Frontiers of Experimental Condensed Matter Physics

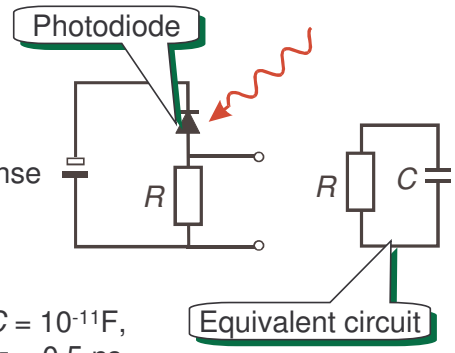
- Part C, Atomic scale measurements
- Atomic distance scales:
  - Part I: Scanned Probe Microscopies
  - Part II: Electron microscopy
- Atomic and electronic time scales
  Part III: Ultra fast measurements.
  - Limits of detector response
  - Pump-probe methods:
    - Basic concepts
  - Illustrations:
    - Real-time observation of molecular vibrations.
    - Carbon nanotube dynamics,

General refs:
Shah "Ultrafast Spectroscopy…" Springer Ser. in Solid-State Sci. **115** (1996).
Demtröder "Laser Spectroscopy" 2nd Ed Springer (1996) [Chapter 11.4]

Electronic limit to detectors

- Response of detectors
  - Conventional detectors are relatively slow and have time a response slower than 10^{-10}s.
    - Eg: Photodiode has an internal capacitance, *C*, which limits the frequency response

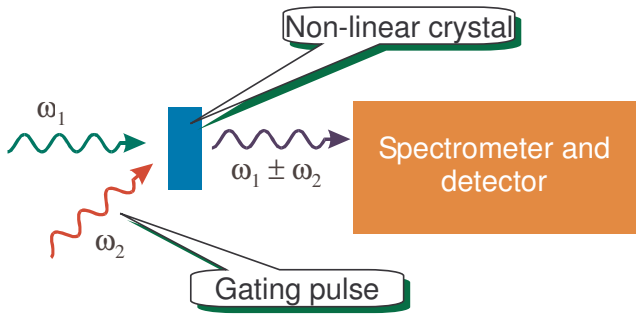
$$f_{\max} = \frac{1}{2\pi CR}$$



    - With $R = 50\ \Omega$, $C = 10^{-11}$F, $f_{max} = 300$ MHz, $\tau = 0.5$ ns.
    - It is very difficult to reduce *C* (or *R*) much below these values.
  - Similar consideration apply to most other detectors: photo- and electron-multipliers, scintillators, image intensifiers etc.
  - One approach is to "gate" a slow detector. That is, to prevent signal reaching the detector except during a pre-defined "opening" of the gate.

Fast methods

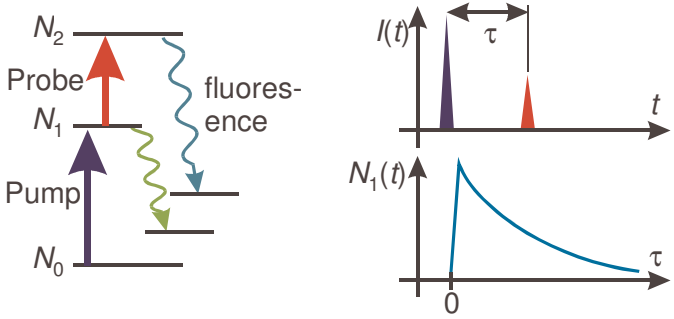
- Gated detector:
  - How to convert a slow detector into a fast one.
  - Example: Non-linear mixing of a process at, ω_1, with a pulsed, gating signal at ω_2. The detector is sensitive to frequency, $\omega_1 + \omega_2$, but does not require time resolution, since the signal can only be present for the duration of the gating pulse.



  - Sub-picosecond resolution is possible using fast, pulsed lasers. Time resolution is limited by the width of the gating pulse. Spectral resolution is limited by the frequency spread in the pulsed laser, ω_2.

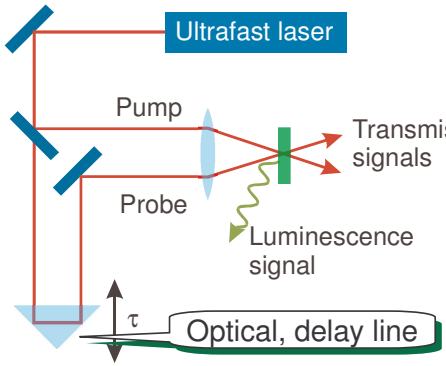
Ultra-fast methods

- Pump-probe techniques
  - The pump probe method overcomes the time limitations described above and allows measurements into the femto-second regime.
  - The dynamics of state, $|1\rangle$, can be followed by first, exciting the state with the "pump" laser. The state of the system after a time delay, τ, is explored by the "probe" laser, which excites from $|1\rangle$ to $|2\rangle$. In the example shown, one could observe the fluorescence signal from state $|2\rangle$, which is indicative of $N_1(t)$.



Transmission/reflection

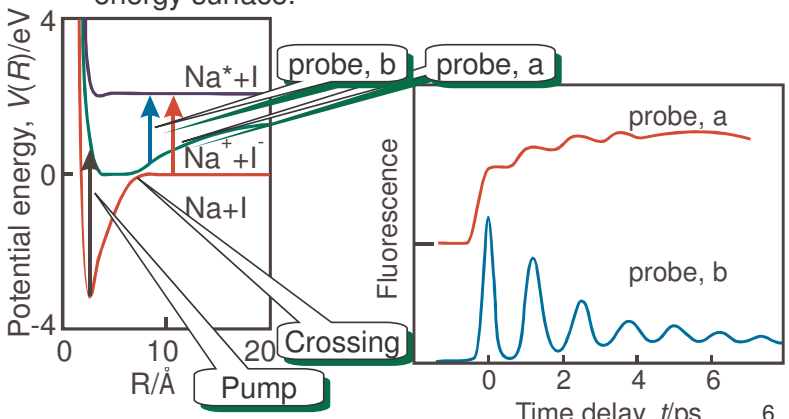
- Transmission/reflection spectroscopy
  - One of the simplest experiments is for both pump and probe to be generated from the same laser.



  - The probe is typically weaker than the pump and forms a smaller spot on the sample (so that a uniformly excited region is probed).
  - In transmission spectroscopy one generally measures the change in transmitted probe, pulse energy as a function of the time delay, τ.
  - At the sample, time resolution is provided by the delay, t, and the detectors can be slow (and include spectral resolution, if required).
  - Time resolution is limited by the laser pulse width; however, coherent process on shorter time scales can be observed.

Femtosecond dynamics of molecules

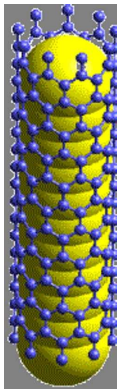
- Vibration of a diatomic molecule in real time.
  - NaI (ionic bond): At small separations the lowest energy state looks like $Na^+ + I^-$. At large internuclear separations, the lowest energy state is Na + I. There is a "crossing" at intermediate separation.
    - The pump excites to the repulsive wall (green curve) and vibration starts. There is leakage at the crossing. The pump excites to a state that radiates (fluorescence) at large R (long lifetime on this scale)
    - Probe, a, (chosen by tuning probe frequency) measures the leakage, which gives dissociation.
    - Probe, b, measures vibration on the green potential-energy surface.



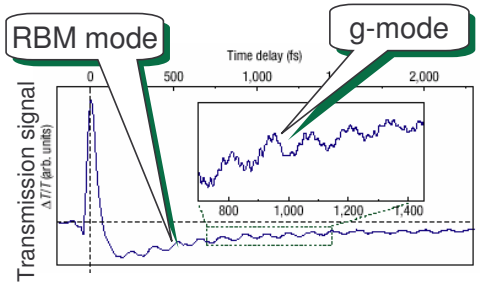
Khundkhar and Zewail Ann. Rev. Phys. Chem. **41** (1990) 15

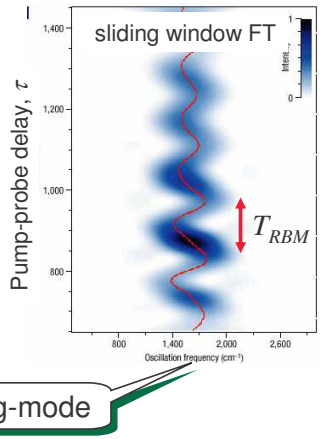
Coherent phonon dynamics

- Single-wall C-nanotubes. www.ncnr.nist.gov/staff/taner/nanotube/



  - There are many vibrational modes:
    - eg. a low frequency, radial breathing mode (RBM) where the diameter oscillates; and a high frequency, g-mode, corresponding to radial deformation of individual carbon rings.
  - Phonons in the medium modify the optical properties and modulate the pump-robe transmission signal. The experiment uses 10-fs, white-light pulses in a geometry similar to p. 5.





  - g-mode frequency is modulated by the RBM (see right).

(Gambetta et al. Nature Physics **2** (2006) 515)