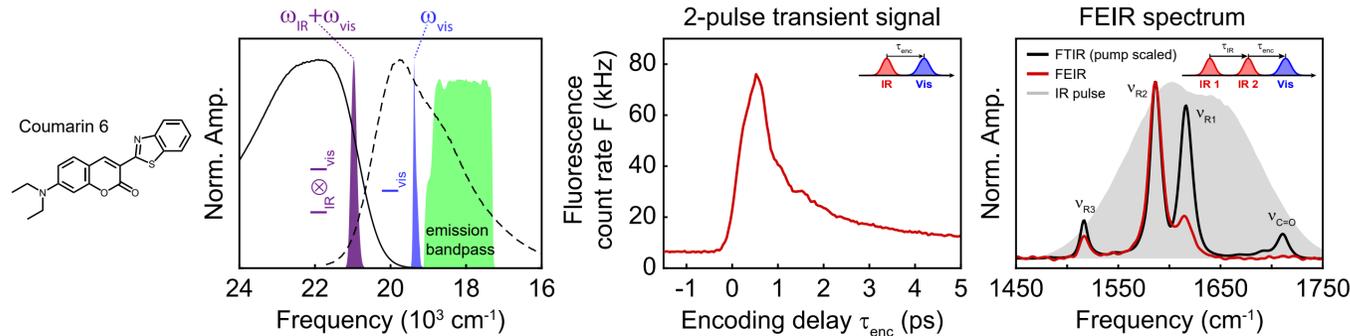
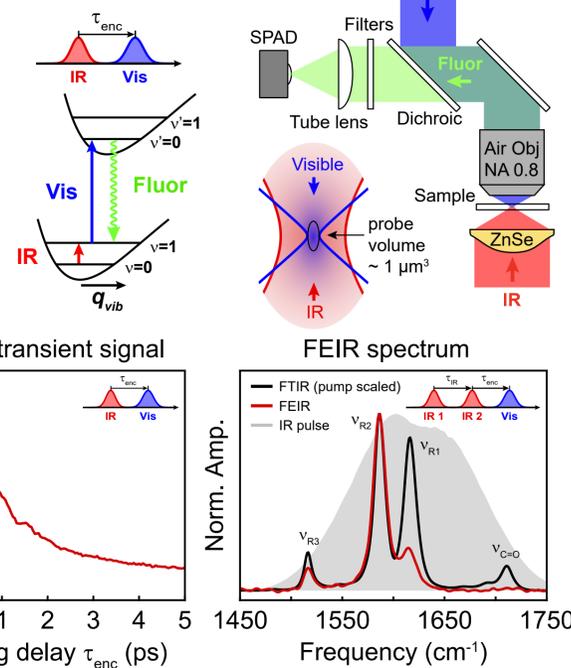


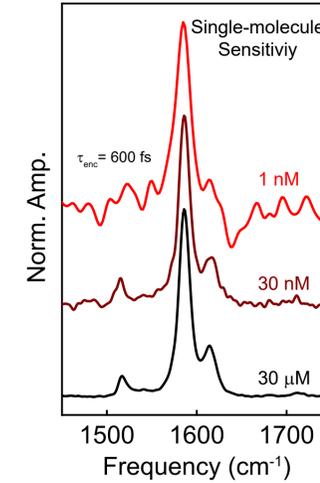
## Principles of FEIR Spectroscopy

IR spectroscopy has limited sensitivity due to low absorption cross-sections, poor mid-IR detectors, and a lack of vibrational luminescence. FEIR spectroscopy overcomes some of these limitations by up-converting the vibrational excitation with a pre-resonant visible pulse, producing a fluorescence signal that can be detected with sensitivity down to the single-molecule limit.

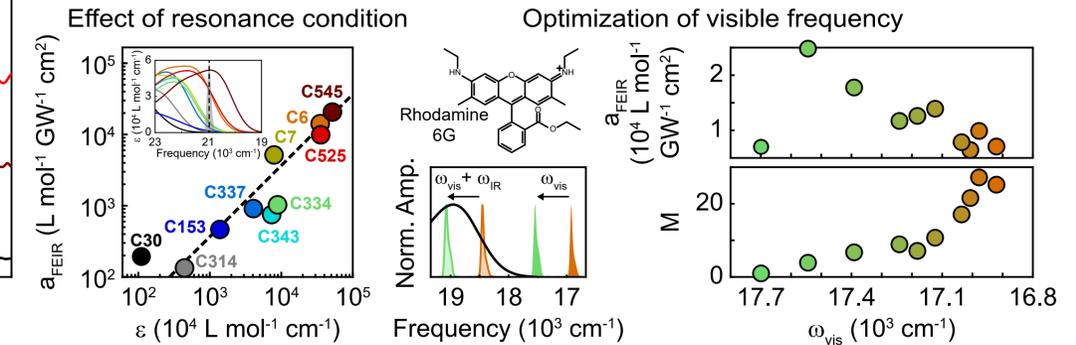


## Single-molecule sensitivity

Detection sensitivity to nM range (~ single-molecule equivalent)

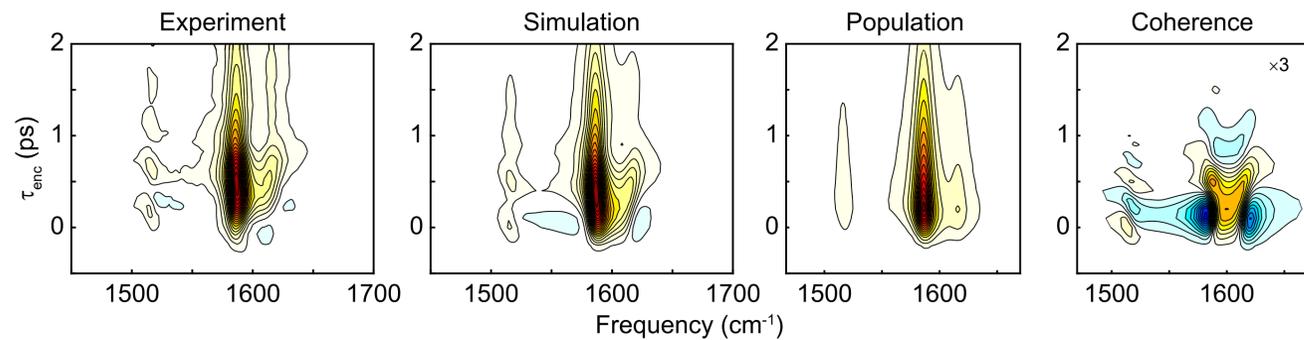
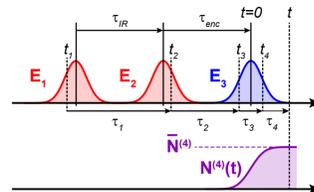


Fine-tuning the resonance condition for a chromophore provides a smooth control over the balance between the FEIR cross-section ( $a_{\text{FEIR}}$ ) and contrast  $M = (F_{\text{IR-on}} - F_{\text{IR-off}}) / F_{\text{IR-off}}$  to determine the best conditions for single-molecule level FEIR measurements.

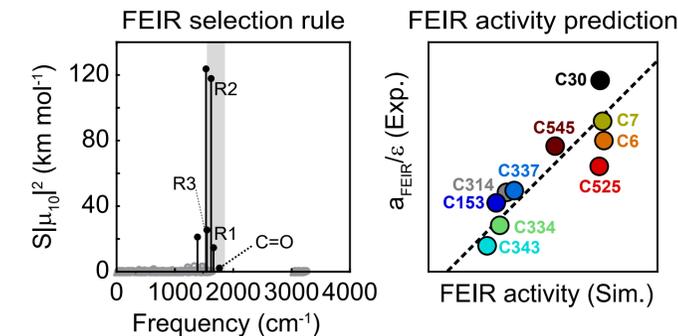


## Simulations of FEIR spectra

FEIR spectroscopy is the fourth-order action spectroscopy where the fluorescence signal is used as an indirect read-out of ground-state vibrational information. We use response function formalism to simulate the  $\tau_{\text{enc}}$ -dependent FEIR spectral surfaces.

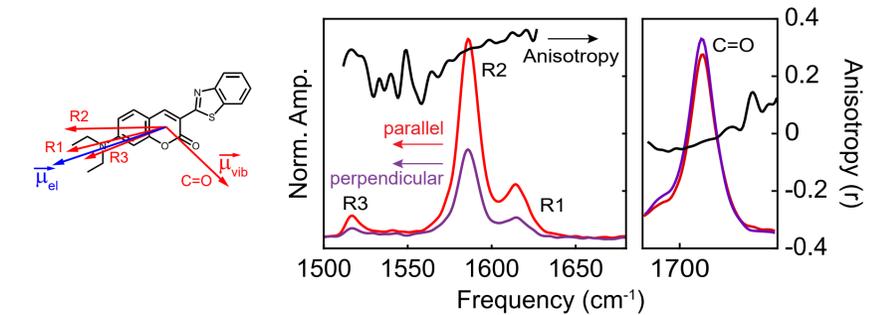


## Computational predictions of FEIR activity

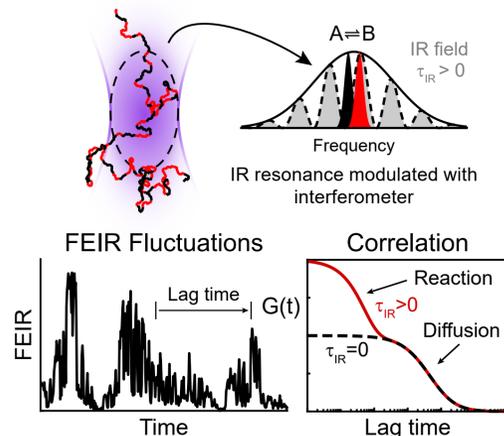


The FEIR activity is jointly determined by strengths of the vibrational transition dipole ( $\mu_{10}$ ) and vibronic coupling which is manifested by the Huang-Rhys factor ( $S$ ). We are developing computational models using electronic structure calculation to predict structures of FEIR active chromophores.

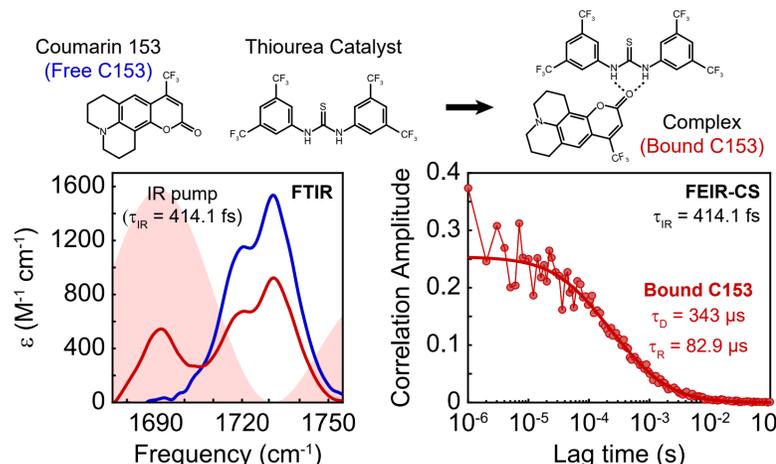
The FEIR activity is modulated by the relative orientation between the vibrational and electronic transition dipoles.



## Chemical Dynamics at the Single Molecule Level



Single-molecule measurements can provide chemical dynamic information with trajectories of molecular properties evolving within the equilibrium states. With selective excitation of specific molecular vibrations, FEIR trajectories can provide information about molecular dynamics at the length scale of a chemical bond.



The dynamics of chemical reactions in solution is hardly accessible with the existing single-molecule techniques due to their structural insensitivity or large perturbation. We are developing single-molecule techniques using structurally sensitive FEIR trajectory to understand chemical dynamics in the solution, such as H/D exchange, diffusion-limited bimolecular reaction, etc.