Pump-probe Raman Scattering Investigation of Graphite:

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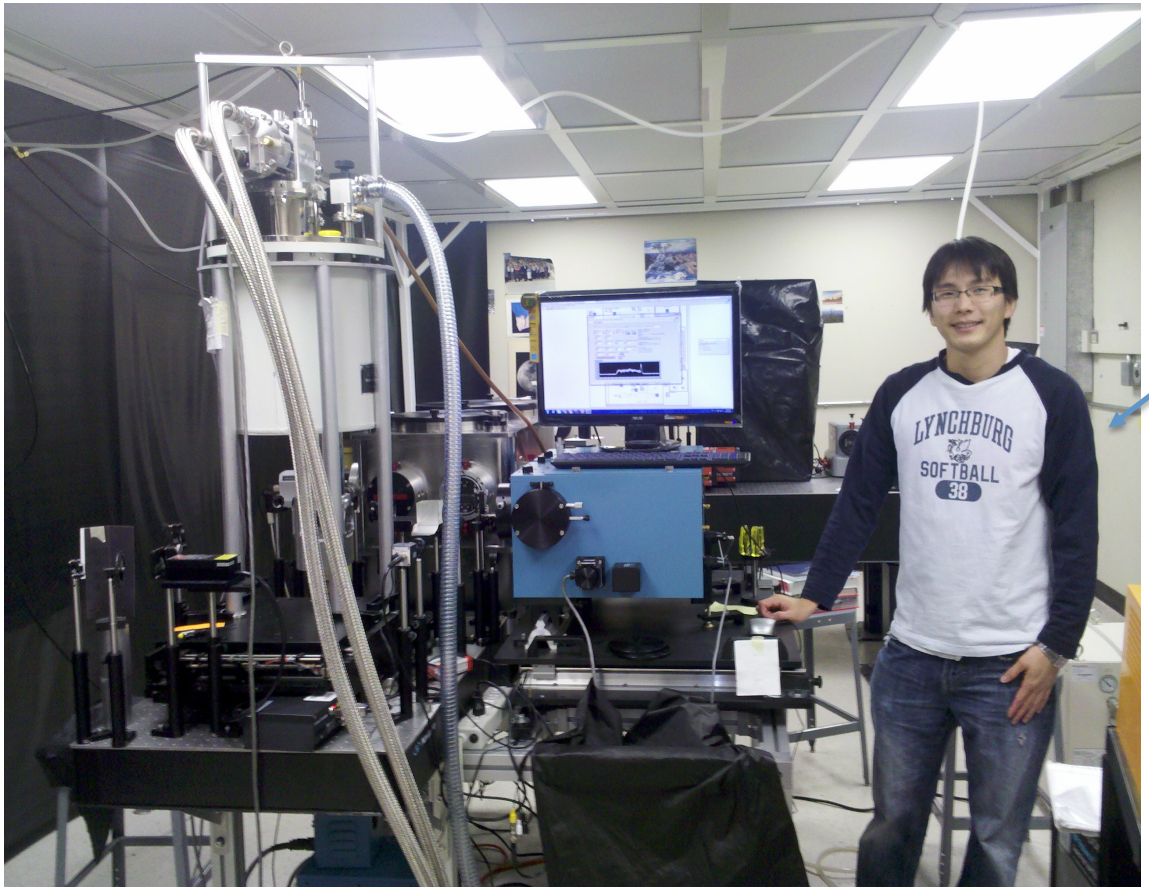
Funding: NSF

Raman experiment setup

McPherson custom triple spectrometer
with off-axis paraboloid optics

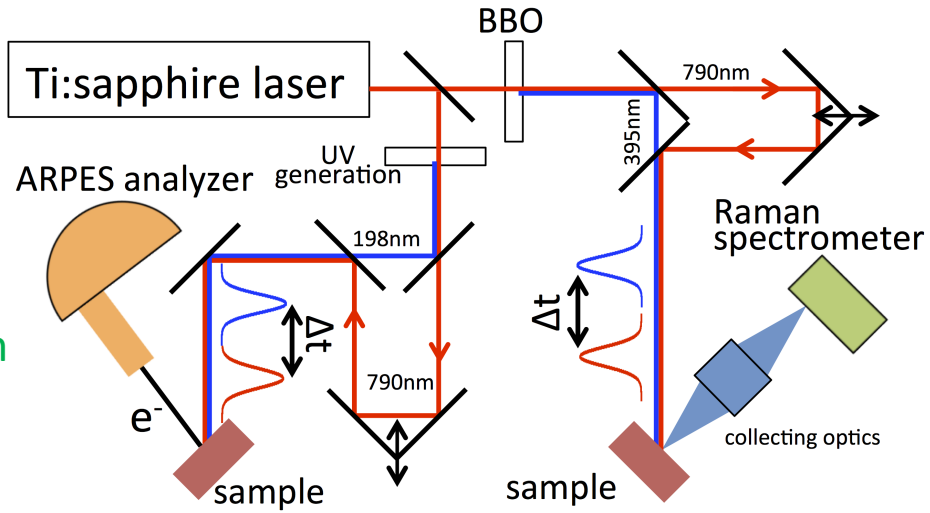


Jhih-An Yang

New state-of the art Raman laboratory with many different laser lines, pump-probe capability

Time Resolved Raman/ARPES Lab

Dessau group
Stephen Parham
Dan Dessau



Reznik group

Ti-Saph fundamental for pump (790 nm, 20kHz rep rate)

Frequency doubled for probe (395 nm)

Time-resolution: 90 fs.

Time=0 and time resolution measured from third harmonic peak

Filter stage for the fundamental (not shown) can compress the beam in energy at the expense of time resolution

Opportunities of pump-probe Raman

1. We typically know what we are probing (specific Raman-active phonons, electronic transitions, etc.)
2. A wide variety of identifiable bosonic features can be monitored: Phonon occupation numbers, phonon frequencies, electronic excitations, magnons, d-d excitations, superconducting gap excitations.
3. Pump an probe energy can be varied over a wide range: allows to resonate with specific excitations both on the pump and probe sides.
4. Cross-correlating with behavior of fermions measured by tr-ARPES.

Challenges of Pump-Probe Raman Experiment

1. Heisenberg uncertainty principle.

Improved time resolution=Degraded energy resolution.

Elastic scattering peak at zero energy becomes super-broad and overwhelms the low energy signal.

2. Low signal.

3. Self-Pumping.

Probe laser itself acts as a pump due to finite time-duration of the pump pulse: Photons that come first drive the system to an excited state and photons that come after Raman-scatter.

Even if there is no pump, one cannot measure an “unpumped” system.

Lots of hard work, persistence, and $$ to overcome these

First Completed Project: Graphite

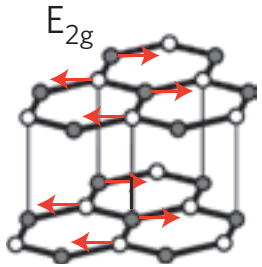
Excellent model system for pump-probe Raman

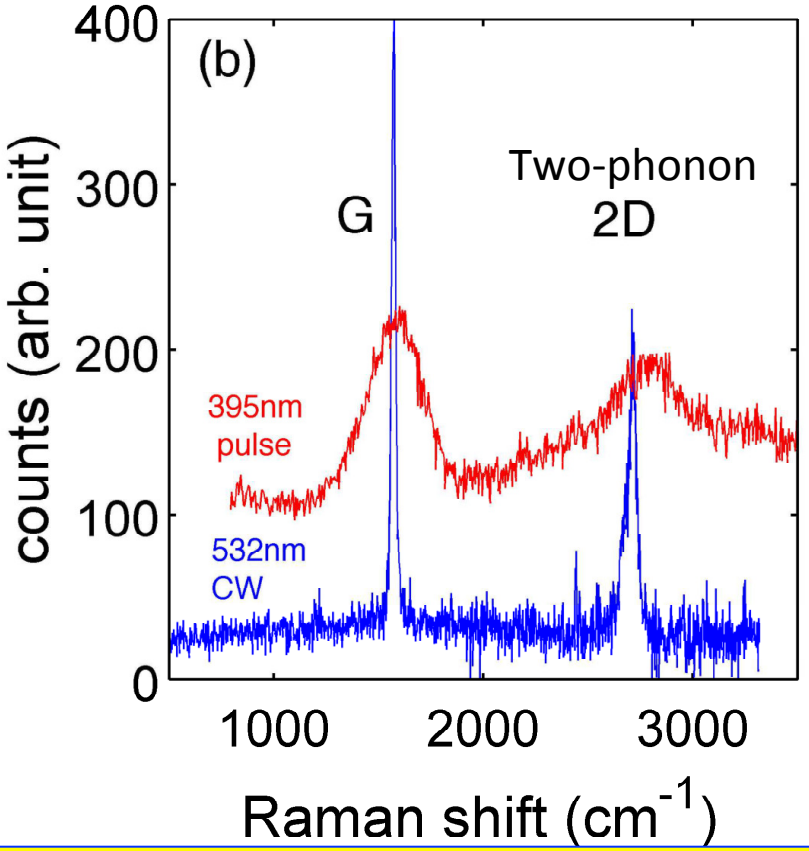
1. Phonons at high energy: Elastic line not a problem even at 90fs resolution
2. Phonons are intense: Relatively easy to get good signal
3. Self-pumping can be controlled by varying intensity of the pump. One can virtually eliminate it by using very low pump power and still see phonons (see item 2)
4. Regular Raman scattering in understood in incredible detail so one can focus on transient processes only.

Manuscript with referees

Graphite spectrum measured with the pulsed vs CW laser system

G-phonon



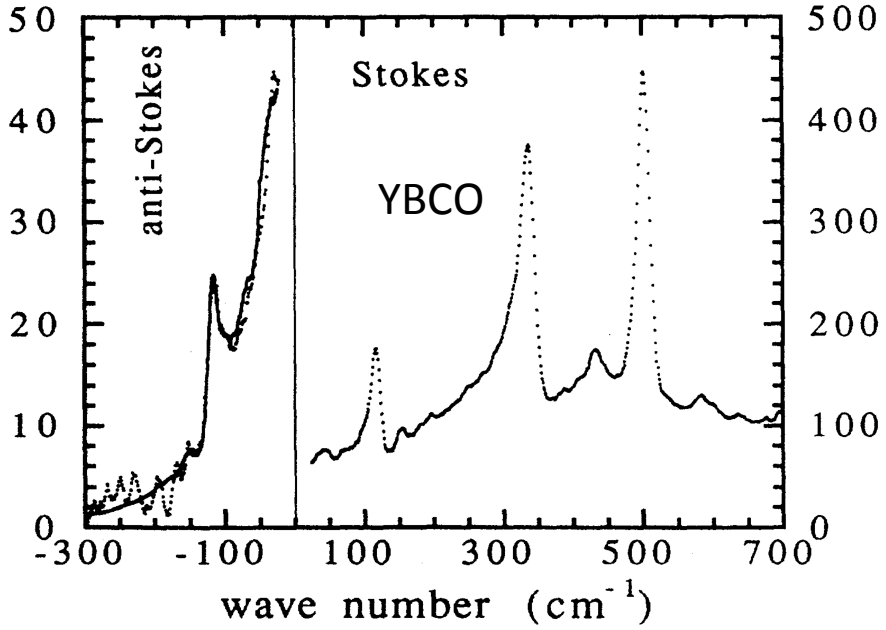


Phonons are broader because increased time resolution leads to decreased energy resolution.

Background is higher due to hot carrier luminescence.

Looking at ratio of Stokes to anti-Stokes to track phonon mode occupation

Anti-Stokes: Energy gain side (negative energy)



Stokes: Energy loss side (positive energy)

Principle of detailed balance:

$$S(-\omega) = S(\omega)e^{-\hbar\omega/k_bT}$$

Phonon occupation number:

$$n = \left(e^{\hbar\omega/k_bT} - 1\right)^{-1}$$

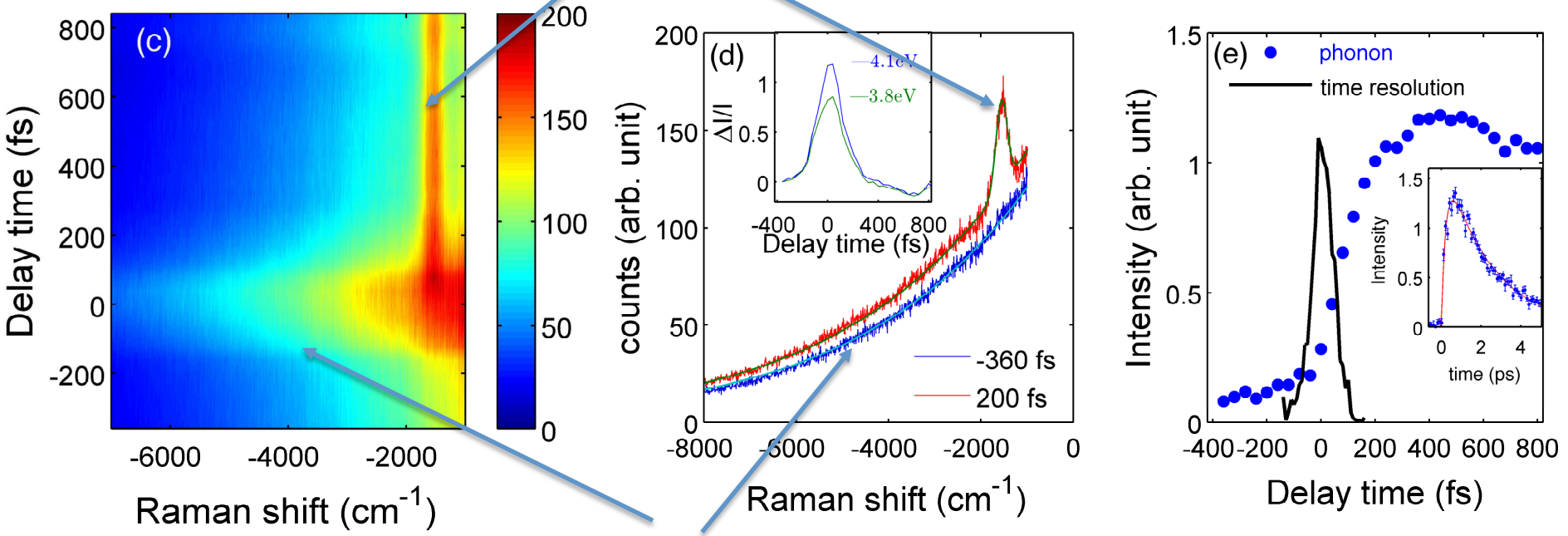
Phonon occupation number can be extracted from the ratio of intensities on the Stokes and anti-Stokes sides.

Qualitative picture: anti-Stokes only.

Time evolution of G-phonon

Energy gain (anti-Stokes side)

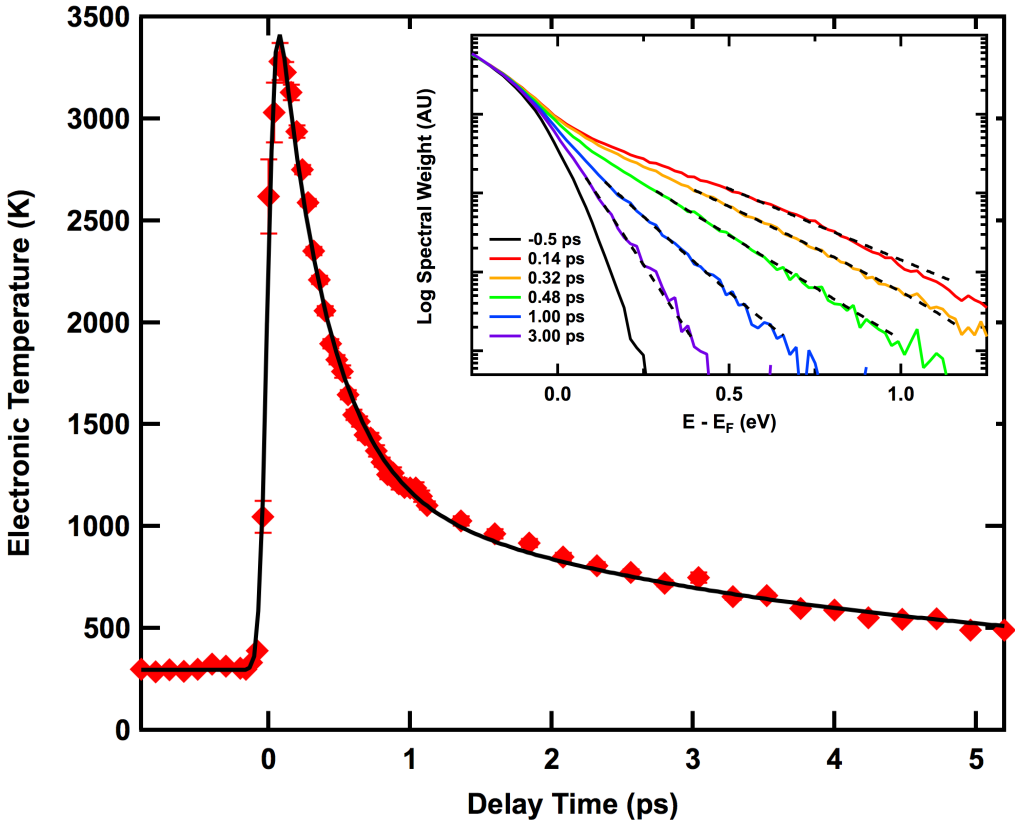
Hot phonon (interesting)



Hot electron luminescence (not interesting)

Phonon unobservable at negative times, i.e. when probe hits BEFORE the pump.
Phonon intensity increases right after the pump pulse and then decays slowly

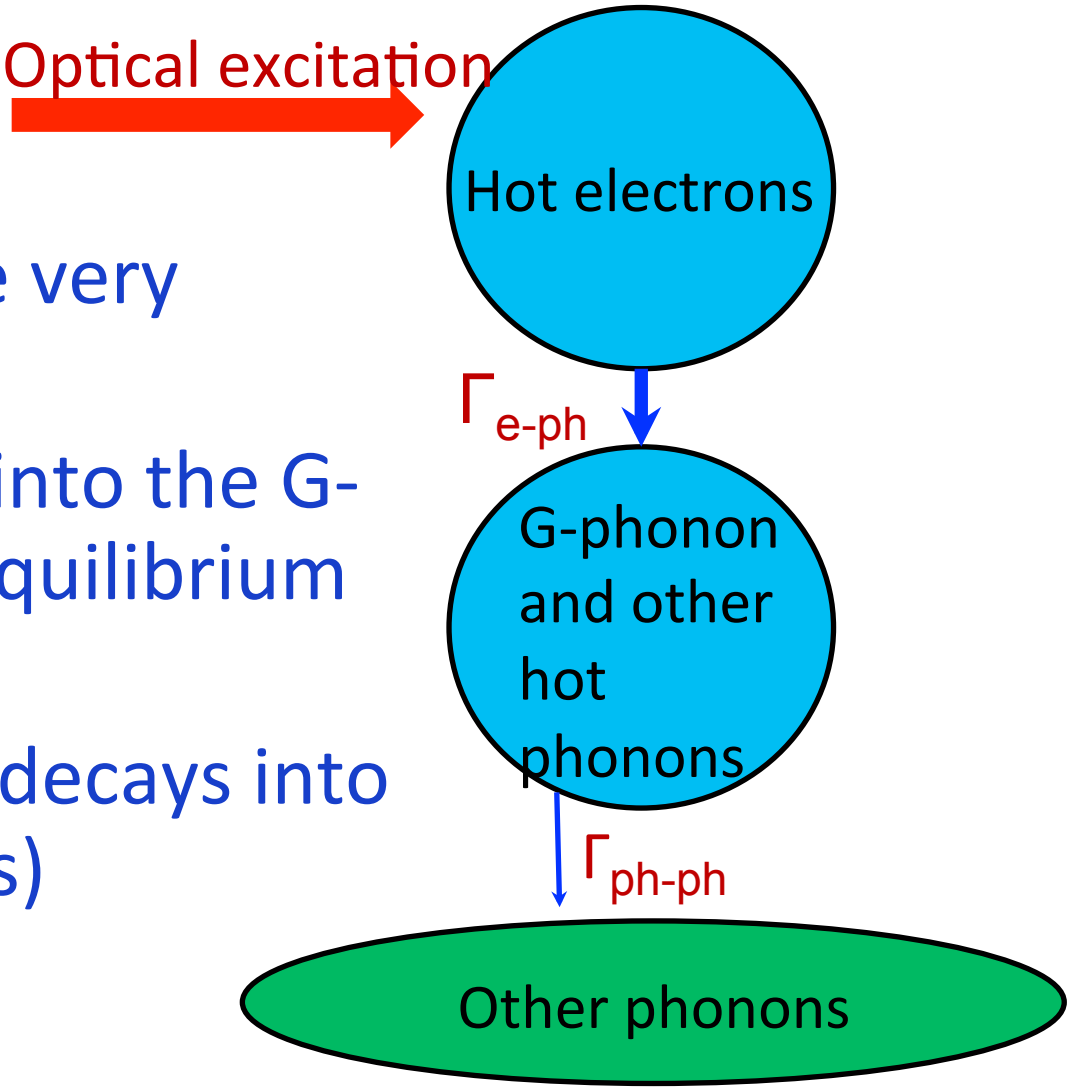
Electronic Temperature as a function of time from tr-ARPES



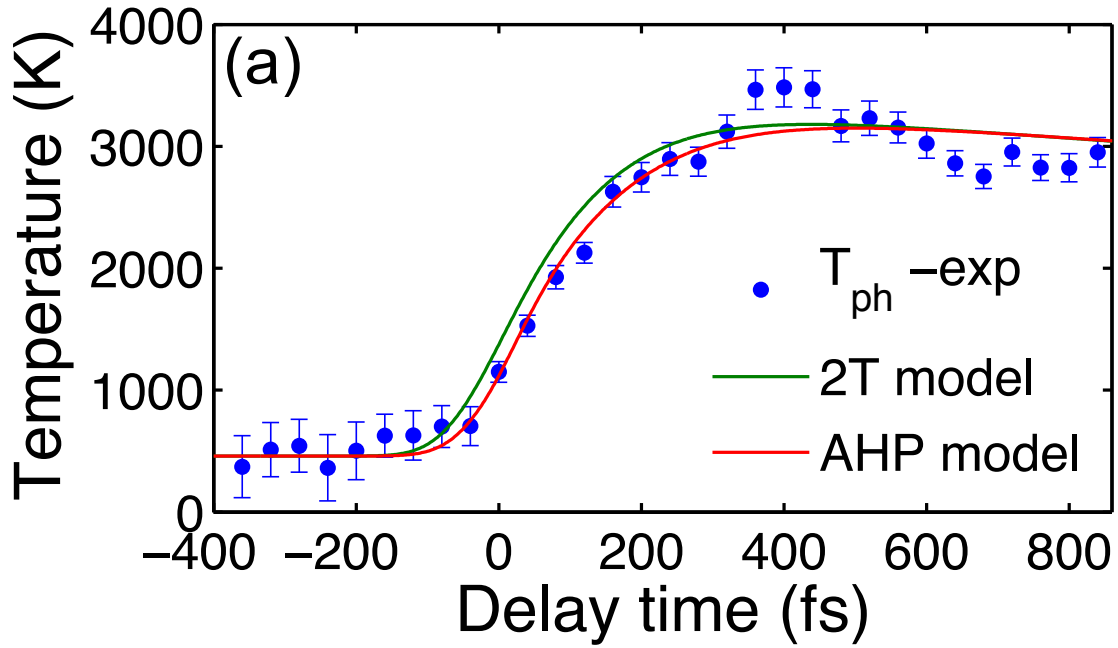
Good fit combining fast and slow time constants: 0.35ps and 3.5ps.

Two-temperature model description of graphite

1. Electrons thermalize very quickly (~10fs)
2. They decay directly into the G-phonon and reach equilibrium with it (~100fs)
3. Then the G-phonon decays into other phonons (~2ps)

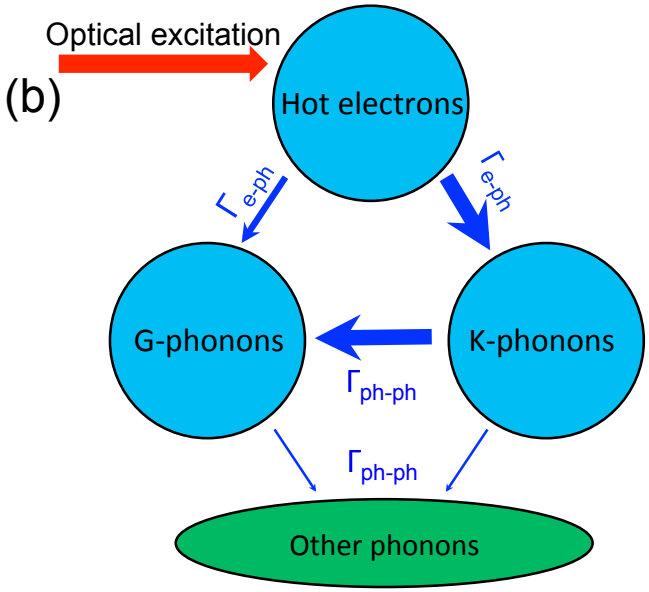


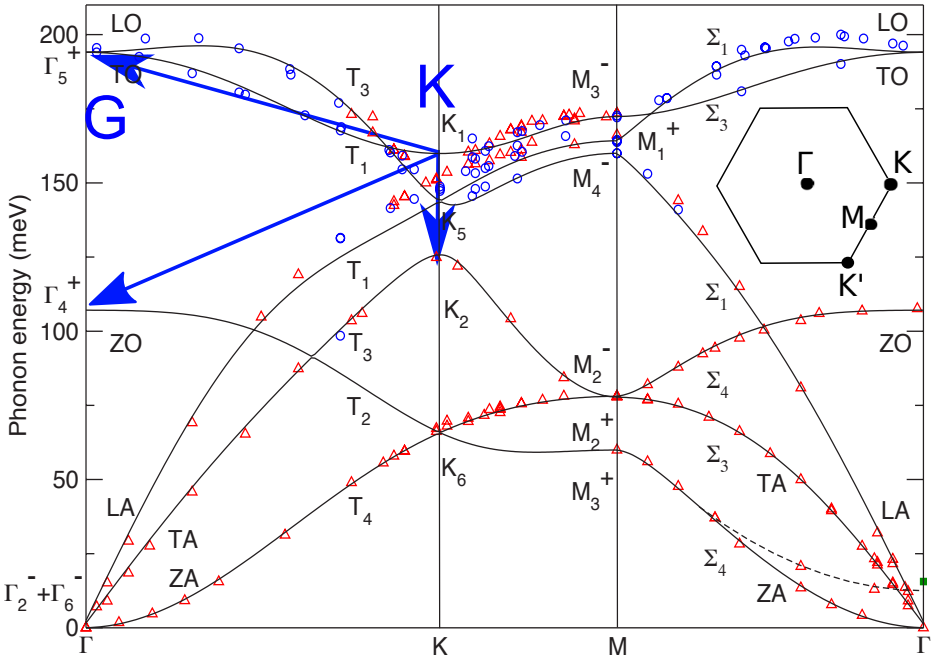
Time delay between two-T model prediction and the leading edge



Time-delay of ~80fs between the expected increase in the phonon intensity (green line) and what is observed (data).

Anharmonic phonon model





Anharmonic phonon model allows for hot phonons to decay into each other on very fast timescales. The resulting time-scale is consistent with ab-initio calculations and the observed time-delay

Where we are and where we are going

- Pump-probe Raman scattering is a highly-selective probe of materials in strongly driven nonequlibrium conditions.
- Our high-resolution setup allows measurements of fast processes in quantum materials such as electron-phonon relaxation, magnon and electron dynamics
- Future work will focus on tuning the pump energy to resonate with specific phonons
- Electronic excitations in addition to magnons will be investigated: d-d transitions, superconducting gap excitations

Need a detailed understanding of the data to figure out what's going on

What is the origin of electronic background?

How do we measure electronic temperature?

What is the Raman process for phonons in graphite?

What is the electronic background?

Luminescence (T. Heinz et. al)

Excited electrons thermalize quickly via electron-electron scattering reaching a few 1000K. (depending on pulse energy)

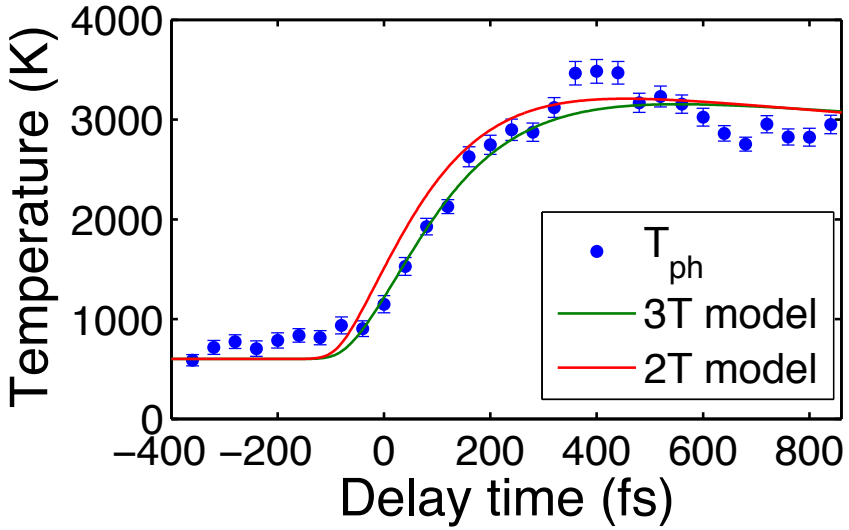
Then they take a long time to reach thermal equilibrium with phonons.

In the meantime they emit a black body PHOTON spectrum.

Reading off electronic temperature from luminescence

1. Luminescence lives for a long time, so intensity is a time-integral of the luminescence signal. Dominant contribution comes from the spectrum at maximum temperature because black body radiation is exponential in 1/Temperature. When pump and probe hit at different times the maximum temperature is smaller than when they hit at the same time, so there is a peak at zero T.
2. Virtually impossible to read off electronic temperature in real time from the luminescence signal.

Two temperature model prediction



Red line based on the electronic temperature obtained from 2D phonon peak.
Green line: Talk of Jhih-An Yang