Optical phonon lifetimes in graphene and graphite by time-resolved incoherent anti-Stokes Raman scattering

Kwangu Kang, Daner Abdula, David Cahill, and Moonsub Shim

Department of Materials Science and Engineering and Materials Research Laboratory, University of Illinois, Urbana, IL

Understand ultrafast energy transfer in graphene

Conventional picture

photons

↓ ~ 2 fs

electron-hole pairs

↓ ≈ 200 fs

optical phonons

↓ ≈ 2 ps

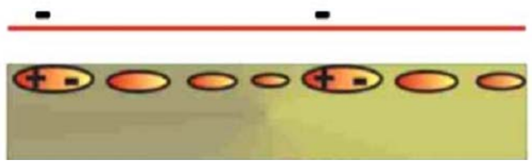
acoustic phonons

↓ ~ 20 ps

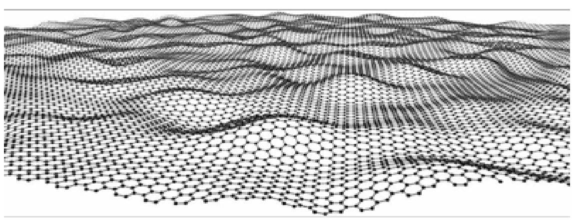
equilibrium

What might be special about graphene?

- coupling to substrate excitations, e.g., SiO_2 surface phonon polaritons



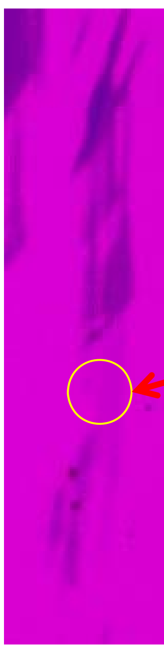
- low frequency ripple excitations



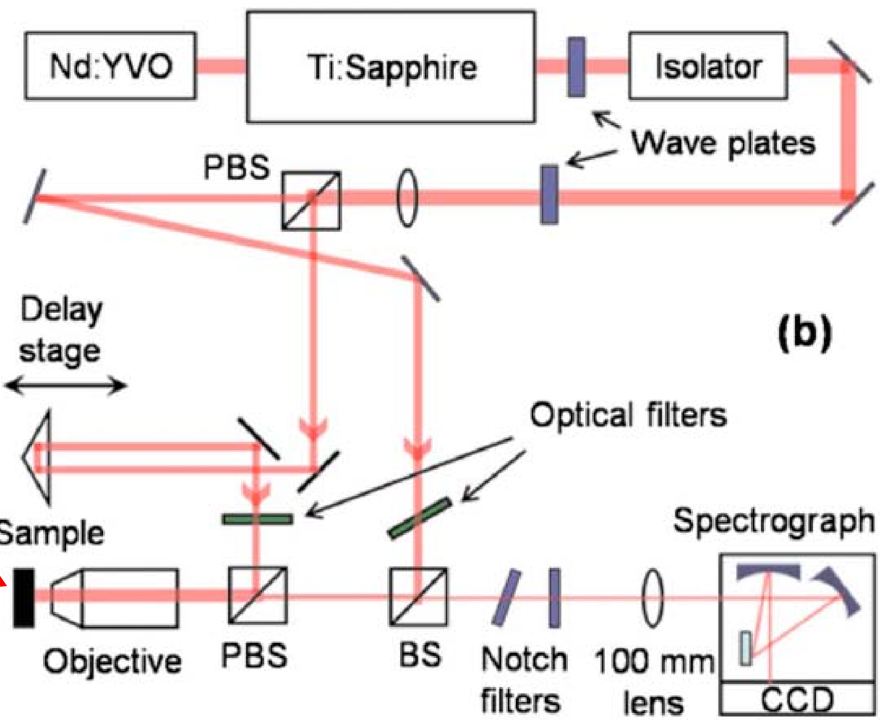
⇒ Understand and control transport of thermal energy at interfaces

TRIARS directly measures phonon lifetimes

- Anti-Stokes Raman intensity is proportional to phonon population.
- Time-Resolved Incoherent Anti-Stokes Raman Scattering (TRIARS) provides a direct measurement of population lifetimes.
  - o hot electron-hole pairs are generated by 500 fs pump pulses
  - o zone-center optical phonons scatter photons from 500 fs probe pulses



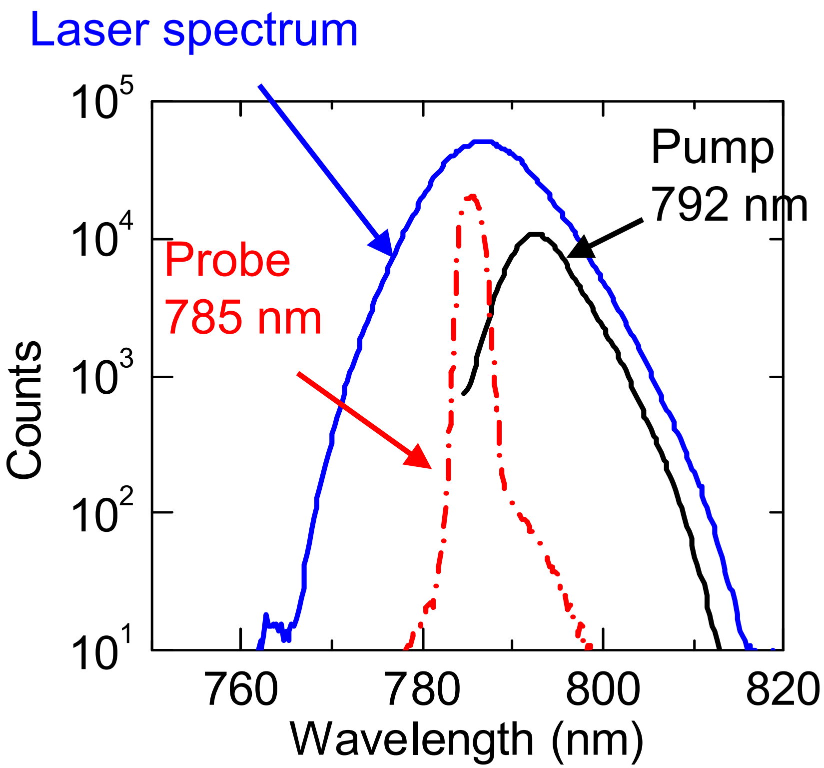
Single layer graphene

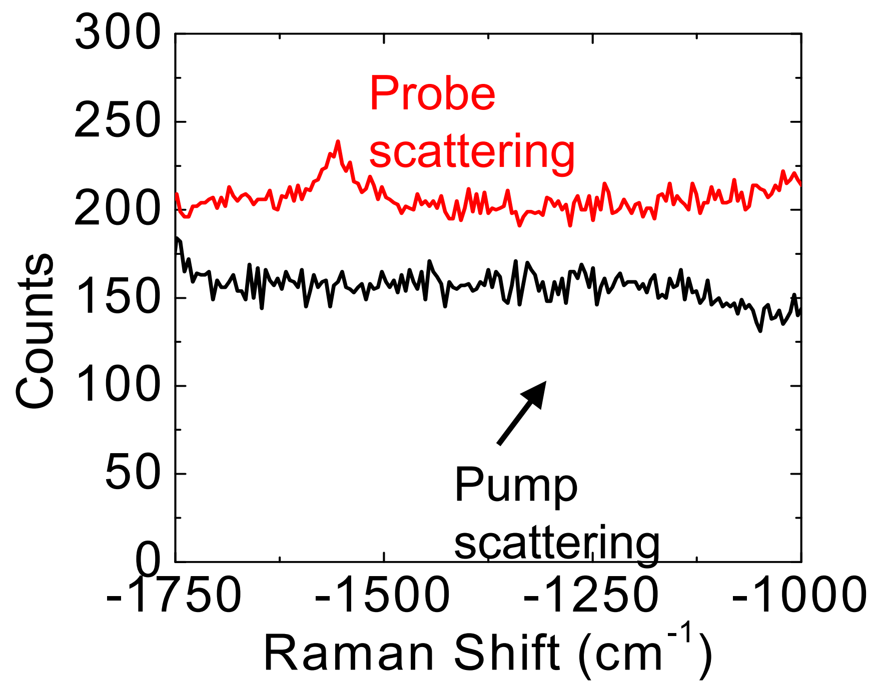


Recent TRIARS studies of phonon lifetimes

- Heinz (Columbia) and co-workers
  - nanotubes, **graphite** (T_1=2.2 ps)
- Dlott (UIUC) and co-workers
  - Molecular liquids (uses IR pump)
- Tsen (ASU) and co-workers
  - III-nitrides
- Kang and Cahill (UIUC) and co-workers
  - Si, nanotubes, **graphite, graphene**

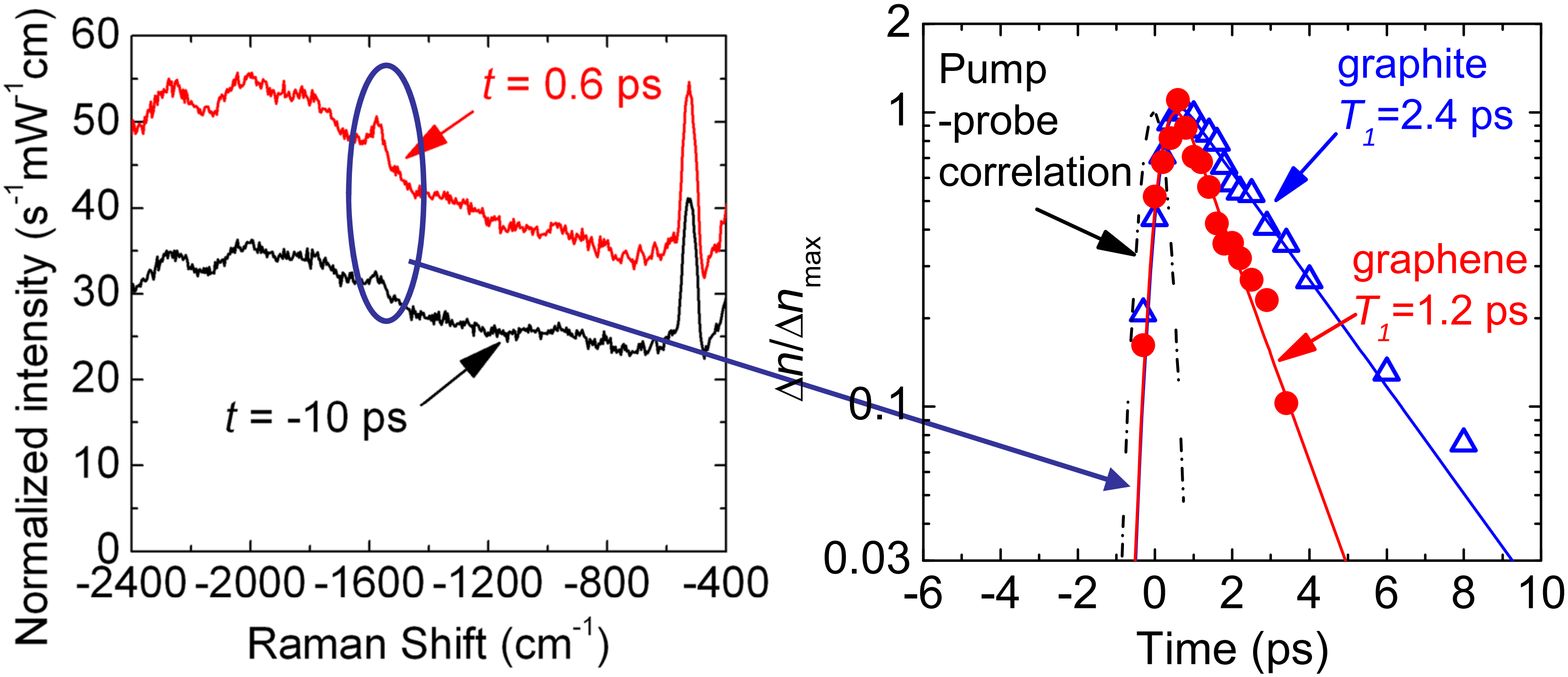
“Two-tint” approach separates pump and probe





- Use of laser oscillator enables tight focusing on small area graphene samples
  - o pump laser fluence is 4 J/m^2; $1/e^2$ radius 4 μm.
  - o N_2 atmosphere; annealed at 300°C.

Convolution of exponential decay with instrument response



Fit the measurement to convolution of *f* and *g*

Correlation of pump and probe

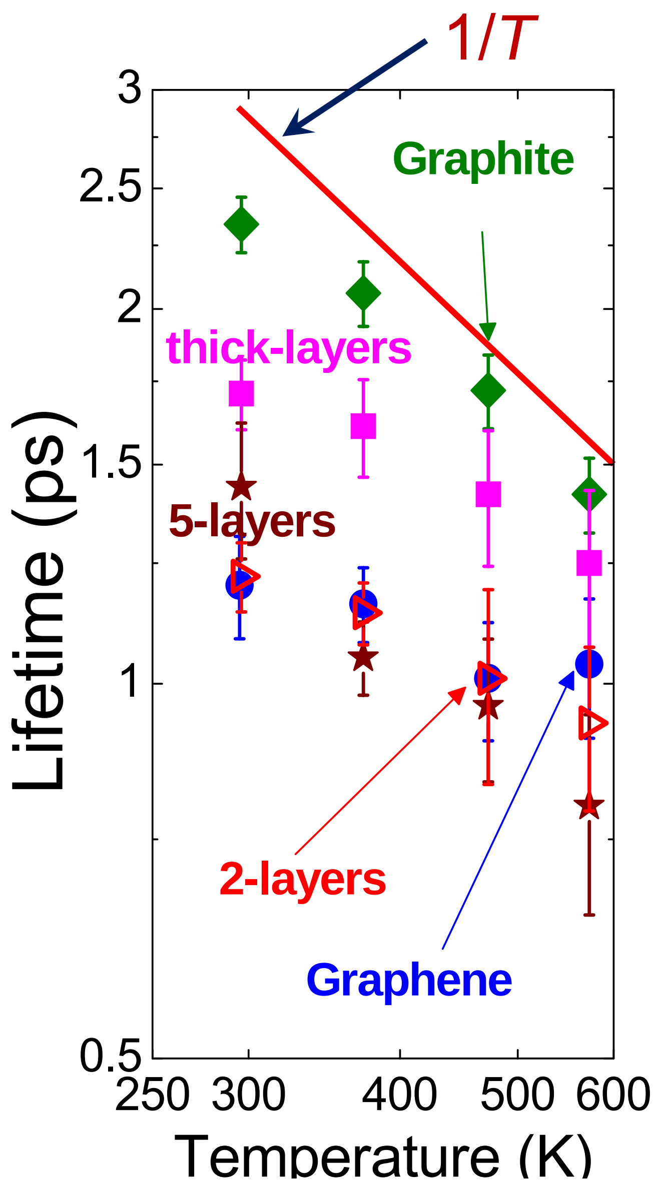
$$f(x) = \frac{\exp\left[\frac{-(x-\mu)^2}{2\sigma^2}\right]}{\sigma\sqrt{2\pi}}$$

Exponential decay

$$g(x) = A\exp\left[-\frac{x}{\tau}\right]$$

Lifetime

Optical phonon lifetime depends on temperature and thickness



Main results:

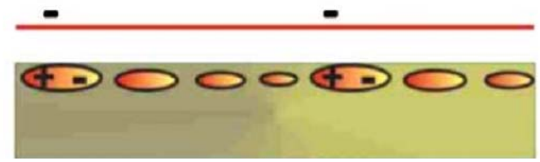
- Approaches 1/T temperature dependence
  - o anharmonic three-phonon decay
- Shorter lifetimes in thinner graphenes
  - o substrate effects?
- No significant difference between single layer and bilayer graphene
  - o ripple excitations unimportant

K. Kang *et al. submitted.*

Estimate thermal conductance of the additional channel for energy transport

Coupling to surface phonon-polaritons?

(optical phonons of graphene are coupled to electronic excitations that are, in turn, coupled to polar phonons of the substrate)



Thermal time conductance of the additional channel

$$G = C / \tau \text{ with } \tau = 2 \text{ ps}$$

C = heat capacity of hot optical phonon ≈20 μJ m^{-2} K^{-1} from classical statistics and 3% of optical phonons are excited (see Yan *et al*. PRL (2009)).

$\Rightarrow G$ = interfacial thermal conductance ≈10 MW m^{-2} K^{-1}

Compare to 24 MW m^{-2} K^{-1} (Freitag 2009) for coupling of graphene electrons to SiO_2 substrate phonons

Summary

- Lifetimes of optical phonon in graphene and graphite are 1.2 ps and 2.4 ps, respectively, at room temperature.
- For graphite and >5-layer graphene, lifetimes approach a ~1/T indicating that three-phonon processes are the dominant decay mechanism.
- Lifetime decreases with decreasing number of layers; possible direct interaction of excitations in graphene with lattice vibrations in the a-SiO_2 substrate.