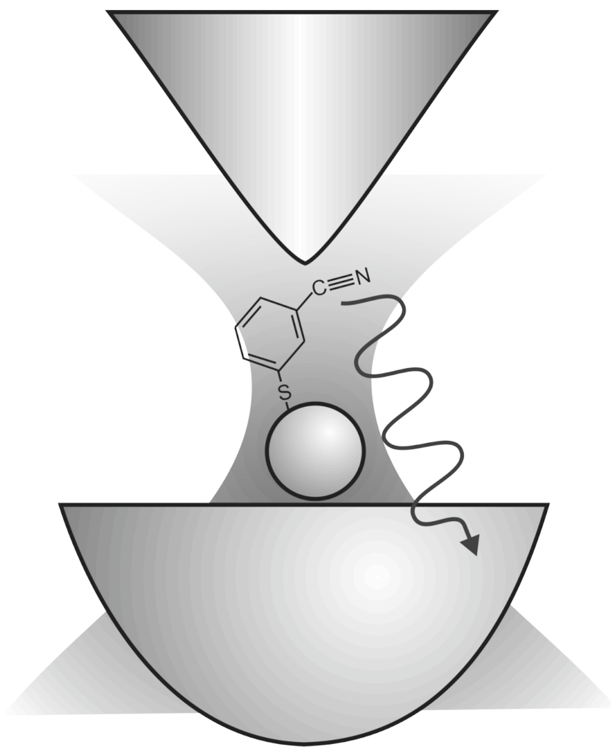
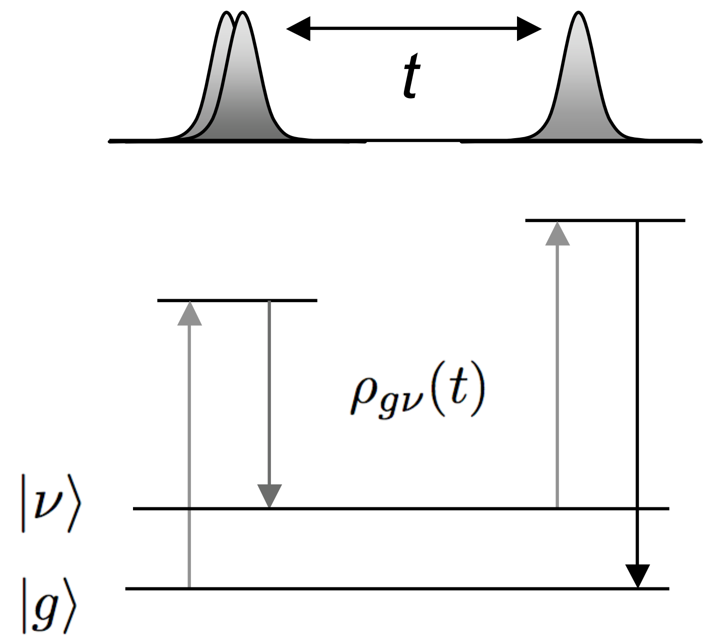
Single Molecule CARS





$$\rho_{g\nu}(t) = \sum_s p(s,t)\, c_g^s(t)\, c_\nu^{s*}(t)$$

Evolving Oscillator

Free propagation without perturbations:

$$\frac{d}{dt}\rho_{g\nu}(t) = -\frac{i}{\hbar}\left[H_0, \rho(t)\right]_{g\nu} - \frac{1}{2}\Gamma_\nu \rho_{g\nu}(t)$$

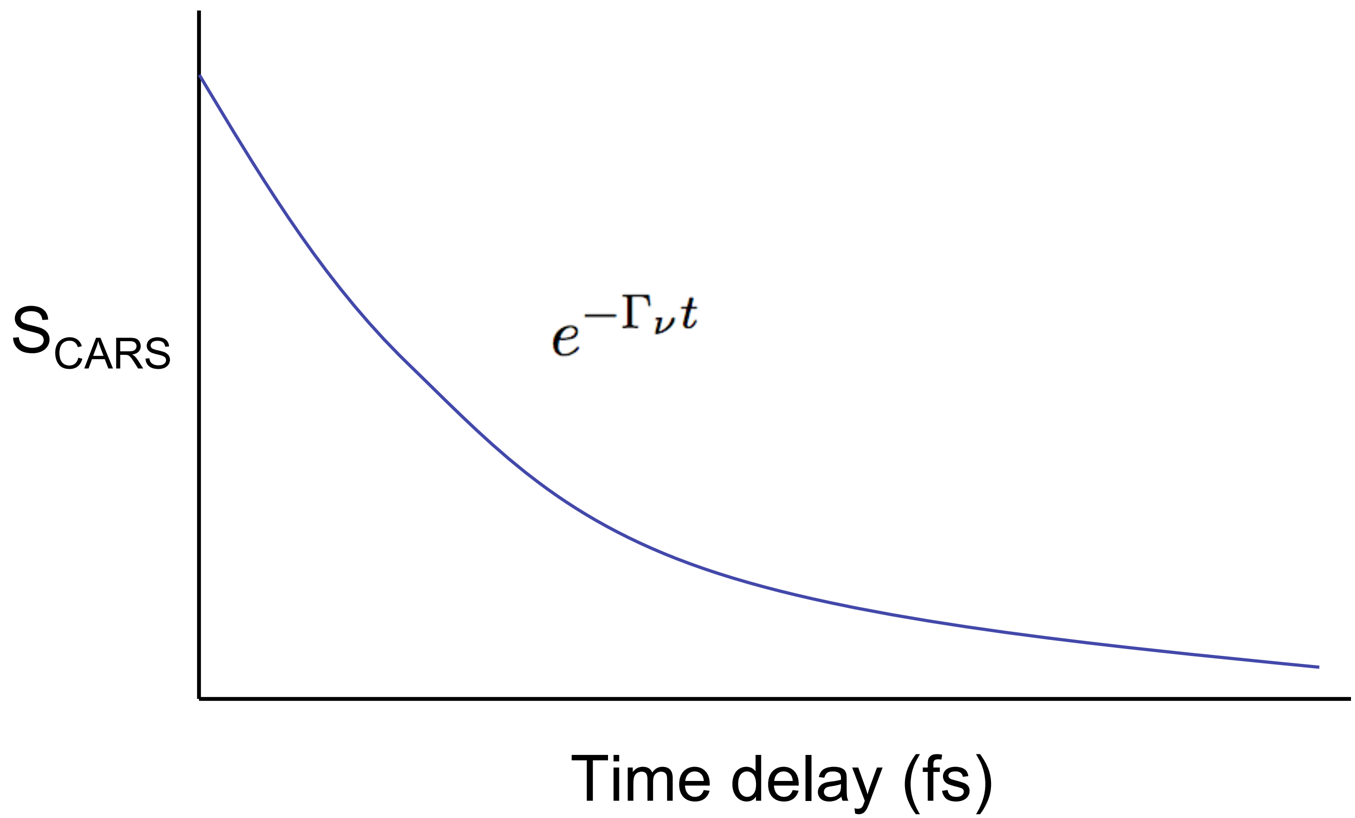
$$= -i\omega_{g\nu}\rho_{g\nu}(t) - \frac{1}{2}\Gamma_\nu \rho_{g\nu}(t)$$

$$\rho_{g\nu}(t) = e^{-(i\omega_{g\nu} + \frac{1}{2}\Gamma_\nu)t}$$

The signal then looks as follows:

$$S(t) = |P(t)|^2 \propto |\langle \mu(t) \rangle|^2 \propto |\rho_{\upsilon\nu}(t)\mu_{g\nu}|^2 \propto \left| e^{-(i\omega_{g\nu} + \frac{1}{2}\Gamma_\nu)t} \right|^2 = e^{-\Gamma_\nu t}$$

Time dependent signal



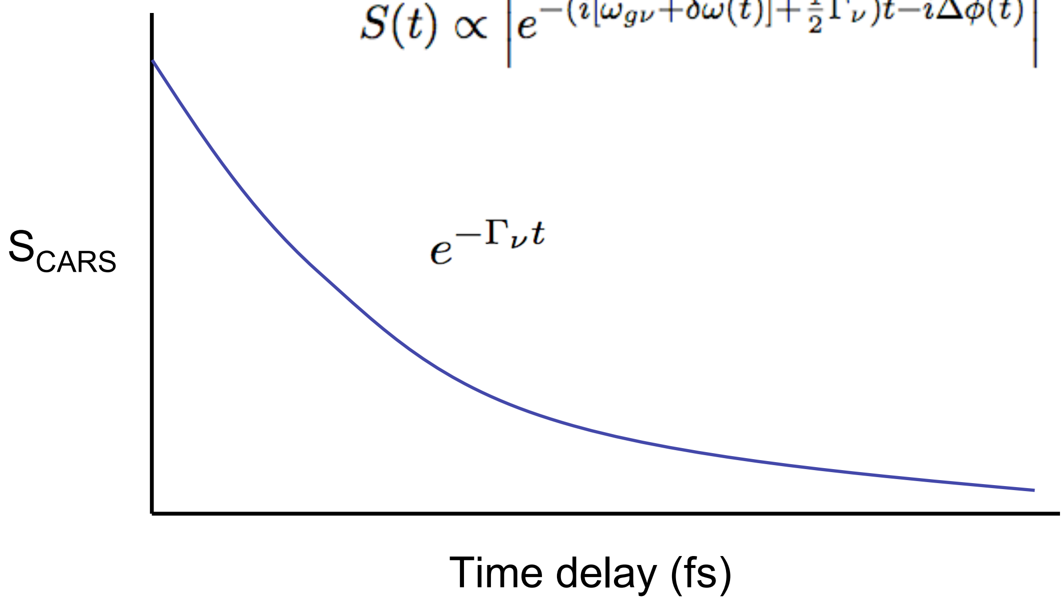
Evolving Oscillator

Free propagation with perturbations:

$$\rho_{g\nu}(t) \approx e^{-(i[\omega_{g\nu}+\delta\omega(t)]+\frac{1}{2}\Gamma_\nu)t-i\Delta\phi(t)}$$

Time-resolved signal:

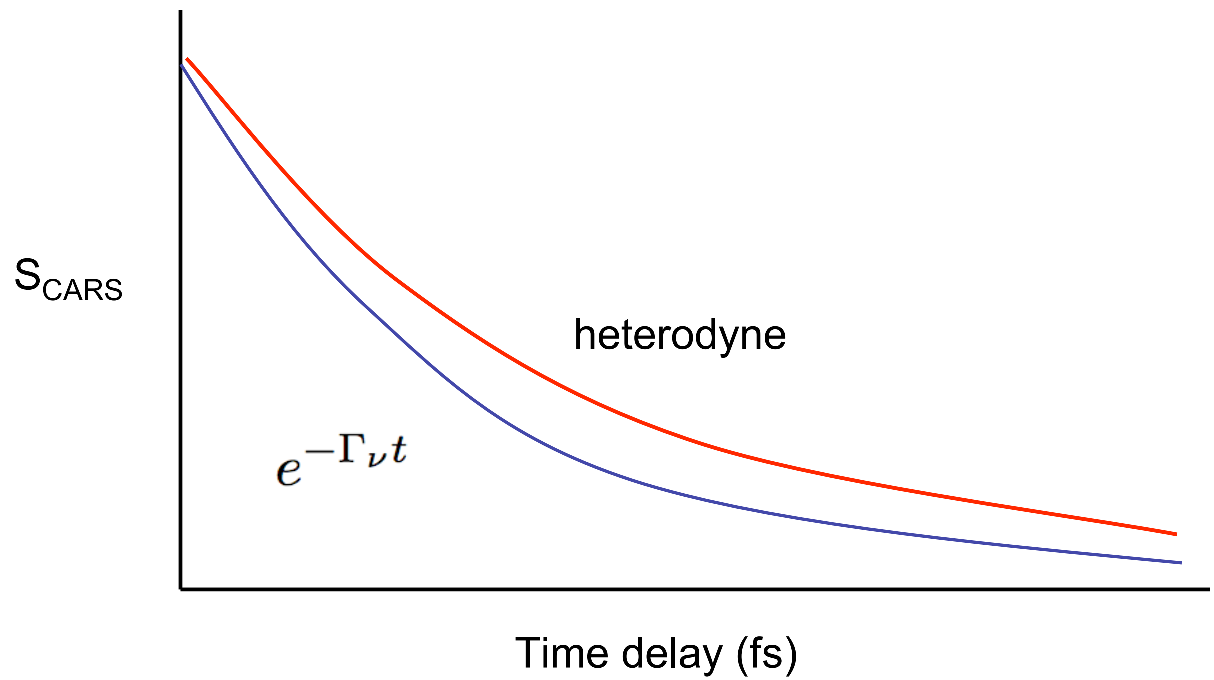
$$S(t) \propto \left|e^{-(i[\omega_{g\nu}+\delta\omega(t)]+\frac{1}{2}\Gamma_\nu)t-i\Delta\phi(t)}\right|^2 = e^{-\Gamma_\nu t}$$



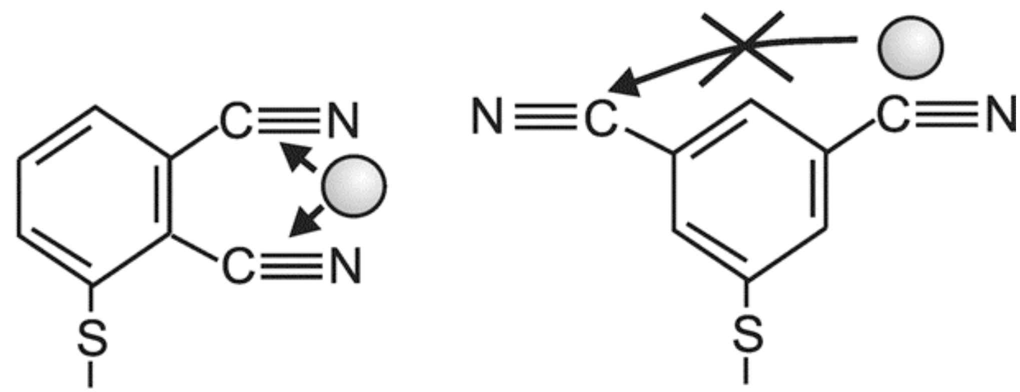
Heterodyne Detection

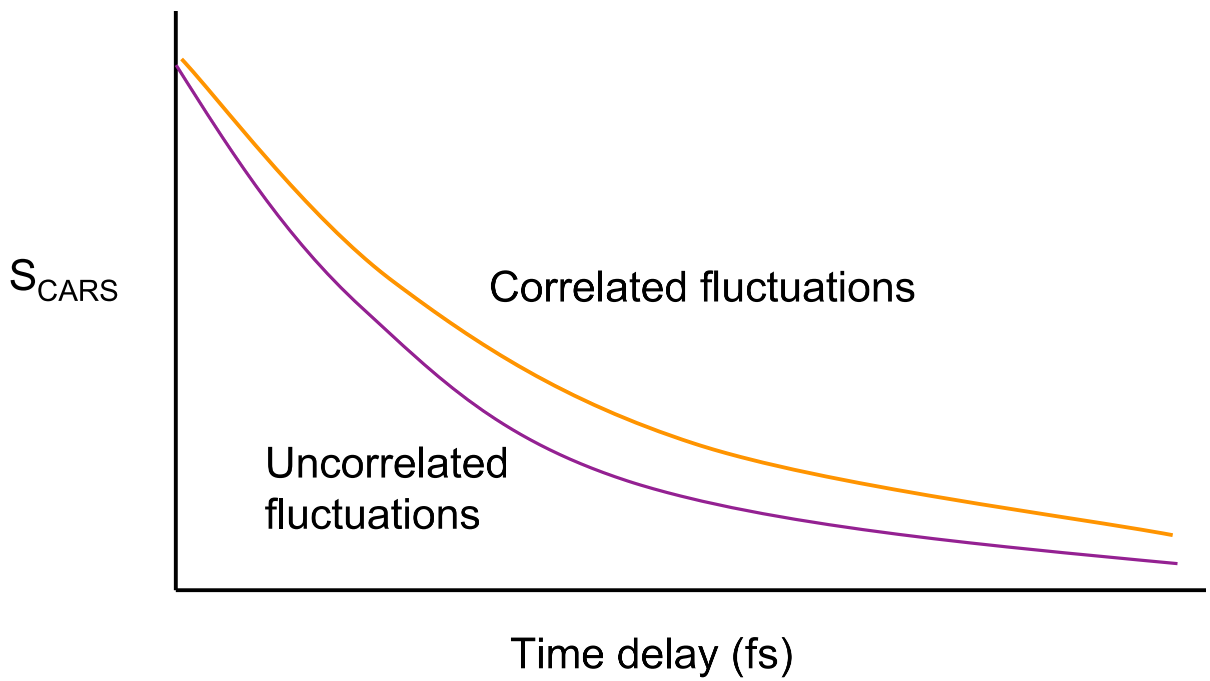
Mixing with another field allows detection of the phase fluctuations:

$$S(t) \propto e^{i\omega_o t} e^{-(i[\omega+\delta\omega(t)]+\frac{1}{2}\Gamma_\nu)t - i\Delta\phi(t)} \propto \sum_s Re\left[e^{-i\delta\omega_s(t)t - i\Delta\phi_s(t)}\right] e^{-\frac{1}{2}\Gamma_\nu t}$$



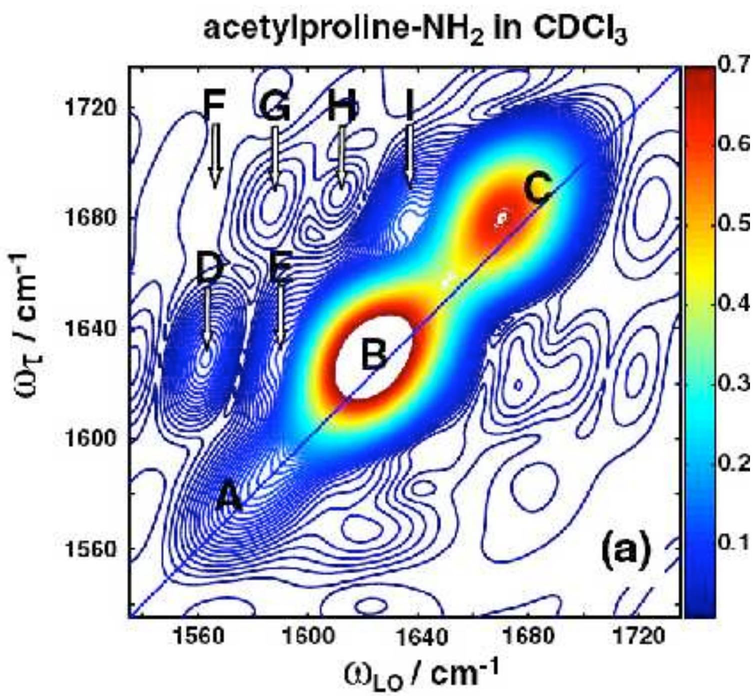
Two oscillators





Measuring intra-molecular correlations

Two-dimensional Infrared Spectroscopy (2D IR):



Crosspeaks show up as a result of dipolar couplings

Conclusion

Heterodyne time-resolved single molecule CARS experiments give new intra-molecular correlation information that does not rely on dipolar couplings.