Mode-selective vibrational modulation of charge transport in organic electronic devices

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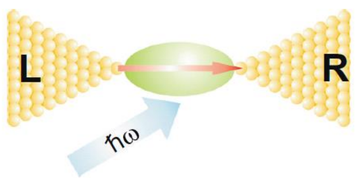
Vibronic Coupling

- Vibronic coupling:
  Interplay between electronic and nuclear dynamics
- Contribute greatly to electronic properties of organic and bio-system, such as photophysics of vision, conformational reorganization, olfactory etc.
- Can mode-selective vibrational excitation be used to
  - **control charge transport in organic devices?**
  - **track charge transfer processes in (bio)molecules?**



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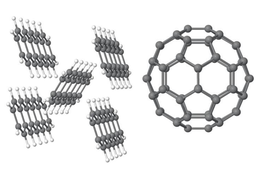
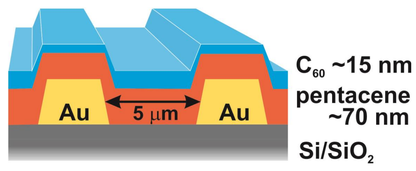
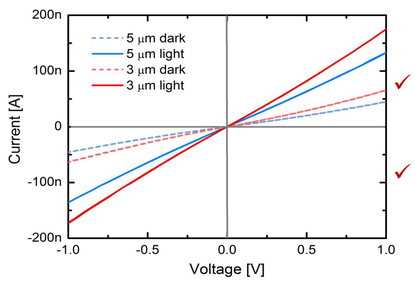
Model System: Pentacene/C_{60}

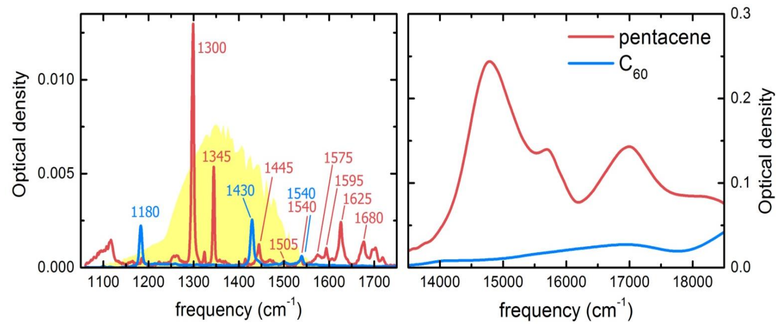






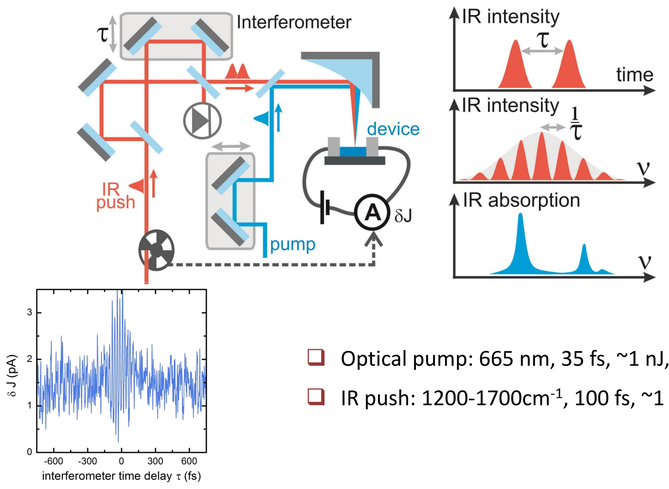
- ✓ Parallel electrodes and open space for good access of mid-infrared pump pulses to the active layer
- ✓ C_{60} to enhance the photocarrier generation in the film

Optical Spectroscopy Characterization of the System



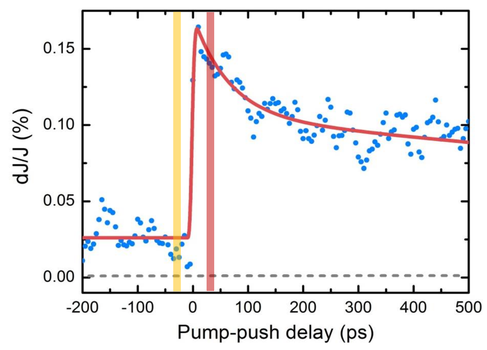
Infrared absorption in the vibrational fingerprint region and optical absorption spectra of pentacene and C60. The yellow shaded contour shows a typical laser spectrum used for infrared push.

Time and Frequency Resolved Pump-Push-Photocurrent (PPP) Setup



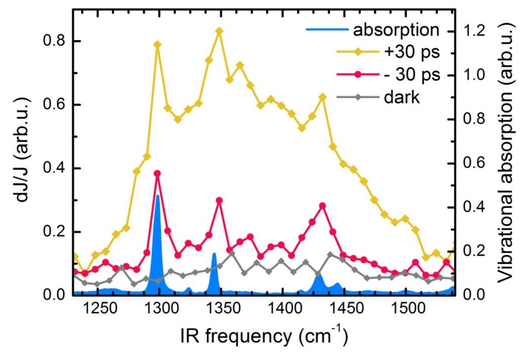
- Optical pump: 665 nm, 35 fs, ~1 nJ, 1 kHz
- IR push: 1200-1700cm^{-1}, 100 fs, ~1 μJ

Results: Time-resolved PPP



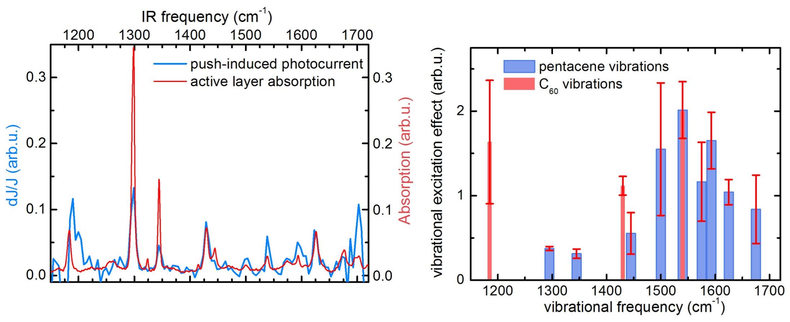
- Increase of *J* already at negative delay
- Excitation of long lived (>1 ms) carriers created by previous pump pulse
- Rapid rise of *J* when IR push arrives
- ~ 100 ps decay component: geminate recombination of newly generated charge pairs

Results: Frequency Resolved PPP



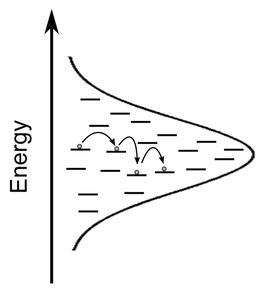
- Broad feature at positive delay: excitation of localized charge pairs to more delocalized states
- No photocurrent without optical pump (“dark”)
- Narrow features match well with vibrational absorption peaks.
  Purely thermal effect???

Photocurrent vs. IR absorption



- No significant frequency shift between absorption and photocurrent
- Photocurrent does not scale linearly with vibrational absorption
- Differences in effect up to 6-fold
- Purely thermal effect can be excluded!

Electron-Phonon Coupling in Hopping Transport



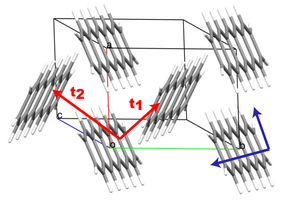
- Miller-Abrahams theory:
  hopping from trap state to higher energy via absorption of phonon
- Hopping rate *k* defined by electron-phonon coupling ν:

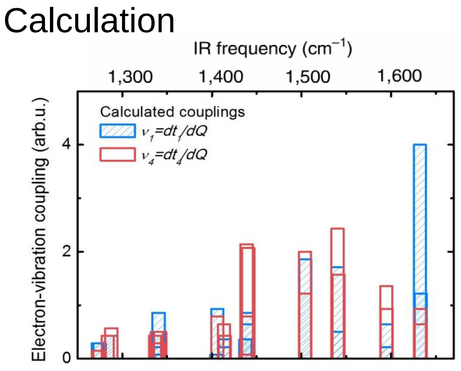
$$k \sim \nu^2 n_D$$

n_D: occupation number of molecular vibrations

- Non-equilibrium population of vibrational states allows mode-selective manipulation of charge transport

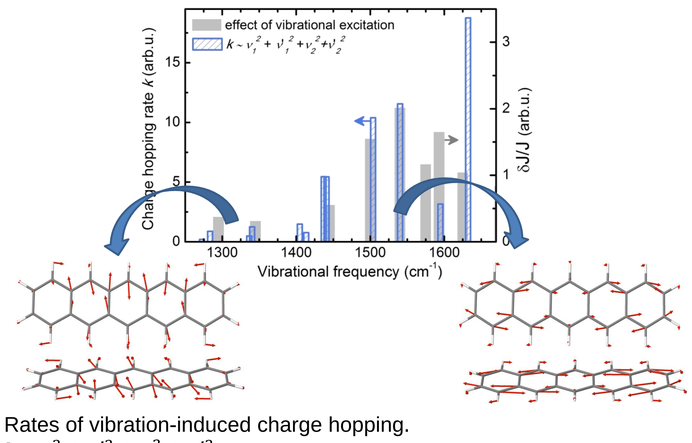
Non-Local Electron-Phonon Coupling by DFT Calculation





- Peierls-type electron-phonon couplings: dependence of the transfer integrals on the distances between adjacent molecules and their relative orientations
- Non-local hole-vibration couplings are defined as the derivatives of the charge transfer integrals with respect to the vibrational coordinates, $n_i=dt_f/dQ_j$

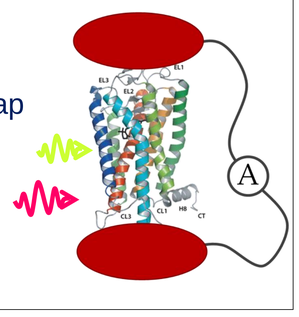
Mode-selective Effect on Charge Transport



Rates of vibration-induced charge hopping.
$k \sim \nu_1^2 + \nu_1'^2 + \nu_2^2 + \nu_1'^2$
where ν_i and ν'_icorrespond to quasi-degenerate molecular vibrations of similar frequencies.

Summary and Outlook

- Vibrational coupling can be directly observed by opto-electronic measurement
- Vibrations along the long axis of pentacene lead to stronger increase of hopping transport than vibrations along the short axis
- Mode-selective and local nature of method opens up a **new way** to map transport paths and understand transport mechanisms in (bio)molecular junctions



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