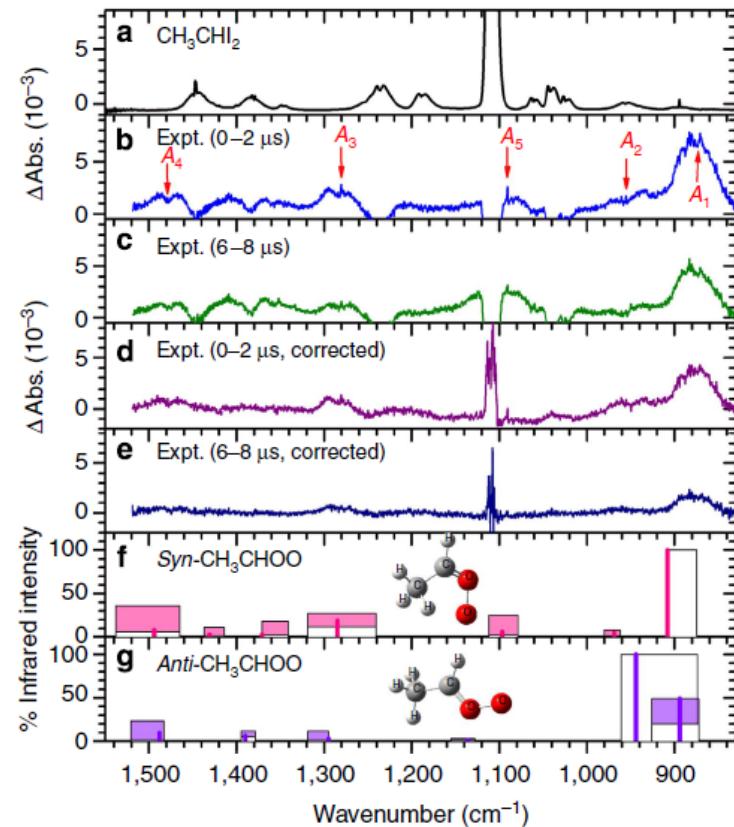
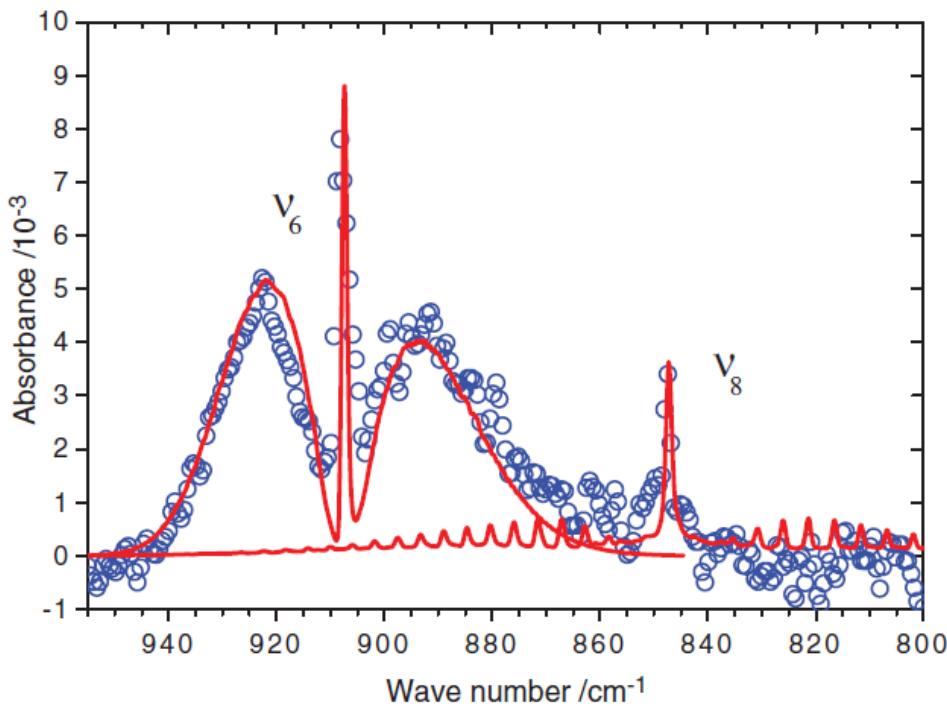
Optics: exciting transitions with light



Wavelength

Pulses in the mid-infrared (IR) to THz can be a probe of chemical dynamics.

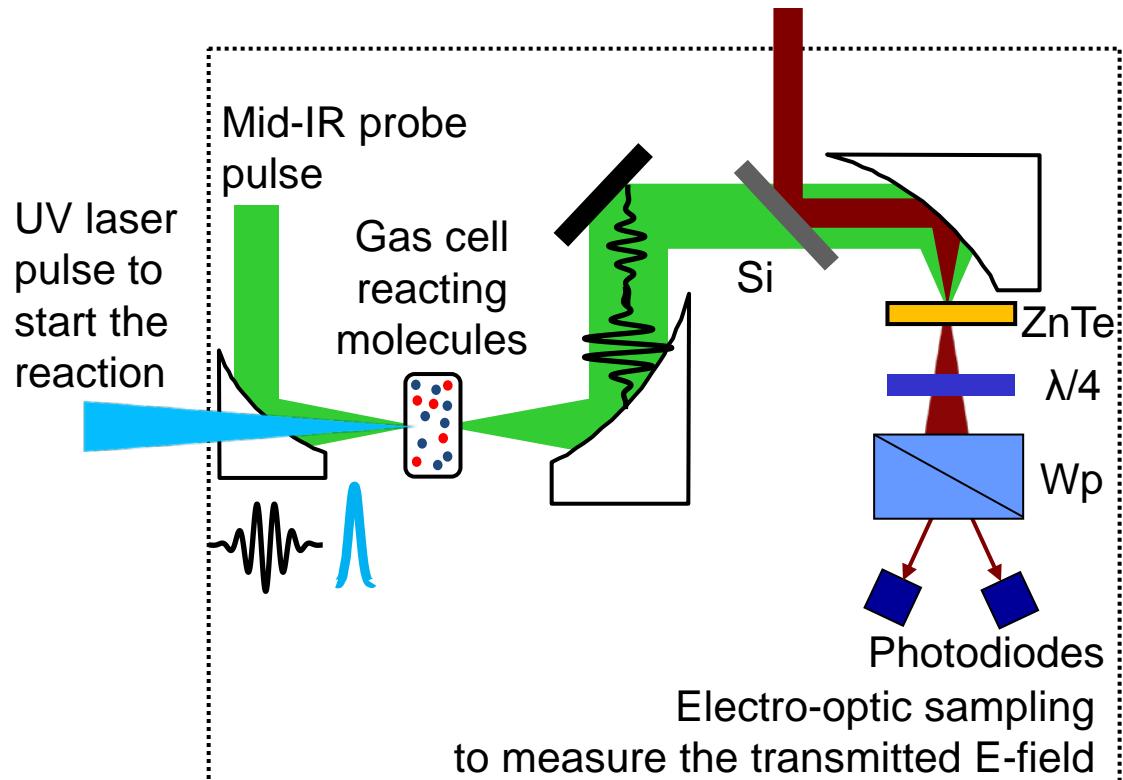
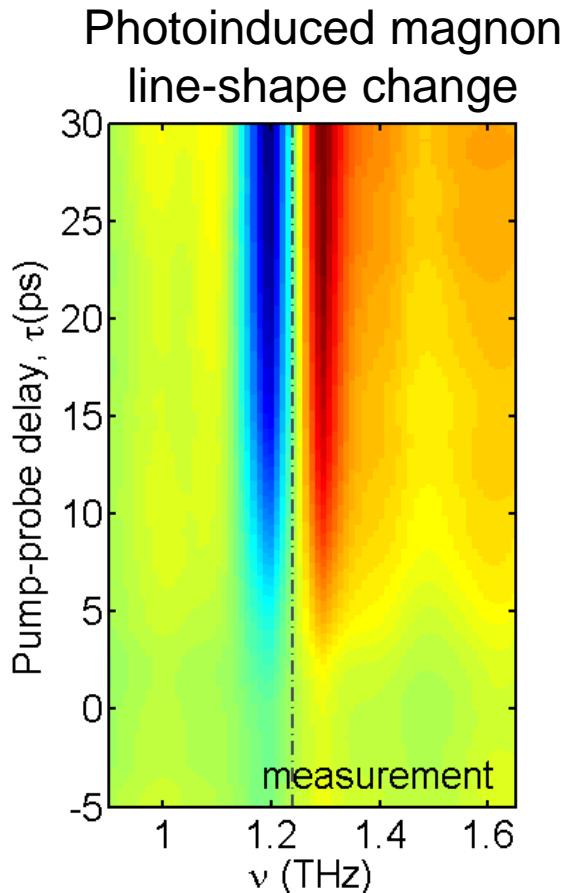
Example: Mid-infrared absorption spectrum of the intermediate state CH_2OO



Su et. al. *Science*, **340**, 841 (2014), and Lin et. al. *Nat. Comm*, **6**, 2012 (2015)

Reaction intermediate states can have distinct mid-IR features. With pulses, we can track reactions dynamics by monitoring these features, as did with magnons.

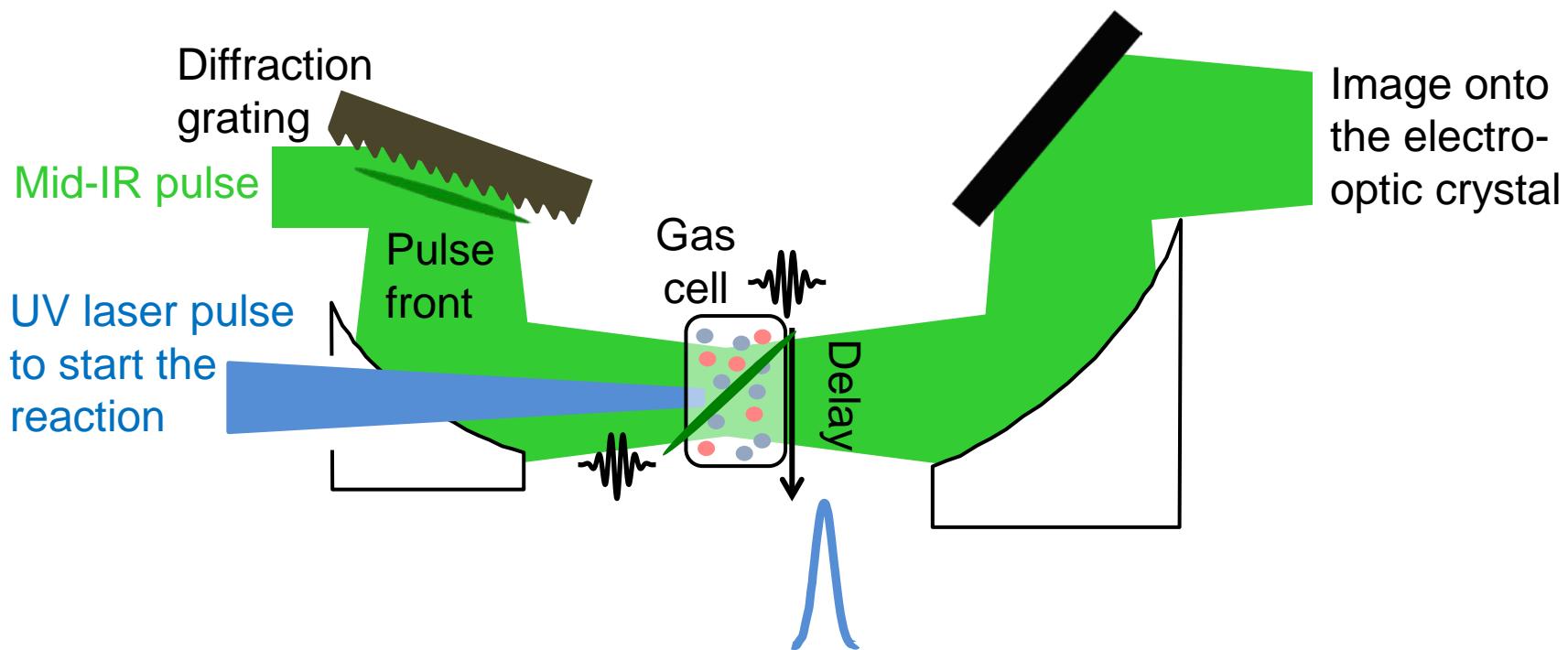
Tracking reaction dynamics through changes in the spectra.



P. Bowlan, et. al., arXiv:1602.03872

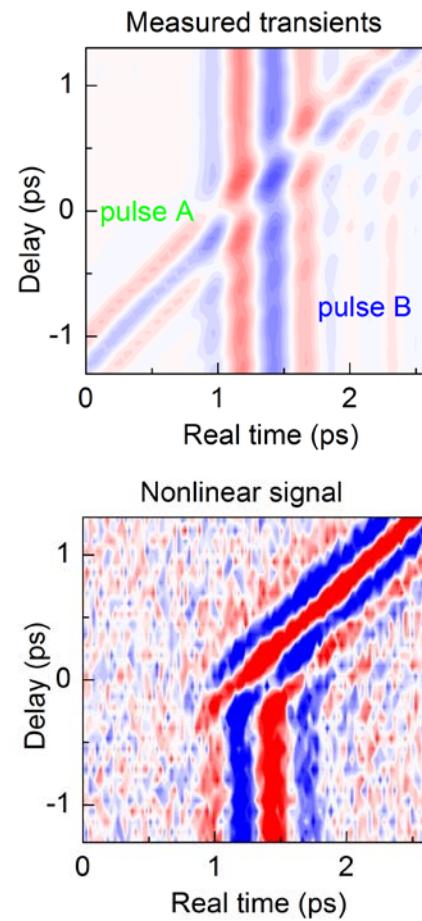
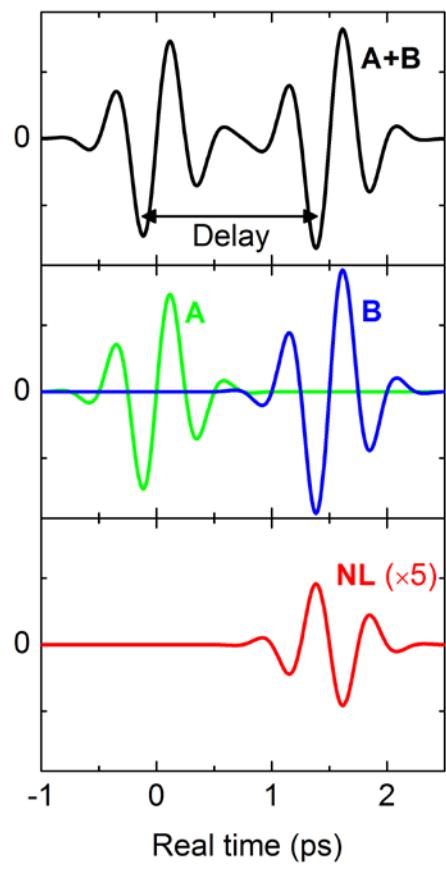
Pump-induced changes in the mid-IR show how the molecules are changing.

Single-shot measurement of the mid-IR absorption dynamics



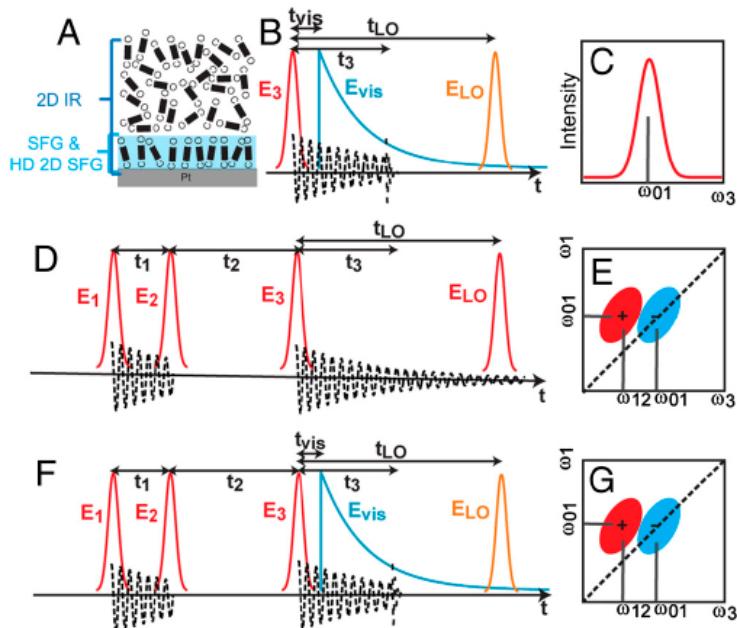
Mapping the pump-probe delay into positon, allows for a faster single-shot measurement of absorption versus delay, spanning a range of up to 100 ps.

Applying 2D coherent mid-IR spectroscopy to learn more about transition states.



Measuring the absorption spectrum in two –dimensions reveals more information about transition states, and their life and coherence times

Time resolving chemical reactions at a catalysis using mid-IR and THz pulses.



Zanni et. al. PNAS, **108**, 52 (2011)

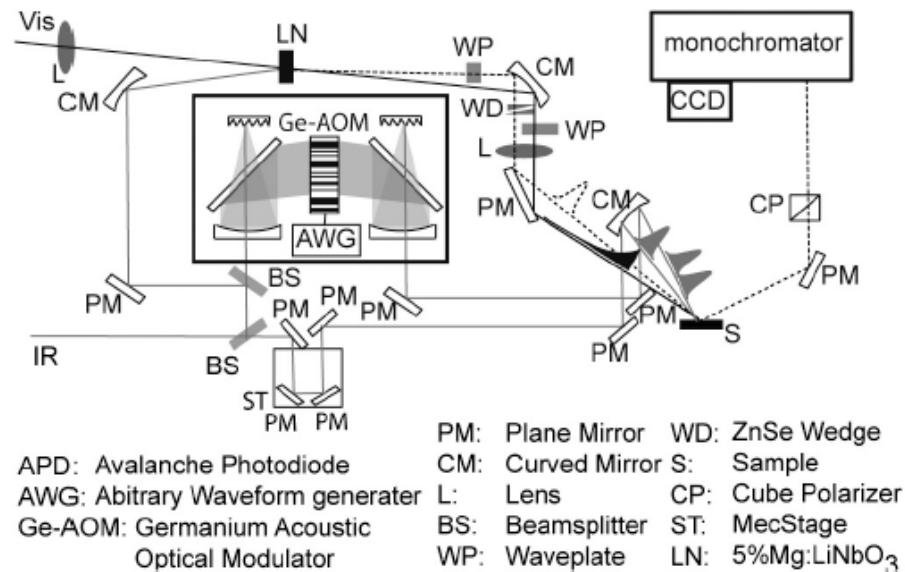
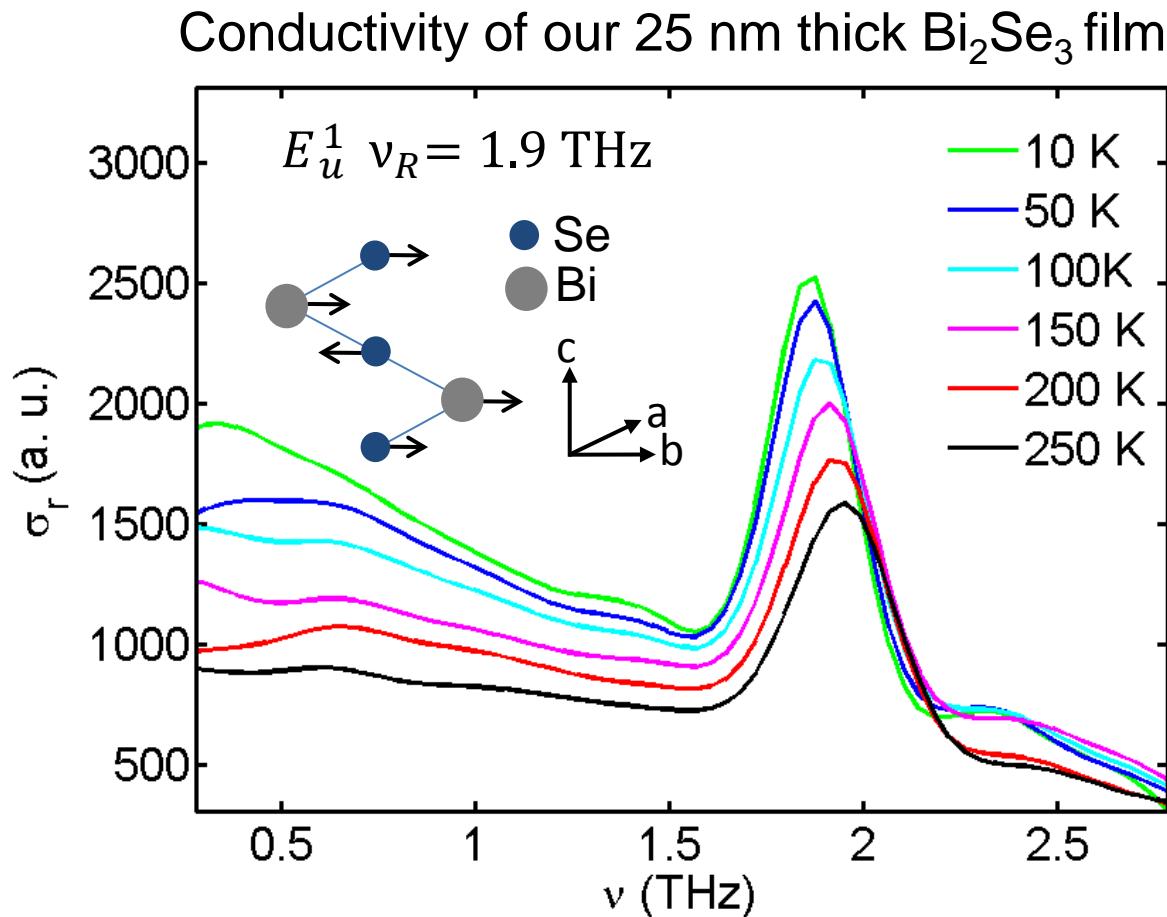


Fig. S1. Schematic illustration of the HD 2D SFG spectrometer.

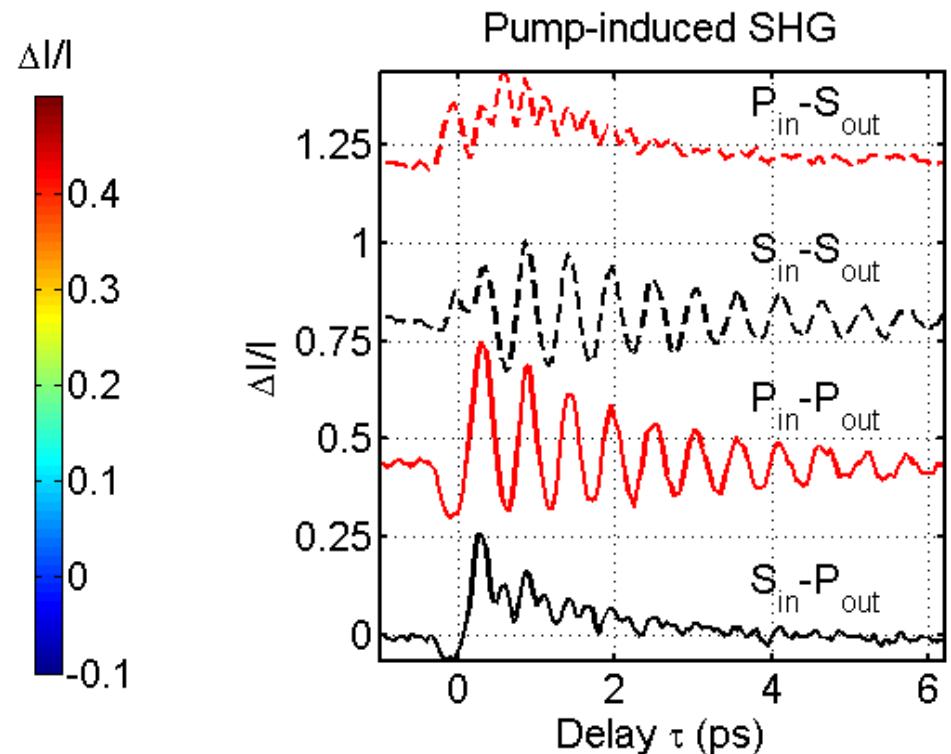
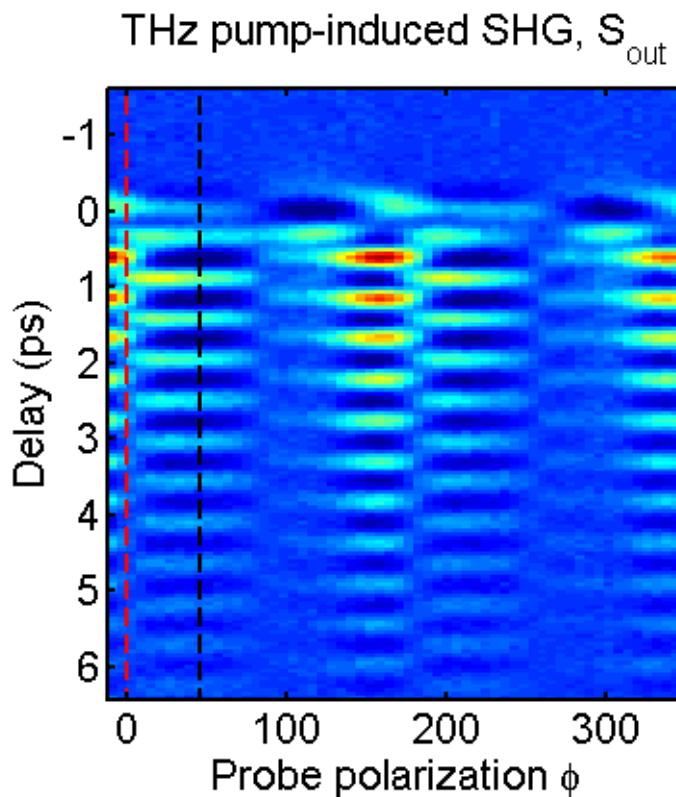
Using two excitation pulses, and sum frequency generation, it is possible to make surface sensitive 2D measurements. Getting the phase information is difficult.

Studying topological insulators requires a surface sensitive probe.



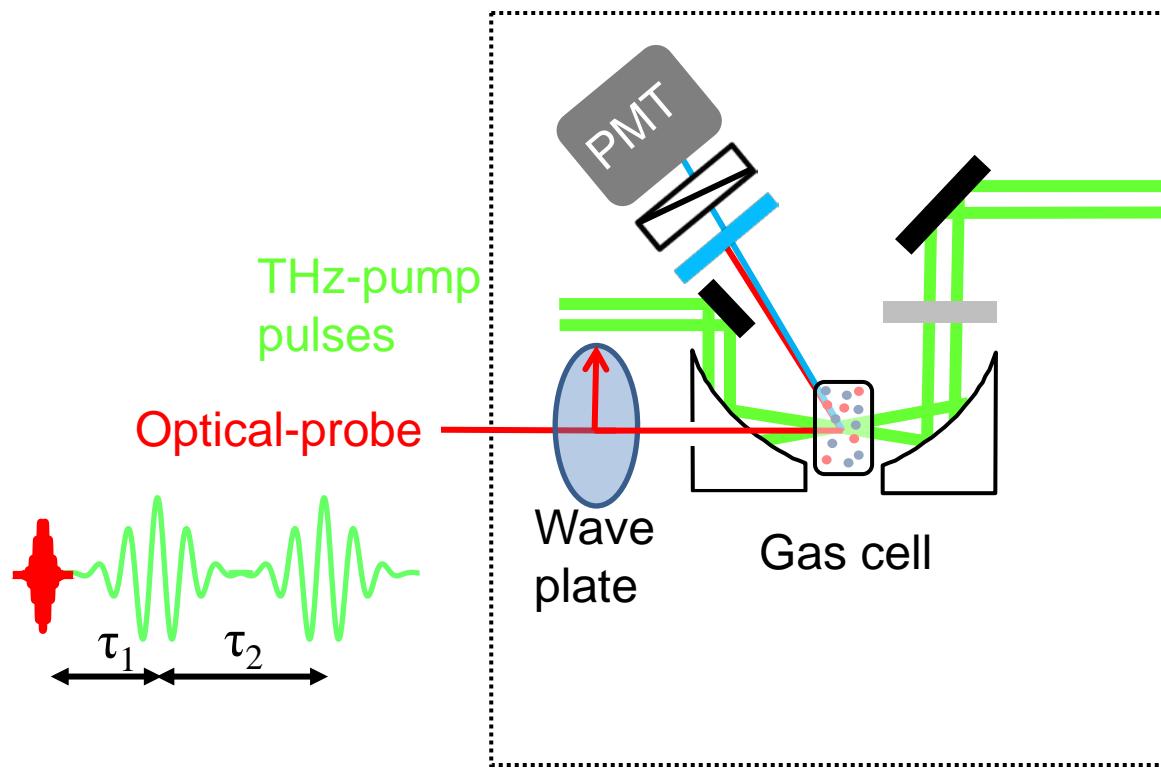
Besides the Drude response, there is also an IR active phonon at ~ 2 THz.

Nonlinear phonon dynamics in Bi_2Se_3



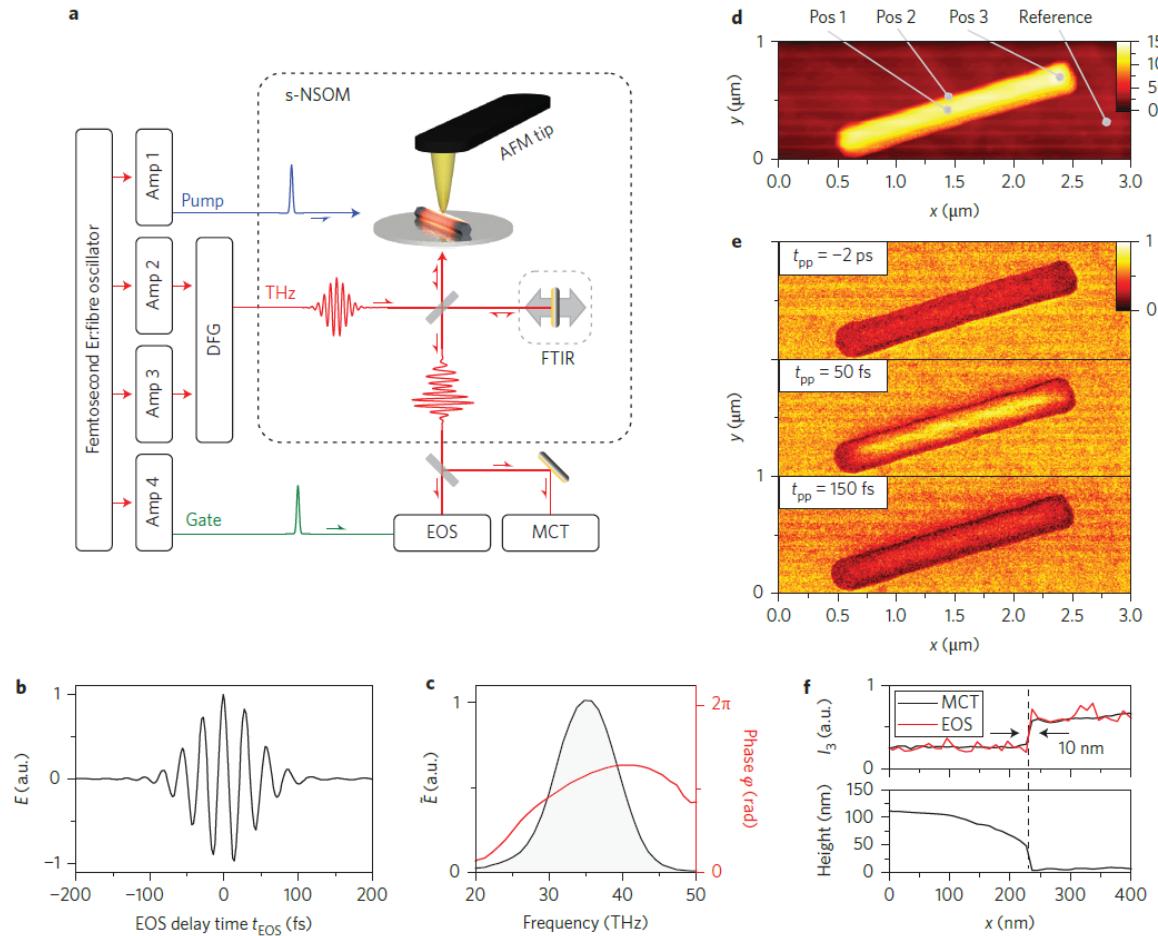
THz excitation results in oscillations of the SHG which follow the phonon frequency and also its second harmonic.

THz-pump, SHG-probe as a surface sensitive coherent 2D spectroscopy



Adding a second pulse to this spectrum could give a two dimensional, spectrum from the surface, for studying catalysis.

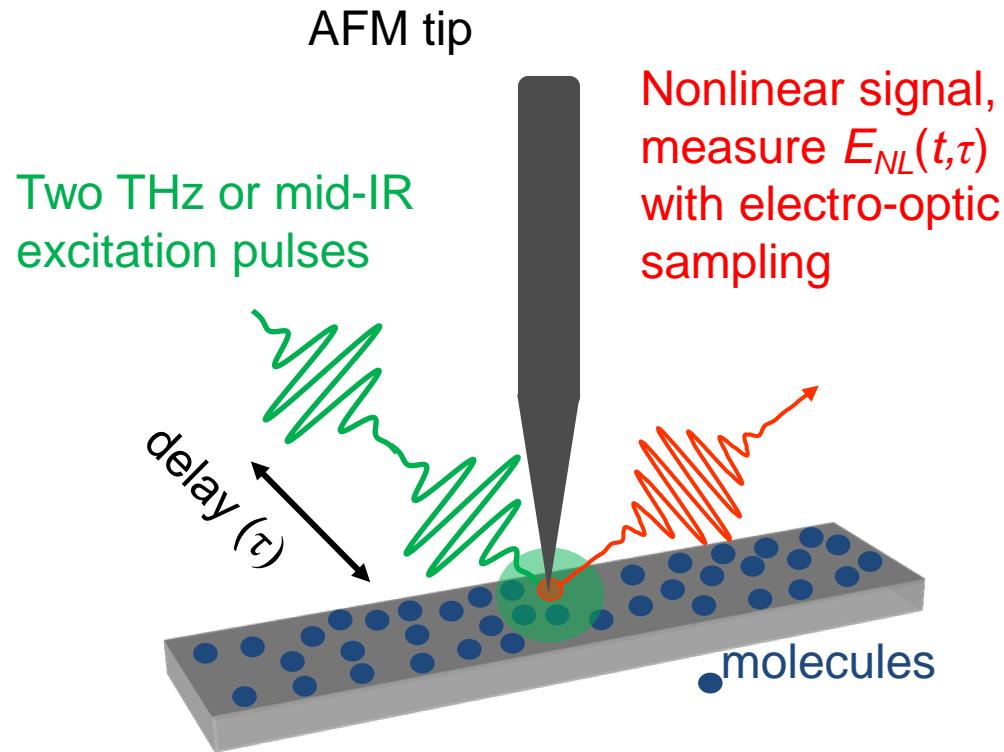
Nanometer and femtosecond spatiotemporal resolution mid-IR spectroscopy



Eisele et. al. Nat. Photon. 5, 841 (2014) and H

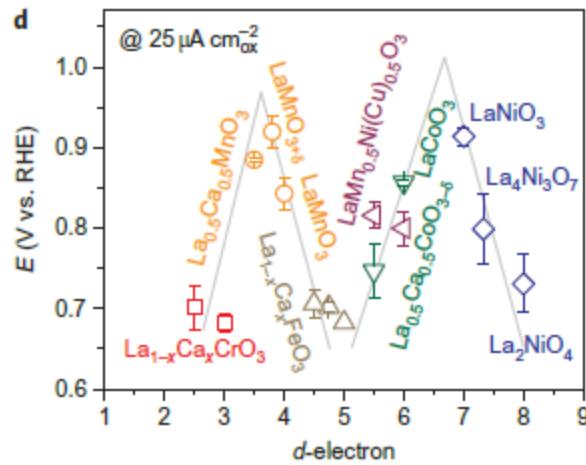
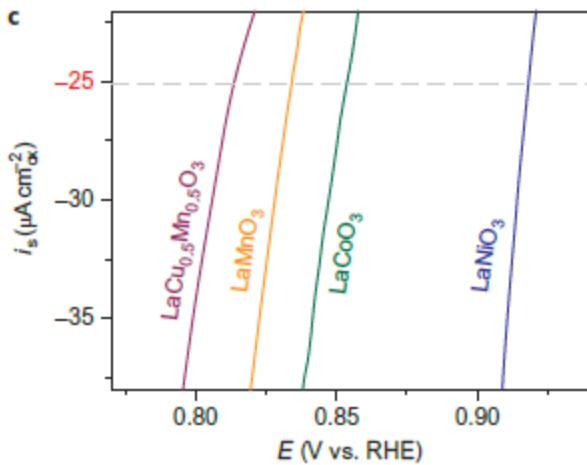
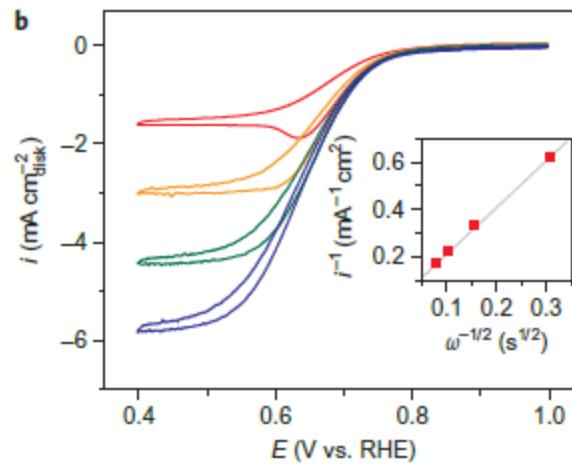
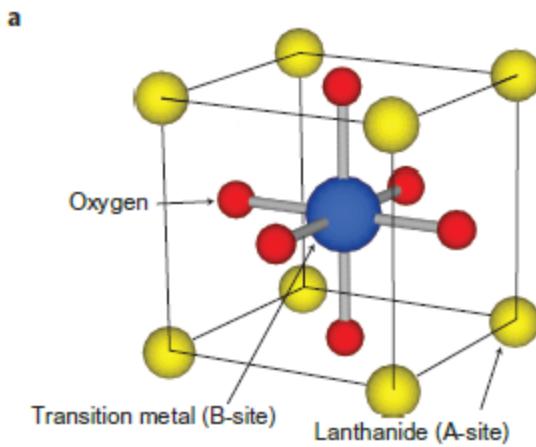
The AFM tip enhances the THz scattering, so that only the light localized to ~10 nm is detected by EOS. Vibrations can further enhance this.

Coherent two-dimensional THz/mid-IR spectroscopy with 10nm spatial resolution



While the mid-IR beams have ~ 20 μm focus size, locking into the top enhanced signal gives only the signal from a 10-nm spatial region.

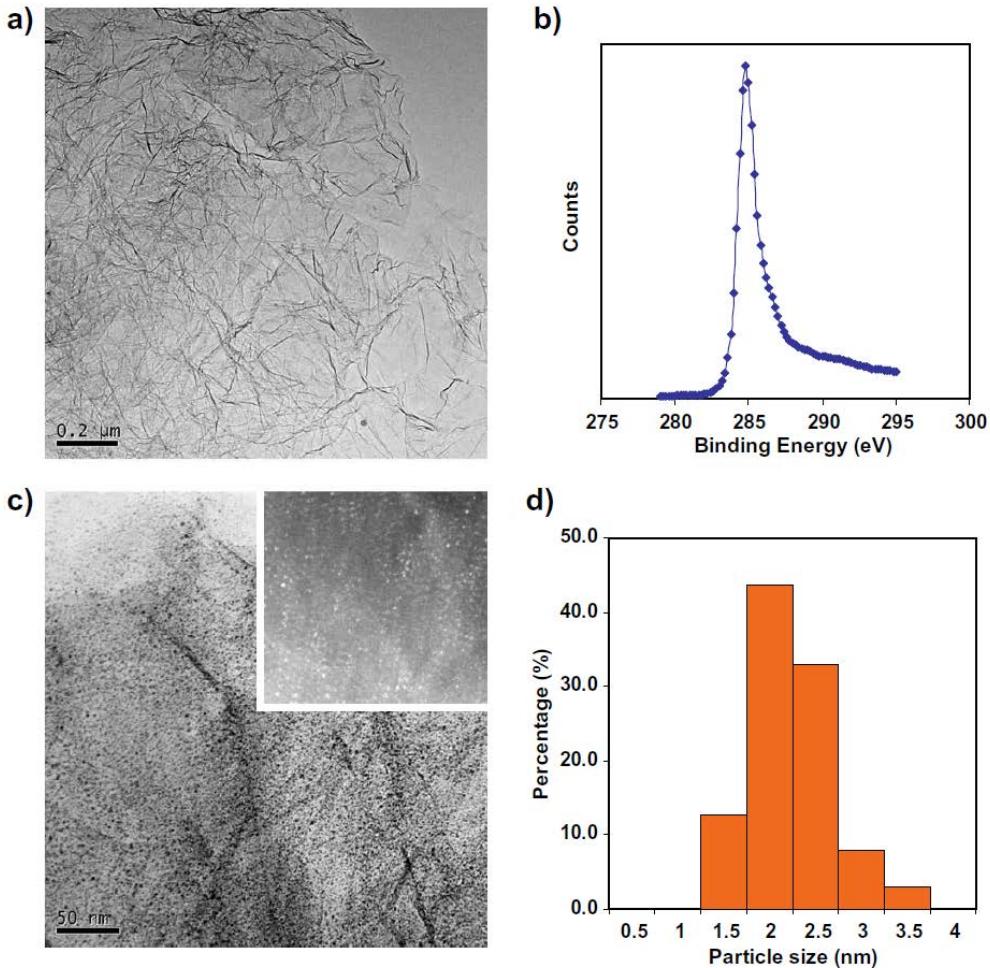
Pervoskite oxides as catalysts



Suntivich et. al. Nature Chemistry. 3, (2011).

We can use surface sensitive techniques to study new catalysts.

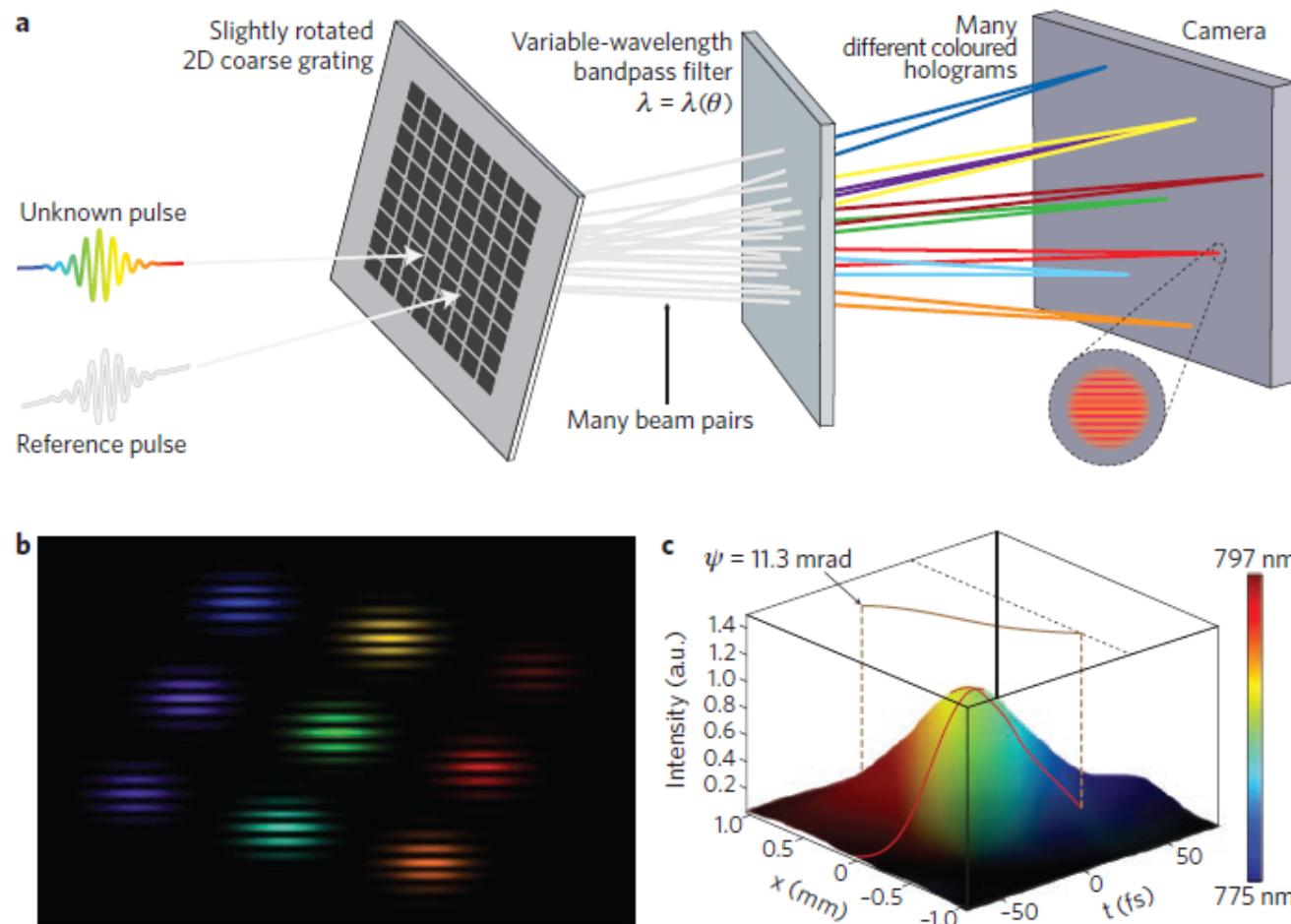
Functionalized graphene for catalysis



Kou et. al. *Electrochemistry Communications*. **11**, (2009).

Embedding catalytic nanoparticles in graphene sheets enhances their activity.

Single-shot spatiotemporal measurements

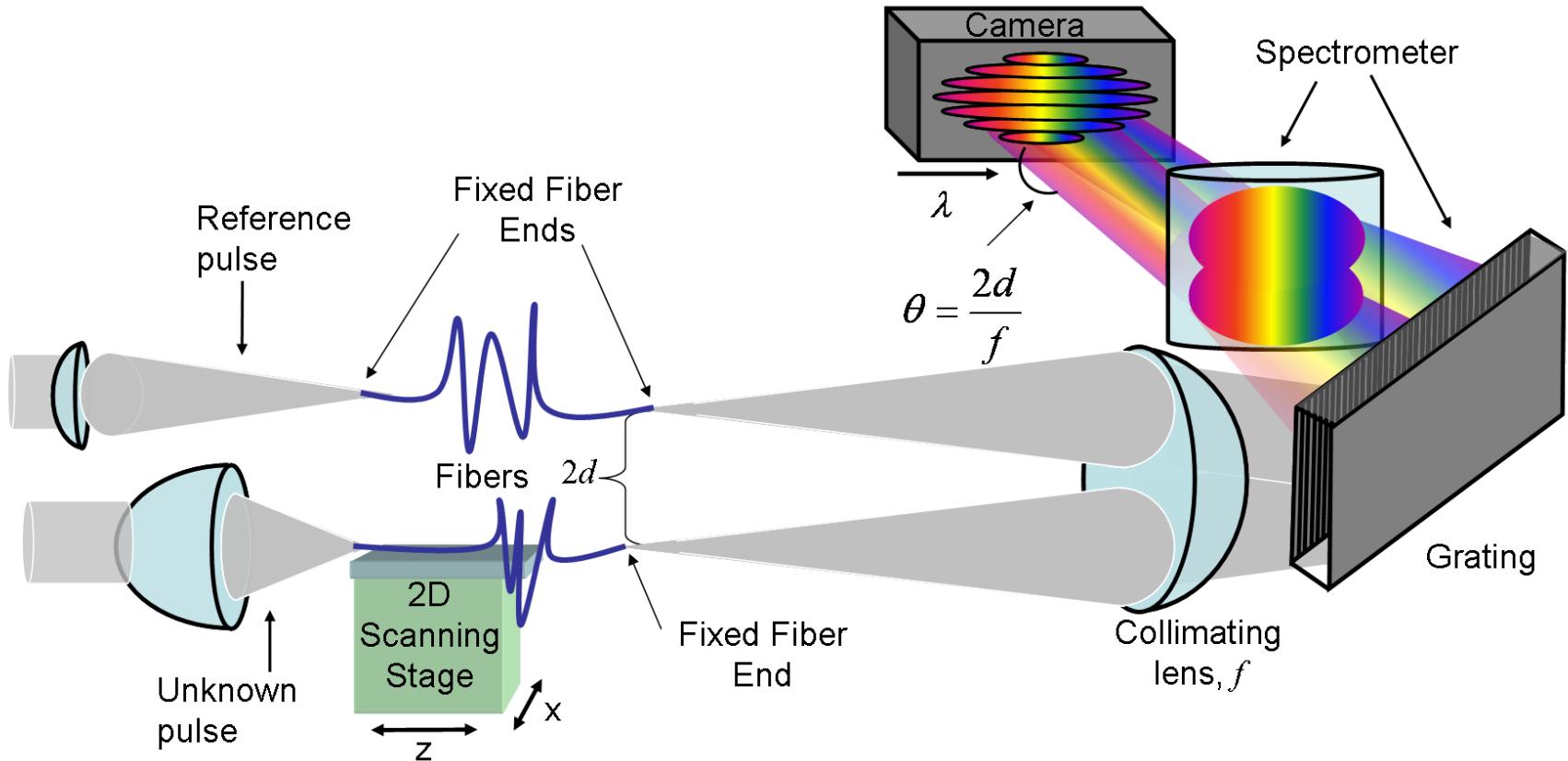


Gabolde, P. et. al., J. Opt. Soc. B. **25**, A25, (2008).

Combining this with up conversion of transmitted mid-IR pulses adds chemical specificity to the measurement.

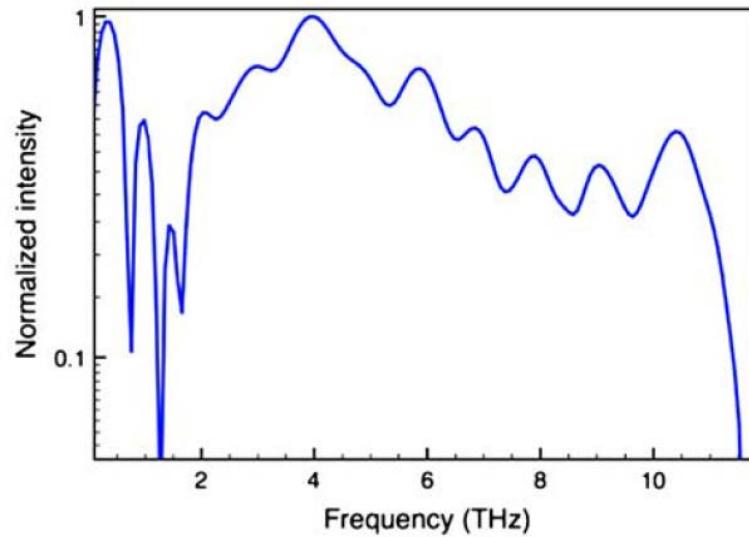
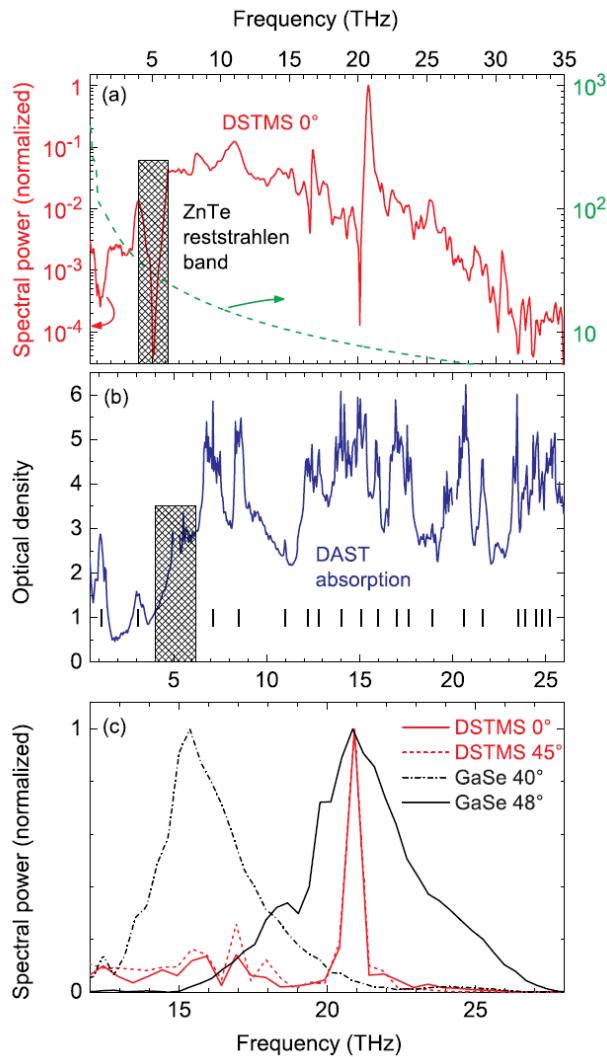
Spatiotemporal pulse measurement

Our spatial resolution is given by the mode size of the fiber, which is currently $5.6 \mu\text{m}$.



By scanning the input end of the reference fiber, we can measure $E(\lambda)$ at different positions, which yields $E(x,y,z,\lambda)$.

Intense, broad-band THz/mid-IR generation with organic crystals



Vicario et. al. J. Mod. Opt. **18**, 62 , (2013).

Somma et. al. Opt. Lett. **40**, 14, (20015).