**Principles of FEIR Spectroscopy**

IR spectroscopy is an insensitive method due to low absorption cross-sections, poor mid-IR detectors, and a lack of vibrational luminescence. FEIR spectroscopy overcomes some of these limitations by encoding the vibrational excitation into a visible fluorescence signal that can be detected with high sensitivity.

Vibrations are pumped with an IR pulse or pulse-pair, then a pre-resonant visible pulse selectively brings these vibrationally excited molecules to their fluorescent electronic state. Spectra are recorded via Fourier transform of the IR pulse-pair delay, and vibrational relaxation processes are monitored by varying the encoding delay. FEIR activity depends on vibronic coupling as well as the relative orientation of vibrational and electronic transition dipoles.

**Toward Single-Molecule FEIR Vibrational Spectroscopy**

To push the sensitivity of FEIR to the single molecule level we are employing 1 MHz repetition-rate pulse trains, photon counting, and confocal fluorescence microscopy. We are currently able to perform measurements where on average only a single molecule is present at a time.

FEIR correlation functions demonstrate single-molecule sensitivity. Although not true single-molecule measurements, possible FEIR correlation spectroscopy experiments could use vibrational spectra to sense spontaneous structural changes in chemically exchanging systems.

Single-molecule measurements can record trajectories of molecular properties evolving within the equilibrium state. Here FEIR spectroscopy could add the sensitivity to time-evolving structure required for studying chemical dynamics. We are seeking new concepts for FEIR measurements that integrate vibrational spectra and ultrafast dynamics from optical delays with trajectories from real-time photon streams.