

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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Comparing md-WPI & FWM signals from an EET dimer. A tale of three bases and two measurement strategies.

5 Jan 11

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Dimer Hamiltonian $H = T + H_{ee}(\hat{Q})$.

nuclear kinetic energy

shorthand for all nuclear coordinate operators

$$H_{ee}(Q) = |gg\rangle V_{gg}(Q) \langle gg| + |ge\rangle V_{ge}(Q) \langle ge| + |eg\rangle V_{eg}(Q) \langle eg| + |ee\rangle V_{ee}(Q) \langle ee| + J(Q) (|eg\rangle \langle ge| + |ge\rangle \langle eg|),$$

in the basis of **site states**. * Alternatively, in the basis of **adiabatic electronic states**,

$$H_{ee}(Q) = |0\rangle E_0(Q) \langle 0| + |1'(Q)\rangle E_{1'}(Q) \langle 1'(Q)| + |1(Q)\rangle E_1(Q) \langle 1(Q)| + |2\rangle E_2(Q) \langle 2|.$$

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

$$P_{one} = |eg\rangle \langle eg| + |ge\rangle \langle ge| \quad \sigma_y = -i|eg\rangle \langle ge| + i|ge\rangle \langle eg|$$

$$\sigma_x = |eg\rangle \langle ge| + |ge\rangle \langle eg| \quad \sigma_z = |eg\rangle \langle eg| - |ge\rangle \langle ge|.$$

* We neglect higher excited states involving high electronic excitations of either monomer such as $|e'g\rangle$ or $|ee'\rangle$ (for the sake of simplicity), rather than including them (for the sake of complication).

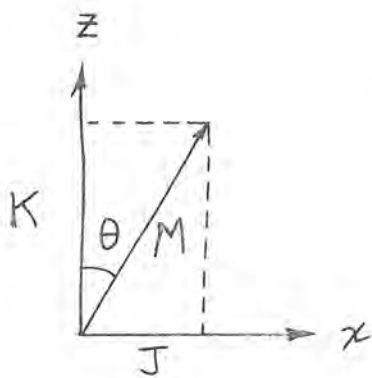
Then

$$|g_g X e_g| = \frac{1}{2} (\rho_{one} + \sigma_z) \quad |g_e X a_e| = \frac{1}{2} (\rho_{one} - \sigma_z)$$

$$|g_g X g_e| = \frac{1}{2} (\sigma_x + i\sigma_y) \quad |g_e X e_g| = \frac{1}{2} (\sigma_x - i\sigma_y)$$

and

$$H_{ee}(Q) = |g_g X g_g| V_{gg}(Q) + \rho_{one} \underbrace{\frac{1}{2} (V_{eg}(Q) + V_{ge}(Q))}_{\equiv L(Q)} \\ + \sigma_z \underbrace{\frac{1}{2} (V_{eg}(Q) - V_{ge}(Q))}_{\equiv K(Q)} + |e_e X e_e| V_{ee}(Q) + \sigma_x J(Q)$$



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

$$H_{ee}(Q) = |g_g X g_g| V_{gg}(Q) + \rho_{one} L(Q) + \sigma_z M(Q) \cos \theta(Q) \\ + \sigma_x M(Q) \sin \theta(Q) + |e_e X e_e| V_{ee}(Q)$$

$$= |g_g X g_g| V_{gg}(Q) + \rho_{one} L(Q) \\ + M(Q) e^{-i \frac{\theta(Q)}{2} \sigma_y} \sigma_z e^{i \frac{\theta(Q)}{2} \sigma_y} + |e_e X e_e| V_{ee}(Q)$$

Thus, the adiabatic eigenenergies appearing on p. ① are ③

$$E_0(Q) = V_{gg}(Q)$$

$$E_{1'}(Q) = L(Q) - M(Q)$$

$$E_1(Q) = L(Q) + M(Q)$$

$$E_2(Q) = V_{ee}(Q) \quad ,$$

while the corresponding adiabatic electronic eigenstates are

$$|0\rangle = |gg\rangle$$

$$\begin{aligned} |1'(Q)\rangle &= e^{-i\frac{\theta(Q)}{2}\sigma_y} |ge\rangle = \left(\cos\frac{\theta(Q)}{2} - i\sigma_y \sin\frac{\theta(Q)}{2} \right) |ge\rangle \\ &= |ge\rangle \cos\frac{\theta(Q)}{2} - |eg\rangle \sin\frac{\theta(Q)}{2} \end{aligned}$$

$$\begin{aligned} |1(Q)\rangle &= e^{-i\frac{\theta(Q)}{2}\sigma_y} |eg\rangle \\ &= |ge\rangle \sin\frac{\theta(Q)}{2} + |eg\rangle \cos\frac{\theta(Q)}{2} \end{aligned}$$

$$|2\rangle = |ee\rangle \quad .$$

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,

$$|0\rangle \equiv |gg\rangle$$

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

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

$$|2\rangle \equiv |ee\rangle \quad .$$

We can now write $H_{el}(\mathbf{Q}) = H_{el} + v(\mathbf{Q})$, with

$$H_{el} \equiv H_{el}(0) = |0\rangle E_0 \langle 0| + |1'\rangle E_1 \langle 1'| + |1\rangle E_1 \langle 1| + |2\rangle E_2 \langle 2|$$

and (from p. 1)

$$\begin{aligned}
v(\mathbf{Q}) = H_{el}(\mathbf{Q}) - H_{el} = & |gg\rangle \langle gg| (V_{gg}(\mathbf{Q}) - V_{gg}) \\
& + |ge\rangle \langle ge| (V_{ge}(\mathbf{Q}) - V_{ge}) \\
& + |eg\rangle \langle eg| (V_{eg}(\mathbf{Q}) - V_{eg}) \\
& + |ee\rangle \langle ee| (V_{ee}(\mathbf{Q}) - V_{ee}) \\
& + (|eg\rangle \langle ge| + |ge\rangle \langle eg|) (J(\mathbf{Q}) - J)
\end{aligned}$$

We want $v(\mathbf{Q})$ in the exciton rep'n and so seek

$$\langle 0|v(\mathbf{Q})|0\rangle = V_{gg}(\mathbf{Q}) - V_{gg} \equiv \delta V_{gg}(\mathbf{Q}) ; \langle 2|v(\mathbf{Q})|2\rangle = \delta V_{ee}(\mathbf{Q})$$

$$\begin{aligned}
\langle 1'|v(\mathbf{Q})|1'\rangle &= \left(\cos \frac{\theta}{2} \langle ge| - \sin \frac{\theta}{2} \langle eg| \right) v(\mathbf{Q}) \left(|ge\rangle \cos \frac{\theta}{2} - |eg\rangle \sin \frac{\theta}{2} \right) \\
&\downarrow \\
&= (V_{ge}(\mathbf{Q}) - V_{ge}) \cos^2 \frac{\theta}{2} + (V_{eg}(\mathbf{Q}) - V_{eg}) \sin^2 \frac{\theta}{2} \\
&\quad - (J(\mathbf{Q}) - J) \sin \theta \\
&\downarrow \\
&= (V_{ge}(\mathbf{Q}) - V_{ge}) \frac{1}{2} (1 + \cos \theta) + (V_{eg}(\mathbf{Q}) - V_{eg}) \frac{1}{2} (1 - \cos \theta) \\
&\quad - (J(\mathbf{Q}) - J) \sin \theta
\end{aligned}$$

$$\begin{aligned}
\langle 1'|v(\mathbf{Q})|1'\rangle &\equiv \frac{\delta V_{ge}(\mathbf{Q}) + \delta V_{eg}(\mathbf{Q})}{2} + \frac{\delta V_{ge}(\mathbf{Q}) - \delta V_{eg}(\mathbf{Q})}{2} \cos \theta \\
&\quad - \delta J(\mathbf{Q}) \sin \theta
\end{aligned}$$

$$\begin{aligned}
\langle 1|v(\mathbf{Q})|1\rangle &= \frac{\delta V_{ge}(\mathbf{Q}) + \delta V_{eg}(\mathbf{Q})}{2} - \frac{\delta V_{ge}(\mathbf{Q}) - \delta V_{eg}(\mathbf{Q})}{2} \cos \theta \\
&\quad + \delta J(\mathbf{Q}) \sin \theta
\end{aligned}$$

(5)

$$\begin{aligned}
\langle 1|v(Q)|1'\rangle &= \frac{\delta V_{ge}(Q)}{2} \sin\theta - \frac{\delta V_{eg}(Q)}{2} \sin\theta \\
&\quad \delta J(Q) \left(\cos^2\frac{\theta}{2} - \sin^2\frac{\theta}{2} \right) \\
&= \frac{\delta V_{ge}(Q) - \delta V_{eg}(Q)}{2} \sin\theta + \delta J(Q) \cos\theta \\
&= \langle 1'|v(Q)|1\rangle .
\end{aligned}$$

Whence, in the exciton basis,

$$\begin{aligned}
v(Q) &= |0\rangle\langle 0| \delta V_{gg}(Q) + |1'\rangle\langle 1'| \left[\frac{\delta V_{ge}(Q) + \delta V_{eg}(Q)}{2} + \frac{\delta V_{ge}(Q) - \delta V_{eg}(Q)}{2} \cos\theta \right. \\
&\quad \left. - \delta J(Q) \sin\theta \right] + |1\rangle\langle 1| \left[\frac{\delta V_{ge}(Q) + \delta V_{eg}(Q)}{2} - \frac{\delta V_{ge}(Q) - \delta V_{eg}(Q)}{2} \cos\theta \right. \\
&\quad \left. + \delta J(Q) \sin\theta \right] + (|1\rangle\langle 1'| + |1'\rangle\langle 1|) \left[\frac{\delta V_{ge}(Q) - \delta V_{eg}(Q)}{2} \sin\theta + \delta J(Q) \sin\theta \right] \\
&\quad + |2\rangle\langle 2| \delta V_{ee}(Q) .
\end{aligned}$$

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,

$V(t) = -\underline{\mu} \cdot \underline{E}(t)$, to the Hamiltonian. Here the dipole moment operator

$$\begin{aligned}
\underline{\mu} &= \underline{\mu}_a + \underline{\mu}_b = \underline{m}_a (|eg\rangle\langle 00| + |ee\rangle\langle ge|) \\
&\quad + \underline{m}_b (|ge\rangle\langle 00| + |ee\rangle\langle eg|) + H.c.
\end{aligned}$$

in the site representation.

We can also write (from p. (3))

(6)

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

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

and use substitution to obtain

$$\begin{aligned} \underline{\mu} = & \underline{m}_a \left(-|1'(Q)\rangle \langle 0| \sin \frac{\theta(Q)}{2} + |1(Q)\rangle \langle 0| \cos \frac{\theta(Q)}{2} \right. \\ & \left. + |2\rangle \langle 1'(Q)| \cos \frac{\theta(Q)}{2} + |2\rangle \langle 1(Q)| \sin \frac{\theta(Q)}{2} \right) \\ & + \underline{m}_b \left(|1'(Q)\rangle \langle 0| \cos \frac{\theta(Q)}{2} + |1(Q)\rangle \langle 0| \sin \frac{\theta(Q)}{2} \right. \\ & \left. - |2\rangle \langle 1'(Q)| \sin \frac{\theta(Q)}{2} + |2\rangle \langle 1(Q)| \cos \frac{\theta(Q)}{2} \right) + \text{H.c.} \end{aligned}$$

$$\begin{aligned} \underline{\mu} = & |1'(Q)\rangle \langle 0| \left(-\underline{m}_a \sin \frac{\theta(Q)}{2} + \underline{m}_b \cos \frac{\theta(Q)}{2} \right) \\ & + |1(Q)\rangle \langle 0| \left(\underline{m}_a \cos \frac{\theta(Q)}{2} + \underline{m}_b \sin \frac{\theta(Q)}{2} \right) \\ & + |2\rangle \langle 1'(Q)| \left(\underline{m}_a \cos \frac{\theta(Q)}{2} - \underline{m}_b \sin \frac{\theta(Q)}{2} \right) \\ & + |2\rangle \langle 1(Q)| \left(\underline{m}_a \sin \frac{\theta(Q)}{2} + \underline{m}_b \cos \frac{\theta(Q)}{2} \right) + \text{H.c.} \end{aligned}$$

in the adiabatic representation.

In the exciton basis, we therefore have

$$\begin{aligned} \underline{\mu} = & |1'\rangle \langle 0| \left(-\underline{m}_a \sin \frac{\theta}{2} + \underline{m}_b \cos \frac{\theta}{2} \right) \\ & + |1\rangle \langle 0| \left(\underline{m}_a \cos \frac{\theta}{2} + \underline{m}_b \sin \frac{\theta}{2} \right) \\ & + |2\rangle \langle 1'| \left(\underline{m}_a \cos \frac{\theta}{2} - \underline{m}_b \sin \frac{\theta}{2} \right) \\ & + |2\rangle \langle 1| \left(\underline{m}_a \sin \frac{\theta}{2} + \underline{m}_b \cos \frac{\theta}{2} \right) + \text{H.c.} \end{aligned}$$

The electric field consists of four pulses

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$$\underline{E}(t) = \sum_{I=A,B,C,D} \underline{E}_I(t); \quad \underline{E}_I(t) = \underline{e}_I E_I f_I(t-t_I(\tau)) \cos \Phi_I(t-t_I(\tau)).$$

$f_I(t)$ is an envelope function localized around $t=0$ and having a temporal width $\sim \sigma_I$. The phase function has the form $\Phi_I(t) = \omega_I t + \phi_I$ and the arrival time $t_I(t) = t_I + \underline{n}_I \cdot \underline{r} / c$. \underline{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; 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 $t_D \ll t_A \leq t_B \leq t_C$).

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = (H + V(t)) |\Psi(t)\rangle$$

with an initial condition $|\Psi(t \ll t_A(\tau))\rangle = e^{-iH(t-t_A(\tau))/\hbar} |gg\rangle |\Psi_0\rangle$.

$|\Psi_0\rangle$ could be an eigenstate of

$$\langle 0 | T + H_{el}(\omega) | 0 \rangle = T + E_0(\omega) \text{ or a wave packet -}$$

an arbitrary linear superposition of such nuclear eigenstates.

In the interaction picture, $|\tilde{\Psi}(t)\rangle = e^{iH(t-t_A(\epsilon))/\hbar} |\Psi(t)\rangle;$

$$|\tilde{\Psi}(t \ll t_A(\epsilon))\rangle = |gg\rangle |\Psi_0\rangle \quad (= \text{constant}). \quad (8)$$

$$i\hbar \frac{\partial}{\partial t} |\tilde{\Psi}(t)\rangle = e^{iH(t-t_A(\epsilon))/\hbar} \{-H + H + V(t)\} |\Psi(t)\rangle \\ = \tilde{V}(t) |\tilde{\Psi}(t)\rangle.$$

$$\tilde{V}(t) = e^{iH(t-t_A(\epsilon))/\hbar} V(t) e^{-iH(t-t_A(\epsilon))/\hbar}$$

The formal solution is

$$|\tilde{\Psi}(t)\rangle = |gg\rangle |\Psi_0\rangle + \frac{1}{i\hbar} \int_{-\infty}^t d\tau \tilde{V}(\tau) |\tilde{\Psi}(\tau)\rangle.$$

The perturbative solution through 3rd order is

$$|\tilde{\Psi}(t)\rangle = \left\{ 1 + \frac{1}{i\hbar} \int_{-\infty}^t d\tau \tilde{V}(\tau) + \left(\frac{1}{i\hbar}\right)^2 \int_{-\infty}^t d\tau \int_{-\infty}^{\tau} d\bar{\tau} \tilde{V}(\tau) \tilde{V}(\bar{\tau}) \right. \\ \left. + \left(\frac{1}{i\hbar}\right)^3 \int_{-\infty}^t d\tau \int_{-\infty}^{\tau} d\bar{\tau} \int_{-\infty}^{\bar{\tau}} d\bar{\bar{\tau}} \tilde{V}(\tau) \tilde{V}(\bar{\tau}) \tilde{V}(\bar{\bar{\tau}}) \right\} |gg\rangle |\Psi_0\rangle.$$

Introducing the notation $[t] = e^{-iHt/\hbar}$ and

returning to the Schrödinger picture gives

$$|\Psi(t)\rangle = \left\{ [t-t_A(\epsilon)] + \frac{1}{i\hbar} \int_{-\infty}^t d\tau [t-\tau] V(\tau) [\tau-t_A(\epsilon)] \right. \\ \left. + \left(\frac{1}{i\hbar}\right)^2 \int_{-\infty}^t d\tau \int_{-\infty}^{\tau} d\bar{\tau} [t-\tau] V(\tau) [\tau-\bar{\tau}] V(\bar{\tau}) [\bar{\tau}-t_A(\epsilon)] \right. \\ \left. + \left(\frac{1}{i\hbar}\right)^3 \int_{-\infty}^t d\tau \int_{-\infty}^{\tau} d\bar{\tau} \int_{-\infty}^{\bar{\tau}} d\bar{\bar{\tau}} [t-\tau] V(\tau) [\tau-\bar{\tau}] V(\bar{\tau}) [\bar{\tau}-\bar{\bar{\tau}}] V(\bar{\bar{\tau}}) [\bar{\bar{\tau}}-t_A(\epsilon)] \right\} |gg\rangle |\Psi_0\rangle.$$

We introduce pulse propagators,

(9)

$$P_I(t; \tau) = \frac{i}{\hbar} \int_{-\infty}^t d\tau' [t_I(\tau) - \tau'] \underline{\mu} \cdot \underline{E}_I(\tau') [\tau - t_I(\tau)],$$

and, for the various interpulse delays, use the notation

$$t_{IJ}(\tau) = t_I(\tau) - t_J(\tau) = t_{IJ} + \underline{n}_{IJ} \cdot \underline{r} / c.$$

Then

$\underline{n}_{IJ} \equiv \underline{n}_I - \underline{n}_J$,
not a unit vector in general

$$\begin{aligned} |\Psi(t)\rangle = & [t - t_A(\tau)] \left\{ 1 + \sum_{I=A,B,C,D} [t_{AI}(\tau)] P_I(t; \tau) [t_{IA}(\tau)] \right. \\ & + \sum_{IJ} [t_{AI}(\tau)] P_I(t; \tau) [t_{IJ}(\tau)] P_J(\tau; \bar{\tau}) [t_{JA}(\tau)] \\ & \left. + \sum_{IJK} [t_{AI}(\tau)] P_I(t; \tau) [t_{IJ}(\tau)] P_J(\tau; \bar{\tau}) [t_{JK}(\tau)] P_K(\bar{\tau}; \bar{\tau}) [t_{KA}(\tau)] \right\} |gg\rangle |\Psi_0\rangle. \end{aligned}$$

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

$\{|gg\rangle, |ge\rangle, |eg\rangle, |ee\rangle\}$ and $\{|0\rangle, |1'\rangle, |1\rangle, |2\rangle\}$, and use generic electronic states $\{|E\rangle\}$ 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 $\sigma \ll |2\pi/\Omega|$, so that EET can be neglected for the duration of a laser pulse, or $\sigma \ll |2\pi/\nu| \approx |2\pi/(V_{ge} - V_{eg})|$,

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,

$$\langle \Xi | P_I(t; \tau) | \bar{\Xi} \rangle \approx \frac{i}{\hbar} \int_{-\infty}^t d\tau [t_I(\tau) - \tau]_{\Xi\bar{\Xi}} \mu_{\Xi\bar{\Xi}} \cdot E_I(\tau) [\tau - t_I(\tau)]_{\bar{\Xi}\Xi}$$

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

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

$$p_I^{(\Xi\bar{\Xi})}(t; \tau) \equiv \frac{i}{2\hbar} \int_{-\infty}^t d\tau [t_I(\tau) - \tau]_{\Xi\bar{\Xi}} [\tau - t_I(\tau)]_{\bar{\Xi}\Xi} f_I(\tau - t_I(\tau)) e^{-i\omega_I(\tau - t_I(\tau))}$$

It then follows that

$$\langle \Xi | P_I(t; \tau) | \bar{\Xi} \rangle \approx E_I(\Xi\bar{\Xi})_I e^{-i\varphi_I} p_I^{(\Xi\bar{\Xi})}(t; \tau)$$

$$(\Xi\bar{\Xi})_I \equiv \mu_{\Xi\bar{\Xi}} \cdot \hat{e}_I$$

← Here assumed real

For the corresponding downward transition

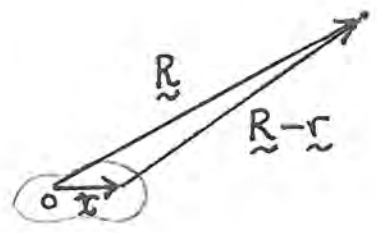
$\Xi \rightarrow \bar{\Xi}$, we have

$$\langle \bar{\Xi} | P_I(t; \tau) | \Xi \rangle \approx E_I(\bar{\Xi} \Xi)_I e^{i\varphi_I} P_I^{(\bar{\Xi} \Xi)}(t; \tau)$$

with $P_I^{(\bar{\Xi} \Xi)}(t; \tau) = -\left(P_I^{(\Xi \bar{\Xi})}(t; \tau)\right)^\dagger$ (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 $\underline{R} = R\hat{n}$ distant from the sample that arises due to the trilinear dipole moments $\mu_{ABC}^\dagger(t)$ of the laser-illuminated chromophores. In the fluorescence-detected



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

$$\begin{aligned} * \langle \bar{\Psi} | K \bar{\Xi} | P_I | \Xi \rangle | \Psi \rangle &= E_I(\bar{\Xi} \Xi)_I e^{i\varphi_I} \langle \bar{\Psi} | P_I^{(\bar{\Xi} \Xi)} | \Psi \rangle \\ &= \langle \bar{\Psi} | K \bar{\Xi} | P_I^\dagger | \Xi \rangle | \bar{\Psi} \rangle^* = -\langle \bar{\Psi} | K \Xi | P_I | \bar{\Xi} \rangle | \bar{\Psi} \rangle^* \\ &= -\langle \bar{\Psi} | E_I(\Xi \bar{\Xi})_I e^{-i\varphi_I} P_I^{(\Xi \bar{\Xi})} | \bar{\Psi} \rangle^* \\ &= -E_I(\Xi \bar{\Xi})_I e^{i\varphi_I} \langle \bar{\Psi} | P_I^{(\Xi \bar{\Xi})\dagger} | \bar{\Psi} \rangle ; \end{aligned}$$

Comparison of 1st and last lines establishes the equality stated.

mid-WPI measurement, one uses fluorescence - or some other (12) 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 \underline{R} at time t , we need the molecular state at the earlier time $t - |\underline{R} - \underline{r}|/c \cong t - \frac{R}{c} + \frac{\underline{r} \cdot \underline{n}}{c}$.

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 $t_D(\underline{r}) = t_D + \underline{n}_D \cdot \underline{r}/c$. Thus the relevant time arguments of the free-evolution operators $[t]$ appearing in molecular state expression on p. (9) are either of the form

$$t - |\underline{R} - \underline{r}|/c - t_A(\underline{r}) \cong t - t_A - R/c + \underline{r} \cdot (\underline{n} - \underline{n}_A)/c$$

or

$$t_{IJ}(\underline{r}) = t_{IJ} + \underline{n}_{IJ} \cdot \underline{r}/c$$

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

$$\left| \frac{\underline{r} \cdot \underline{n}_{IJ}}{c} \right| \approx \frac{a}{c} \theta_{IJ} \ll \sigma, \quad ,$$

where a is the "sample size" (i.e. the diameter of a laser spot). * This criterion, that the divergence of the beams across the sample be much less than the distance light travels in time σ , implies that

$$\frac{a}{c} \theta_{IS} \ll \sigma \ll \begin{cases} \frac{2\pi}{\omega} & \text{when the pulses "freeze" energy transfer} \\ \frac{2\pi}{|\omega|} & \text{when the pulses "freeze" vibrational motion} \end{cases}$$

It is therefore reasonable to choose interbeam angles sufficiently small that $a \theta_{IS}/c$ is negligible on both of these timescales (energy transfer $\hat{=}$ vibrational motion), regardless of which one is shorter. The only remaining timescale, on which $\frac{a \theta_{IS}}{c}$ may not be negligible, is the optical timescale $\sim 2\pi/\omega$, the optical period of light resonant with an electronic excitation. We can write

$$[t + \frac{a \theta_{IS}}{c}]_{\xi\xi} = \sum_{\xi'} [t]_{\xi\xi'} [\frac{a \theta_{IS}}{c}]_{\xi'\xi}$$

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 follows that

* The FWM signal beams will be seen shortly to emerge in the directions $\underline{n}_A - \underline{n}_B + \underline{n}_C$ and $\underline{n}_B - \underline{n}_A + \underline{n}_C$; nonnegligible signal field can only be observed at points $\underline{R} = R\underline{n}$ for which \underline{n} closely approximates one of these two directions. The conditions limiting geometrical broadening are therefore the same in FWM and md-WPI experiments.

$$\begin{aligned}
 [t + n_{II} \cdot \tau / c]_{\xi\xi} &\approx [t]_{\xi\xi} [n_{II} \cdot \tau / c]_{\xi\xi} \\
 &= [t]_{\xi\xi} e^{-i\eta_{\xi} \sqrt{\omega_{II}} n_{II} \cdot \tau / c}
 \end{aligned}$$

$$[t + n_{II} \cdot \tau / c]_{\xi\xi} \approx [t]_{\xi\xi} e^{-i\eta_{\xi} (\underline{k}_I - \underline{k}_J) \cdot \tau}$$

where the excitation number of state ξ ,

$$\eta_{\xi} = \begin{cases} 0 & ; \quad \xi = 0 \text{ (g)} \\ 1 & ; \quad \xi = 1, 1' \text{ (ge, eg)} \\ 2 & ; \quad \xi = 2 \text{ (ee)} \end{cases}$$

and the wavevector $\underline{k}_I = \sqrt{\omega_I} n_I / c$ of the 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.

$$\begin{aligned}
 \langle ee | \Psi(t) \rangle &= \langle z | \Psi(t) \rangle = \langle z | \Psi_{AC}(t) \rangle + \langle z | \Psi_{AD}(t) \rangle \\
 &\quad + \langle z | \Psi_{BC}(t) \rangle + \langle z | \Psi_{BD}(t) \rangle
 \end{aligned}$$

AB and \boxed{CD} terms cannot play any role because signal contributions containing either of them would carry a phase factor $e^{\pm i(\omega_A + \omega_B)}$ or $e^{\pm i(\omega_C + \omega_D)}$ 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 $\xi = ge, eg$ (or $1', 1$), we need

$$\langle \xi | \Psi(t) \rangle = \langle \xi | \Psi_A(t) \rangle + \langle \xi | \Psi_B(t) \rangle + \langle \xi | \Psi_C(t) \rangle + \langle \xi | \Psi_D(t) \rangle$$

$$+ \langle \xi | \Psi_{ABC}(t) \rangle + \langle \xi | \Psi_{ABD}(t) \rangle + \langle \xi | \Psi_{ACD}(t) \rangle + \langle \xi | \Psi_{BCD}(t) \rangle$$

$$\langle 03 | \Psi(t) \rangle = \langle 01 | \Psi(t) \rangle$$

$$= [t - t_A(\xi)]_{00} | \Psi_0 \rangle + \langle 01 | \Psi_{AB}(t) \rangle + \langle 01 | \Psi_{AC}(t) \rangle$$

$$+ \langle 01 | \Psi_{AD}(t) \rangle + \langle 01 | \Psi_{BC}(t) \rangle + \langle 01 | \Psi_{BD}(t) \rangle + \langle 01 | \Psi_{CD}(t) \rangle$$

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

$$\mu_{ABC}(t) = 2 \text{Re} \sum_{\xi} \left\{ \langle \Psi_0 | [-t + t_A(t)]_{00} \mu_{0\xi} \langle \xi | \Psi_{ABC}(t) \rangle \right.$$

$$+ \langle \Psi_{BC}(t) | 0 \rangle \mu_{0\xi} \langle \xi | \Psi_A(t) \rangle + \langle \Psi_B(t) | \xi \rangle \mu_{\xi 0} \langle 0 | \Psi_{AC}(t) \rangle + \langle \Psi_C(t) | \xi \rangle \mu_{\xi 0} \langle 0 | \Psi_{AB}(t) \rangle$$

$$\left. + \langle \Psi_{BC}(t) | Z \rangle \mu_{Z\xi} \langle \xi | \Psi_A(t) \rangle + \langle \Psi_B(t) | \xi \rangle \mu_{\xi Z} \langle Z | \Psi_{AC}(t) \rangle \right\} ;$$

The sum is over $\xi = 1', 1$ or ge, eg depending on the choice of basis.

The quadrilinear excited-state populations are

(16)

$$S^{(ee)}(t) = S^{(2)}(t)$$

$$= 2\text{Re} \left\{ \langle \Psi_{BC}(t) | Z X Z | \Psi_{AD}(t) \rangle + \langle \Psi_{BD}(t) | Z X Z | \Psi_{AC}(t) \rangle \right\}$$

and, for $\xi = ge, eg$ (or $1, 1$),

$$S^{(\xi)}(t) = 2\text{Re} \left\{ \langle \Psi_D(t) | \xi X \xi | \Psi_{ABC}(t) \rangle + \langle \Psi_C(t) | \xi X \xi | \Psi_{ABD}(t) \rangle \right.$$

$$\left. + \langle \Psi_B(t) | \xi X \xi | \Psi_{ACD}(t) \rangle + \langle \Psi_{BCD}(t) | \xi X \xi | \Psi_A(t) \rangle \right\}$$

The electric field generated in the far field by the oscillating dipole moments $\mu_{ABC}(t)$ of the various laser-illuminated chromophore pairs (p. 15) is

$$\underline{E}_{ABC}(t) = \frac{1}{cR^2} \sum_{\underline{r}} \left[\ddot{\mu}_{ABC} \left(t - \frac{R}{c} + \frac{\underline{r} \cdot \underline{n}}{c} \right) \times \underline{n} \right] \times \underline{n}$$

dimer locations

$$= -\frac{1}{c^2 R} \sum_{\underline{r}} (1 - \underline{n} \cdot \underline{n}) \cdot \ddot{\mu}_{ABC} \left(t - \frac{R}{c} + \frac{\underline{r} \cdot \underline{n}}{c} \right)$$

$$\underline{E}_{ABC}(t) \cong \frac{\rho \omega^2}{c^2 R} (1 - \underline{n} \cdot \underline{n}) \cdot \int_V d^3r \mu_{ABC} \left(t - \frac{R}{c} + \frac{\underline{r} \cdot \underline{n}}{c} \right);$$

ρ 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 $\ddot{\mu} \approx -\omega^2 \mu$.