Objectives:
1. Introduce Sum-Over-States (SOS) approaches derived from time-dependent perturbation theory for resonant NLO polarizabilities.
2. Reduce the general SOS forms down to simple, intuitive expressions.

Note: Citations to the contents of these slides should reference the following textbook:
Although potentially useful for qualitatively describing nonresonant SHG (e.g., in collagen) and the background in CARS, the adiabatic nonlinear polarizability cannot be reliably used to describe the most interesting measurements, performed near a vibrational or electronic resonance.

Alternative formalism: Time-dependent perturbation theory.

Final result:

$$\beta^{ijk}_{00}(-2\omega ; \omega, \omega) = \sum_m S_m (2\omega) \bar{\mu}_{0m} \otimes \alpha^{(1)}_{m0}$$  
Electronic SHG

Two-photon absorption matrix

$$\beta^{ijk}_{00}(-\omega_3 ; \omega_1, \omega_2) = \sum_n S_n (\omega_2) \alpha^{(1)}_{0n} \otimes \bar{\mu}_{n0}$$  
Vibrational SFG

Transition moment

Complex-valued lineshape function

Garth J. Simpson
From the top: The near-resonant polarizability describes a two-wave process including both “excitation” and coherent emission.

\[
\alpha^{ij}(-\omega; \omega) = \sum_n \frac{\mu^{i}_n \mu^{j}_n}{\hbar \omega_{n0} - \hbar \omega - i\hbar \Gamma_{n0}} + \frac{\mu^{j}_n \mu^{i}_n}{\hbar \omega_{n0} + \hbar \omega + i\hbar \Gamma_{n0}}
\]

\[
\approx \frac{\mu^{i}_0 \mu^{j}_0}{\hbar \omega_{n0} - \hbar \omega - i\hbar \Gamma_{n0}} + NR
\]

(Near resonance)

Garth J. Simpson
Near resonance for systems initially in the ground state, only the first (red) term contributes significantly.

\[ \alpha_{ij} (-\omega; \omega) = -\sum_n \frac{\mu_{in}^i \mu_{jn}^j}{\hbar \omega_{n0} - \hbar \omega - i\hbar \Gamma_{n0}} + \frac{\mu_{jn}^j \mu_{in}^i}{\hbar \omega_{n0} + \hbar \omega + i\hbar \Gamma_{n0}} \]

In blue, the \(-\hbar \omega\) term comes first in the interaction-ordering, corresponding to enhancement with a lower lying state (stimulated emission).

*Note the sign convention on the damping term \(+i\Gamma\), which must be positive for stimulated emission to arise.

Garth J. Simpson
The Contracted SOS

End results:

\[
\beta_{ijk}^{(-2\omega; \omega, \omega)} = -\frac{1}{\hbar} \sum_n \frac{\mu_{0n}^{i} \alpha_{n0}^{jk}}{\omega_{n0} - 2\omega - i\Gamma_{n0}} + NR_{ijk}^{i}
\]

In SHG, the hyperpolarizability is dominated by the one-photon transition moment \( \mu_{0n} \) and the two-photon absorption matrix \( \alpha_{n0} \).

\[
\beta_{ijk}^{(-\omega_{sum}; \omega_{vis}, \omega_{ir})} = -\frac{1}{\hbar} \sum_n \frac{\alpha_{0n}^{ij} \mu_{n0}^k}{\omega_{n0} - \omega_{ir} - i\Gamma_{n0}} + NR_{ijk}^{i}
\]

In SFG, the hyperpolarizability is dominated by the Raman polarizability matrix \( \alpha_{0n} \) and the one-photon infrared transition moment \( \mu_{n0} \).

How do we get these different outcomes from time-dependent perturbation theory? We start with 3! = 6 different pathways to consider.
Next, we pick the two pathways relevant to the resonance of interest.

For vibrational SFG (one-photon resonance with $\omega_2$):

The two terms from the six possible that describe this interaction:

$$\beta^{ijk}(\omega_{\text{sum}}; \omega_{\text{vis}}, \omega_{\text{ir}}) = \frac{-1}{2\hbar^2} \sum_p \sum_r \frac{\mu^i_{0r} \mu^j_{rp} \mu^k_{p0}}{(\omega_{r0} - \omega_{\text{sum}} - i\Gamma_{r0}) (\omega_{r0} - \omega_{\text{sum}} - i\Gamma_{r0})} + \frac{\mu^j_{0r} \mu^i_{rp} \mu^k_{p0}}{(\omega_{r0} - \omega_{\text{sum}} - i\Gamma_{r0})} \cdot \frac{\mu^k_{p0}}{(\omega_{p0} - \omega_{\text{ir}} - i\Gamma_{p0})} + NR^{ijk}$$

$$= \frac{-1}{2\hbar} \sum_p \frac{\alpha^{jk}_{0p} \mu^k_{p0}}{(\omega_{p0} - \omega_{\text{ir}} - i\Gamma_{p0})} + NR^{ijk}$$
The Contracted SOS

The answer: Contraction of the SOS expressions! Group the pathways into pairs sharing the desired resonance enhancement with $\omega_2$.

Close to vib. resonance, the molecular tensor is given by the direct product of the anti-Stokes Raman tensor and the one-photon transition moment.

But this is just the SOS expression for anti-Stokes Raman!

$$\beta_{00}^{ijk} (-\omega_3; \omega_1, \omega_2) = -\frac{1}{2\hbar^2} \sum_n \sum_m \left\{ \frac{\mu_{0m}^i \mu_{mn}^j \mu_{n0}^k}{(\omega_n - \omega_2 - i\Gamma_n)(\omega_m - \omega_3 - i\Gamma_m)} + \frac{\mu_{0m}^i \mu_{mn}^j \mu_{n0}^k}{(\omega_n - \omega_2 - i\Gamma_n)(\omega_m + \omega_2 + i\Gamma_m)} \right\}$$

$$\beta_{00}^{ijk} (-\omega_3; \omega_1, \omega_2) = -\frac{1}{2\hbar} \sum_n \frac{\mu_{n0}^k}{(\omega_n - \omega_2 - i\Gamma_n)} \left\{ \frac{1}{\hbar} \sum_m \frac{\mu_{0m}^i \mu_{mn}^j}{(\omega_m - \omega_3 - i\Gamma_m)} + \frac{\mu_{0m}^i \mu_{mn}^j}{(\omega_m + \omega_2 + i\Gamma_m)} \right\}$$

$$\beta_{00}^{ijk} (-\omega_3; \omega_1, \omega_2) = -\frac{1}{2\hbar} \sum_n \left\{ \frac{\alpha_{0n}^{ij} \mu_{n0}^k}{\omega_n - \omega_2} \right\} + NR$$

Garth J. Simpson
The CATS signal responsible for the nonresonant bkg in CARS is dominated by two-photon resonances.

The CARS signal is dominated by the direct product of two coherent Raman transitions.

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Garth J. Simpson
1. Time-dependent perturbation theory provides a framework for recovering both the resonant and nonresonant molecular response.
2. Contraction allows re-expression without additional assumption or approximation.
3. Simple inspection of the energy level diagram allows identification of the contracted form that is consistent with the particular resonant NLO process probed, with the remaining contributions contained within a nonresonant background term.

References: