These notes compare fluorescence detected two-dimensional photo echo spectroscopy in the widely used four-wave mixing approach with a fluorescence detected wave-packet interferometry (md-WPI) version, using the example of an energy-transfer dimer. They will form the basis for a chapter in my forthcoming graduate-level molecular spectroscopy textbook. A similar analysis should apply to any form of action-signal detection of a phase-coherent electronic interferogram, including photoelectron detection, for example.

My University of Oregon colleague, Andy Marcus, who has developed a phase-modulation electronic coherence spectroscopy technique (pm-ECS) for carrying out experiments of this kind, brought to my attention the importance of including the different quantum yields for different electronic states in calculating the md-WPI signal.

The analysis presented here is framed in a sufficiently general way that it applies in the basis of electronic site states, exciton states, or adiabatic electronic states. It uses pulse propagators to describe the interaction of the arbitrarily oriented system with a sequence of polarized femtosecond laser pulses. Although the basic expressions are given in terms of wave packet overlaps using pure nuclear states, the generalization to mixed states in a density matrix treatment is automatic and straightforward.

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25 January 2011
Comparing mid-WPI FWM signals from an EET dimer. A tale of three bases and two measurement strategies.

Dimer Hamiltonian \[ H = T + H_{el}(Q) \]

\[ H_{el}(Q) = \langle e g | V_{gg}(Q) | e g \rangle + \langle e e | V_{ee}(Q) | e e \rangle \\
+ \langle e g | V_{eg}(Q) | e e \rangle + \langle e e | V_{ee}(Q) | e g \rangle \\
+ J(Q) (\langle e g | e g + \langle e e | e g \rangle) \] in the basis of site states. Alternatively, in the basis of adiabatic electronic states,

\[ H_{el}(Q) = \langle 0 | E_0(Q) | 0 \rangle + \langle 1' | E_{1'}(Q) | 1' \rangle \\
+ \langle 1 | E_{1}(Q) | 1 \rangle + \langle 2 | E_{2}(Q) | 2 \rangle \]

The relationship between these two expressions for the electronic Hamiltonian is easy to determine. Set

\[ \theta_{one} = \langle e g | e g \rangle + \langle e e | e g \rangle \]
\[ \sigma_y = -i(\langle e g | e g \rangle + \langle e e | e g \rangle) \]
\[ \sigma_x = \langle e g | e g \rangle + \langle e e | e g \rangle \]
\[ \sigma_z = \langle e g | e g \rangle - \langle e e | e g \rangle \].

* We neglect higher excited states involving high electronic excitations of either monomer such as \( | e' g \rangle \) or \( | e e' \rangle \) (for the sake of simplicity), rather than including them (for the sake of complication).
Then
\[ \text{legXgel} = \frac{1}{2} \left( \sigma_{\text{one}} + \sigma_z \right) \quad \text{legXael} = \frac{1}{2} \left( \sigma_{\text{one}} - \sigma_z \right) \]
\[ \text{legXge} = \frac{1}{2} \left( \sigma_x + i \sigma_y \right) \quad \text{legXegl} = \frac{1}{2} \left( \sigma_x - i \sigma_y \right) \]
and
\[ H_{e\ell}(Q) = \text{legXgel} \text{V}_{gg}(Q) + \sigma_{\text{one}} \frac{1}{2} \left( \text{V}_{eg}(Q) + \text{V}_{ge}(Q) \right) \]
\[ + \sigma_z \frac{1}{2} \left( \text{V}_{eg}(Q) - \text{V}_{ge}(Q) \right) + \text{leexeel} \text{V}_{ee}(Q) + \sigma_z J(Q) \]
\[ \equiv K(Q) \]

\[ M(Q) = \sqrt{J^2(Q) + K^2(Q)} \]

\[ H_{e\ell}(Q) = \text{legXgel} \text{V}_{gg}(Q) + \sigma_{\text{one}} L(Q) + \sigma_z M(Q) \cos \theta(Q) \]
\[ + \sigma_x M(Q) \sin \theta(Q) + \text{leexeel} \text{V}_{ee}(Q) \]
\[ = \text{legXgel} \text{V}_{gg}(Q) + \sigma_{\text{one}} L(Q) \]
\[ + M(Q) e^{-i \frac{\theta(Q)}{2} \sigma_y} e^{i \frac{\theta(Q)}{2} \sigma_y} + \text{leexeel} \text{V}_{ee}(Q) \].
Thus, the adiabatic eigenenergies appearing on p. 1 are

\[ E_0(Q) = V_{gg}(Q) \]
\[ E_1(Q) = L(Q) - M(Q) \]
\[ E_2(Q) = L(Q) + M(Q) \]
\[ E_2(Q) = V_{ee}(Q) \]

while the corresponding adiabatic electronic eigenstates are

\[ |10\rangle = |g g\rangle \]
\[ |11\rangle = e^{-\frac{i\theta(Q)}{2} \sigma_y} |g e\rangle = (\cos \frac{\theta(Q)}{2} - i \sigma_y \sin \frac{\theta(Q)}{2}) |g e\rangle = |g e\rangle \cos \frac{\theta(Q)}{2} - |e g\rangle \sin \frac{\theta(Q)}{2} \]
\[ |11\rangle = e^{-\frac{i\theta(Q)}{2} \sigma_y} |e g\rangle = |g e\rangle \sin \frac{\theta(Q)}{2} + |e g\rangle \cos \frac{\theta(Q)}{2} \]
\[ |12\rangle = |e e\rangle \]

Yet another electronic basis is also popular. We identify the adiabatic electronic states at the fixed nuclear configuration corresponding to the equilibrium position "Q = 0" of the electronic ground state as the exciton basis,

\[ |10\rangle \equiv |g g\rangle \]
\[ |11\rangle \equiv |g e\rangle = |g e\rangle \cos \frac{\theta}{2} - |e g\rangle \sin \frac{\theta}{2} \]
\[ |12\rangle \equiv |e g\rangle \]
\[ |12\rangle \equiv |e e\rangle \]
We can now write \( H_{el}(Q) = H_{el} + \nu(Q) \), with

\[
H_{el} \equiv H_{el}(0) = 10\langle E_0 \rangle 01 + 11\langle E_4 \rangle 11 + 12\langle E_2 \rangle 21
\]

and (from p. 1)

\[
\nu(Q) = H_{el}(Q) - H_{el} = \iota_{ag}\langle ag| (V_{ag}(Q) - V_{ag}) + 1_{ge}\langle ge| (V_{ge}(Q) - V_{ge}) + 1_{ee}\langle ee| (V_{ee}(Q) - V_{ee}) + (1_{eg}\langle eg| + 1_{ge}\langle ge|) (S(Q) - I)
\]

We want \( \nu(Q) \) in the exciton rep'n and so seek

\[
\langle 0|\nu(Q)|10\rangle = V_{gg}(Q) - V_{gg} = 0 \quad ; \quad \langle 2|\nu(Q)|2\rangle = \delta V_{ee}(Q)
\]

\[
\langle 1'|\nu(Q)|1'\rangle = (\cos \frac{\Theta}{2} \langle ge| - \sin \frac{\Theta}{2} \langle eg|) \nu(Q) (\langle ge| \cos \frac{\Theta}{2} - \langle eg| \sin \frac{\Theta}{2})
\]

\[
\overset{\downarrow}{=} (V_{ge}(Q) - V_{ge}) \cos^2 \frac{\Theta}{2} + (V_{eg}(Q) - V_{eg}) \sin^2 \frac{\Theta}{2}
\]

\[
- (S(Q) - I) \sin \Theta
\]

\[
= (V_{ge}(Q) - V_{ge}) \frac{1}{2} (1 + \cos \Theta) + (V_{eg}(Q) - V_{eg}) \frac{1}{2} (1 - \cos \Theta)
\]

\[
- (S(Q) - I) \sin \Theta
\]

\[
\langle 1'|\nu(Q)|1'\rangle \approx \frac{\delta V_{ge}(Q) + \delta V_{eg}(Q)}{2} + \frac{\delta V_{ge}(Q) - \delta V_{eg}(Q)}{2} \cos \Theta
\]

\[
- \delta S(Q) \sin \Theta
\]

\[
\langle 1|\nu(Q)|1\rangle = \frac{\delta V_{ge}(Q) + \delta V_{eg}(Q)}{2} - \frac{\delta V_{ge}(Q) - \delta V_{eg}(Q)}{2} \cos \Theta
\]

\[
+ \delta S(Q) \sin \Theta
\]
\[ \langle 1' | \mathcal{V}(Q) | 1 \rangle = \frac{\delta V_{ge}(Q)}{Z} \sin \theta - \frac{\delta V_{eg}(Q)}{Z} \sin \theta \]

\[ = \frac{\delta V_{ge}(Q) - \delta V_{eg}(Q)}{Z} \sin \theta + \delta J(Q) \cos \theta \]

\[ = \langle 1' | \mathcal{V}(Q) | 1 \rangle . \]

Whence, in the exciton basis,

\[ \mathcal{V}(Q) = 10 \times 1 \delta V_{eg}(Q) + 11' \times 1' \left[ \frac{\delta V_{ge}(Q) + \delta V_{eg}(Q)}{Z} + \frac{\delta V_{ge}(Q) - \delta V_{eg}(Q)}{Z} \cos \theta \right. \]

\[ - \delta J(Q) \sin \theta \left. \right] + 11 \times 1 \left[ \frac{\delta V_{ge}(Q) + \delta V_{eg}(Q)}{Z} - \frac{\delta V_{ge}(Q) - \delta V_{eg}(Q)}{Z} \cos \theta \right. \]

\[ + \delta J(Q) \sin \theta \left. \right] + (11 \times 1' + 1' \times 1) \left[ \frac{\delta V_{ge}(Q) - \delta V_{eg}(Q)}{Z} \sin \theta + \delta J(Q) \sin \theta \right. \]

\[ + 12 \times 2 \delta V_{ee}(Q) \]. \]

In order to compare FWM and fluorescence-detected WPI approaches to multi-dimensional electronic spectroscopy measurements on EET systems, we add a time-dependent field interaction term,

\[ \mathcal{V}(t) = -\mu \cdot E(t) \] to the Hamiltonian. Here the dipole moment operator

\[ \mu = \mu_a + \mu_b = m_a (1e_a X 00l + 1e_l X g_1) \]

\[ + m_b (1e_a X 00l + 1e_l X g_1) + H.c. \]

in the site representation.
We can also write (from p. 3)

$$|ge\rangle = |1'(0)\rangle \cos \frac{\theta(0)}{2} + |1(0)\rangle \sin \frac{\theta(0)}{2}$$

$$|eg\rangle = -|1'(0)\rangle \sin \frac{\theta(0)}{2} + |1(0)\rangle \cos \frac{\theta(0)}{2}$$

and use substitution to obtain

$$\mathcal{M} = \sum_{a} \left( -|1'(0)\rangle \cos \frac{\theta(0)}{2} + |1(0)\rangle \sin \frac{\theta(0)}{2} \right)$$

$$+ \frac{m_a}{2} \left( |1'(0)\rangle \sin \frac{\theta(0)}{2} + |1(0)\rangle \cos \frac{\theta(0)}{2} \right)$$

$$+ \frac{m_b}{2} \left( |1'(0)\rangle \cos \frac{\theta(0)}{2} + |1(0)\rangle \sin \frac{\theta(0)}{2} \right)$$

$$- |2 \times 1'(0)\rangle \cos \frac{\theta(0)}{2} + |2 \times 1(0)\rangle \sin \frac{\theta(0)}{2}$$

In the adiabatic representation.

In the exciton basis, we therefore have

$$\mathcal{M} = |1'(0)\rangle \cos \frac{\theta(0)}{2} + |1(0)\rangle \sin \frac{\theta(0)}{2} \right)$$

$$+ |1\rangle \cos \frac{\theta(0)}{2} + |1\rangle \sin \frac{\theta(0)}{2} \right)$$

$$+ |1'\rangle \cos \frac{\theta(0)}{2} + |1\rangle \sin \frac{\theta(0)}{2} \right)$$

$$+ |2 \times 1\rangle \cos \frac{\theta(0)}{2} + |2 \times 1\rangle \sin \frac{\theta(0)}{2} \right) + \text{H.c.}$$
The electric field consists of four pulses

\[ E(t) = \sum_{I=A,B,C,D} E_I(t) = \sum_{I=A,B,C,D} E_I(t) = E_I(t - t_I(t)) \cos \left( \frac{2\pi}{\lambda_I} (t - t_I(t)) \right). \]

\( t_I(t) \) is an envelope function localized around \( t = 0 \) and having a temporal width \( \sigma_I \). The phase function has the form \( \Phi_I(t) = \frac{n_I}{c} t + \theta_I \) and the arrival time \( t_I = \frac{n_I}{c} t + \theta_I \). \( n_I \) is a unit vector in the direction of propagation of the \( I \)th pulse, and \( c \) is the speed of light.

The pulses arrive in sequence, so we will typically assume \( t_A \leq t_B \leq t_C \leq t_D \). But when we consider spectral interferometry, we will instead assume \( t_D \leq t_C \leq t_B \leq t_A \).

\[ \frac{i}{\hbar} \frac{\partial}{\partial t} |\psi(t)\rangle = (H + V(t)) |\psi(t)\rangle \]

with an initial condition \( |\psi(t < t_A(c))\rangle = e^{-iH(t-t_A(c))/\hbar} |\psi_0\rangle \).

\( |\psi_0\rangle \) could be an eigenstate of the Hamiltonian \( H_{2\Omega} \), or a wave packet - an arbitrary linear superposition of such nuclear eigenstates.
In the interaction picture, \( |\tilde{\Psi}(t)\rangle = e^{-i\mathcal{H}(t-t_A)\frac{\hbar}{i}} |\tilde{\Psi}(t)\rangle \).

\( 1_{\tilde{\Psi}}(t) = 1_{\Psi(t)}(t_A) \) \( (= \text{constant}) \).

\[
\frac{\hbar}{\partial t} |\tilde{\Psi}(t)\rangle = e^{-i\mathcal{H}(t-t_A)\frac{\hbar}{i}} \left\{ -\mathcal{H} + \mathcal{V}(t) \right\} |\tilde{\Psi}(t)\rangle
\]

\[
= \mathcal{V}(t) |\tilde{\Psi}(t)\rangle.
\]

\[
\mathcal{V}(t) = e^{-\mathcal{H}(t-t_A)\frac{\hbar}{i}} \mathcal{V}(t) e^{-i\mathcal{H}(t-t_A)\frac{\hbar}{i}}.
\]

The formal solution is

\[
|\tilde{\Psi}(t)\rangle = 1_{\Psi(\infty)}(t) + \frac{i}{\hbar} \int_{-\infty}^{t} d\tau \mathcal{V}(\tau) |\tilde{\Psi}(\tau)\rangle.
\]

The perturbative solution through 3rd order is

\[
|\tilde{\Psi}(t)\rangle = \left\{ 1 + \frac{i}{\hbar} \int_{-\infty}^{t} d\tau \mathcal{V}(\tau) + \left( \frac{i}{\hbar} \right)^2 \int_{-\infty}^{t} d\tau \int_{-\infty}^{\tau} d\tau' \mathcal{V}(\tau) \mathcal{V}(\tau') \right\}
\]

\[
\left\{ 1 + \frac{i}{\hbar} \int_{-\infty}^{t} d\tau \int_{-\infty}^{\tau} d\tau' \int_{-\infty}^{\tau'} d\tau'' \mathcal{V}(\tau) \mathcal{V}(\tau') \mathcal{V}(\tau'') \right\} |\tilde{\Psi}(t)\rangle.
\]

Introducing the notation \([+\tau] = e^{-i\mathcal{H}\tau}/\hbar\) and returning to the Schrödinger picture gives

\[
|\Psi(t)\rangle = \left\{ [t-t_A(\tau)] + \frac{i}{\hbar} \int_{-\infty}^{t} d\tau [t-\tau] \mathcal{V}(\tau) [\tau-t_A(\tau)]
\right.
\]

\[
+ \left( \frac{i}{\hbar} \right)^2 \int_{-\infty}^{t} d\tau \int_{-\infty}^{\tau} d\tau' \mathcal{V}(\tau) [\tau-\tau'] \mathcal{V}(\tau') [\tau'-t_A(\tau)]
\]

\[
+ \left( \frac{i}{\hbar} \right)^3 \int_{-\infty}^{t} d\tau \int_{-\infty}^{\tau} d\tau' \int_{-\infty}^{\tau'} d\tau'' \mathcal{V}(\tau) \mathcal{V}(\tau') \mathcal{V}(\tau'') [\tau''-t_A(\tau'')]
\right\} |\Psi(t)\rangle.
\]
We introduce pulse propagators,

\[ P_{ij}(t;\tau) = \frac{i}{\hbar} \int_{-\infty}^{t} d\tau' \left[ t_{ij}(\tau') - \tau \right] \psi_{ji}(\tau') \left[ t - t_{ij}(\tau) \right], \]

and, for the various interpulse delays, use the notation

\[ t_{ij}(\tau) = t_{i}(\tau) - t_{j}(\tau) = t_{ij} + n_{ij} \Delta \tau / c. \]

Then,

\[ |\Psi(t)\rangle = |t - t_A(\tau)\rangle \left\{ 1 + \sum_{I=A,B,C,D} \left[ t_{AI}(\tau) \right] P_{ij}(t;\tau) \left[ t_{IA}(\tau) \right] \right\} + \sum_{IJ} \left[ t_{AI}(\tau) \right] P_{ij}(t;\tau) \left[ t_{IJ}(\tau) \right] P_{IJ}(t;\tau) \left[ t_{JA}(\tau) \right] + \sum_{IK} \left[ t_{AI}(\tau) \right] P_{ij}(t;\tau) \left[ t_{IJ}(\tau) \right] P_{IK}(t;\tau) \left[ t_{JA}(\tau) \right] \right\} |\Psi_0\rangle. \]

We could work out the FWHM and mid-WPI signal expressions using any of the three electronic bases, but here bypass the adiabatic basis in favor of the two fixed bases

\( \{1g5\}, \{1g6\}, \{1e6\}, \{1e7\} \) and \( \{10\}, \{11\}, \{12\}, \{12\} \), and use generic electronic states \( \{15\} \) to refer to either one.

For the sake of the simplification, thereby enabled, we will assume the pulses impinging on the sample are genuinely ultrafast on at least one timescale. Either \( \sigma \ll \frac{1}{2\pi/\tau} \), so that EET can be neglected for the duration of a laser pulse, or \( \sigma \ll \frac{1}{2\pi/(V_{ge} - V_{eg})} \),
so that nuclear dynamics can be neglected for the pulse duration (or both). The former (latter) condition is easier to meet if the energy-transfer coupling is smaller (larger) than the Franck-Condon energies. In the first instance (of small $J$) it is convenient to work in the site basis; in the second (weak electron-vibration coupling) it is natural to use the exciton basis. In the appropriate basis (or bases) then,

$$\langle \tilde{S} | \mathcal{P}_I(t; \tau) | \tilde{S} \rangle \equiv \frac{i}{\hbar} \int_{-\infty}^{+\infty} dt \ [t \tilde{E}_I(t) - \tilde{t}_I(t)]_{\tilde{S}S} \tilde{S} \cdot \mathcal{E} \tilde{E}_I(t) [\tilde{t} - t \tilde{E}_I(t)]_{S \tilde{S}}$$

in which the single-state nuclear propagators $[t]_{SS}$\n
$$\equiv \langle \tilde{S} | [t] \tilde{S} \rangle$$\n
are calculated with $J$ (v) set equal to zero if $| \tilde{S} \rangle$ is a site state (exciton state).

Making the usual rotating-wave approximation and taking the specific example of an upward electronic transition, $\tilde{S} \leftarrow \tilde{E}$, we can further introduce a reduced pulse propagator having matrix elements

$$\mathcal{P}_I^{(\tilde{S} \tilde{E})}(t; \tau) \equiv \frac{i}{\hbar} \int_{-\infty}^{+\infty} dt \ [t \tilde{E}_I(t) - \tilde{t}_I(t)]_{\tilde{S}S} \tilde{S} \cdot \mathcal{E} \tilde{E}_I(t) [\tilde{t} - t \tilde{E}_I(t)]_{S \tilde{S}} \ e^{-i\tilde{O}_I(t-t \tilde{E}_I(t))}$$

It then follows that

$$\langle \tilde{S} | \mathcal{P}_I(t; \tau) | \tilde{E} \rangle \equiv \tilde{E} \langle \tilde{E} | \mathcal{P}_I(t; \tau) | \tilde{S} \rangle \ e^{-i\tilde{O}_I(t-t \tilde{E}_I(t))}$$

$$\langle \tilde{S} | \mathcal{P}_I(t; \tau) | \tilde{S} \rangle \equiv \tilde{M} \langle \tilde{S} | \tilde{S} \rangle \ e^{-i\tilde{O}_I(t-t \tilde{E}_I(t))}$$

Here assumed real
For the corresponding downward transition $\bar{s} \rightarrow \bar{s}$, we have

$$\langle \bar{s} | P_\perp (t; \tau) | \bar{s} \rangle \approx E_{\bar{s}} (\bar{s} \bar{s})_\perp e^{i \varphi_{\bar{s}}} | \bar{s} \rangle \langle \bar{s} | P_\perp (t; \tau) \rangle$$

with $P_\perp (t; \tau) = - (P_\perp (t; \tau))^\dagger$ (see footnote* below).

We will consider two general strategies for measuring a two-dimensional electronic spectroscopy signal and use the third-order perturbative expansion for $|\Psi(t)\rangle$ given on p. 9 to calculate the requisite expectation values in each case. In the FWM approach, one observes a signal electric field at a field point $R = R_1$ distant from the sample that arises due to the trilinear dipole moments $\mu_{ABC}(t)$ of the laser-illuminated chromophores. In the fluorescence-detected

[Diagram of FWM setup]

+ i.e. the portion of the time-dependent dipole moment expectation value proportional to $E_A E_B E_C$.

* $\langle \Psi | P_\perp | s \rangle \langle s | P_\perp \rangle = E_{\bar{s}} (\bar{s} \bar{s})_\perp e^{i \varphi_{\bar{s}}} \langle \bar{s} | P_\perp (t; \tau) \rangle \langle \bar{s} \rangle$

$$= \langle \Psi | P_\perp (t; \tau) \rangle e^{i \varphi_{\bar{s}}} \langle \bar{s} \rangle \langle \bar{s} | P_\perp (t; \tau) \rangle \rangle \langle \bar{s} \rangle$$

$$= - \langle \Psi | E_{\bar{s}} (\bar{s} \bar{s})_\perp e^{-i \varphi_{\bar{s}}} \langle \bar{s} | P_\perp (t; \tau) \rangle \rangle \langle \bar{s} \rangle$$

$$= - E_{\bar{s}} (\bar{s} \bar{s})_\perp e^{i \varphi_{\bar{s}}} \langle \bar{s} \rangle \langle \bar{s} | P_\perp (t; \tau) \rangle \rangle \langle \bar{s} \rangle$$

Comparison of first and last lines establishes the equality stated.
mid-WPI measurement, one uses fluorescence—or some other population-sensitive action signal—to determine a quantum-yield-weighted sum of the quadrilinear populations (proportional to $E_A E_B E_C E_D$) in various excited electronic states.

In order to calculate the trilinear radiated field at a far-field point $R$ at time $t$, we need the molecular state at the earliest time $t - 1R - 1/c = t - \frac{R}{c} + \frac{t - n}{c}$. To determine the quadrilinear excited-state populations, we may use the molecular state $|\psi(t)\rangle$ with its time argument formally set equal to the arrival time of the fourth pulse $t_D(T) = t_P + \Delta_T \cdot \frac{c}{f}$. Thus the relevant time arguments of the free-evolution operators $|\pm \rangle$ appearing in molecular state expression on p. 9 are either of the form

$$t - 1R - 1/c - t_A(T) = t - t_A - \frac{R}{c} + \frac{t - n_A}{c}$$

or

$$t_{\pm}(T) = t_{\pm} + \frac{n_{\pm}}{c}$$

In order to avoid degradation of the time resolution of the experiment by "geometrical broadening" of the interpulse delays, the angle between propagation directions must be small enough that

$$\left| \frac{n_{\pm}}{c} \right| \approx \frac{a}{c} \Theta_{\pm} \ll c$$
where $a$ is the "sample size" (i.e. the diameter of a laser spot). This criterion, that the divergence of the beam across the sample be much less than the distance light travels in time $t$, implies that

$$\frac{a}{c} \theta_{\text{in}} \ll \sigma \ll \frac{2\pi}{12}$$

when the pulses "squeeze" energy transfer

$$\frac{a}{c} \theta_{\text{in}} \ll \sigma \ll \frac{2\pi}{12}$$

when the pulses "squeeze" vibrational motion.

It is therefore reasonable to choose interaction angles sufficiently small that $a \theta_{\text{in}}/c$ is negligible on both of these timescales (energy transfer & vibrational motion), regardless of which one is shorter. The only remaining timescale, on which $\frac{2\pi}{12} \ll \frac{a}{c}$ may not be negligible, is the optical timescale $\sim \frac{2\pi}{\nu}$, the optical period of high-precision electronic excitation. We can write

$$[t + \frac{2\pi}{\nu}/c]_{\pm} = \frac{2\pi}{\nu} \pm [\frac{2\pi}{\nu}/c]_{\pm}$$

and take advantage of the fact that only energy transfer and electron-vibration coupling (which are negligible for time-values of the second argument) can induce electronic transitions. It then follows that

* The FWM signal beam will be seen shortly to emerge in the directions $n_A - n_B + n_C$ and $n_B - n_A + n_C$. Nonnegligible signal field can only be observed at points $E = n_A$ for which $\sigma$ closely approximates one of these two directions. The conditions limiting geometrical broadening are therefore the same in FWM and mid-WPI experiments.
\[ [t + n_{\text{exc}} \cdot \mathbf{r} / c]_{\text{exc}} = [t]_{\text{exc}} [n_{\text{exc}} \cdot \mathbf{r} / c]_{\text{exc}} \]

\[ = [t]_{\text{exc}} \left( -i n_{\text{exc}} \cdot \mathbf{r} / c \right) e^{-i n_{\text{exc}} \cdot \mathbf{r} / c} \]

\[ [t + n_{\text{exc}} \cdot \mathbf{r} / c]_{\text{exc}} \equiv [t]_{\text{exc}} e^{-i n_{\text{exc}} (\mathbf{r} \cdot \mathbf{x} - \mathbf{r} \cdot \mathbf{y}) / c} \]

Where the excitation number of state \( \text{exc} \),

\[ n_{\text{exc}} = \begin{cases} 
0 & ; \text{exc} = 0 \quad (\text{gs}) \\
1 & ; \text{exc} = 1, 1 \quad (\text{ge}, \text{eg}) \\
2 & ; \text{exc} = 2 \quad (\text{ee}) 
\end{cases} \]

and the wavevector \( \mathbf{r} \cdot \mathbf{x} = n_{\text{exc}} \mathbf{r} \cdot \mathbf{x} / c \) of the \( \text{I} \)th beam have been introduced.

In order to calculate the trilinear dipole moment or the quadrilinear population, we need only determine the appropriate contributions to the nuclear amplitude in each of the four electronic states.

\[ \langle \text{ee} | \mathbf{r} \cdot \mathbf{x} | \text{t} \rangle = \langle 2 | \mathbf{r} \cdot \mathbf{x} | \text{t} \rangle = \langle 2 | \mathbf{r} \cdot \mathbf{x} | \text{t} \rangle = \langle 2 | \mathbf{r} \cdot \mathbf{x} | \text{t} \rangle + \langle 2 | \mathbf{r} \cdot \mathbf{x} | \text{t} \rangle + \langle 2 | \mathbf{r} \cdot \mathbf{x} | \text{t} \rangle + \langle 2 | \mathbf{r} \cdot \mathbf{x} | \text{t} \rangle \]

\[ + \langle 2 | \mathbf{r} \cdot \mathbf{x} | \text{t} \rangle + \langle 2 | \mathbf{r} \cdot \mathbf{x} | \text{t} \rangle + \langle 2 | \mathbf{r} \cdot \mathbf{x} | \text{t} \rangle \]

AB and [CD] terms cannot play any role because signal contributions containing either of them would carry a phase factor \( e^{i(g_A + g_B)} \) or \( e^{i(g_C + g_D)} \) whose value is not controlled and averages to zero over many repetitions. The boxed terms, involving the effect of the D-pulse (local oscillator) on the molecular state, are absent from the trilinear dipole calculation.
For $\varepsilon = \text{ge, eg}$ (or $1, 1$), we need

$$
\langle \varepsilon | \psi(t) \rangle = \langle \varepsilon | \psi_A(t) \rangle + \langle \varepsilon | \psi_B(t) \rangle + \langle \varepsilon | \psi_C(t) \rangle + \langle \varepsilon | \psi_D(t) \rangle + \langle \varepsilon | \psi_{ABD}(t) \rangle + \langle \varepsilon | \psi_{ACD}(t) \rangle + \langle \varepsilon | \psi_{BCD}(t) \rangle
$$

$$
+ \langle \varepsilon | \psi_{ABC}(t) \rangle + \langle \varepsilon | \psi_{ABD}(t) \rangle + \langle \varepsilon | \psi_{ACD}(t) \rangle + \langle \varepsilon | \psi_{BCD}(t) \rangle
$$

In terms of these various one-, two-, and three-pulse amplitudes, the trilinear dipole moment expectation value is given by:

$$
\mu_{ABC}(t) = 2 \text{Re} \sum_{\varepsilon} \left\{ \langle \psi_0 | \varepsilon - t + t_A(t) \rangle \langle \varepsilon | \psi_A(t) \rangle + \langle \psi_B(t) | \psi_C(t) \rangle \langle \psi_{AC}(t) \rangle + \langle \psi_B(t) | \psi_C(t) \rangle \langle \psi_{AC}(t) \rangle + \langle \psi_B(t) | \psi_C(t) \rangle \langle \psi_{AC}(t) \rangle \right\}
$$

The sum is over $\varepsilon = 1, 1$ or ge, eg depending on the choice of basis.
The quadrilinear excited-state populations are

\[ S^{(ee)}(t) = S^{(2\gamma)}(t) \]

\[ = 2\text{Re} \left\{ \langle \Psi_B(t)|zXz|\Psi_{AD}(t)\rangle + \langle \Psi_B(t)|zXz|\Psi_{AC}(t)\rangle \right\} \]

and for \( \gamma = \text{ge, eg (or } t'1) \),

\[ S^{(\gamma)}(t) = 2\text{Re} \left\{ \langle \Psi_B(t)|zXz|\Psi_{ABC}(t)\rangle + \langle \Psi_B(t)|zXz|\Psi_{ABD}(t)\rangle \right\} \]

\[ + \langle \Psi_B(t)|zXz|\Psi_{ACD}(t)\rangle + \langle \Psi_B(t)|zXz|\Psi_A(t)\rangle \]

The electric field generated in the far field by the oscillating dipole moment \( \mu_{ABC}(t) \) of the various laser-illuminated chromophore pairs ( \( \rho \), \( \text{Is} \)) is

\[ E_{\text{ABC}}(t) = \frac{1}{cR^2} \sum \left[ \mu_{\text{ABC}} \left( t - \frac{R}{c} + \frac{\mathbf{r} \cdot \mathbf{r}}{c^2} \right) \times \mathbf{n} \right] \times \mathbf{n} \]

\[ = -\frac{1}{c^2R} \sum (1 - \mathbf{r} \cdot \mathbf{n}) \cdot \mu_{\text{ABC}} \left( t - \frac{R}{c} + \frac{\mathbf{r} \cdot \mathbf{r}}{c^2} \right) \]

\[ E_{\text{ABC}}(t) = \frac{\rho \mu}{c^2R} \left( 1 - \mathbf{n} \cdot \mathbf{r} \right) \cdot \left( \int d^3r \mu_{\text{ABC}} \left( t - \frac{R}{c} + \frac{\mathbf{r} \cdot \mathbf{r}}{c^2} \right) \right) \]

\( \rho \) is the number density of dimers within the sample volume \( V \), and we've taken advantage of the relatively narrow range of electronic excitation frequencies to write \( \mu \approx -\mu \).