Set-up for thinking about Segale & Aptkarian's 5-color 4-wave mixing experiments on I_2 in solid Kr

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$$H = |X\rangle\mathcal{H}_X\langle X| + |B\rangle\mathcal{H}_B\langle B| + |E\rangle\mathcal{H}_E\langle E|$$

The nuclear Hamiltonians $\mathcal{H}_X$, $\mathcal{H}_B$, and $\mathcal{H}_E$ include the sum of the kinetic and potential energy operators for all the intramolecular, medium, and interaction degrees of freedom in the corresponding electronic state.

$$V(t) = -\hat{u}\sum_{j=1}^{3} E_j(t) \quad ;$$

$$\hat{u} = m|BX\rangle\langle X| + m'|EX\rangle\langle B| + H.c.$$

both transition dipole moments assumed real

$$E_j(t) = E_j f_j(t - t_j(\underset{\sim}{r}))\cos(\omega_j(t - t_j(\underset{\sim}{r})) + \varphi_j)$$

molecular location

$$t_j(\underset{\sim}{r}) = t_j + \underset{\sim}{r}\cdot\underset{\sim}{n}_j/c$$

t_j: arrival time of j^{th} pulse at the sample origin

$\underset{\sim}{n}_j$: unit vector in direction of propagation of j^{Th} pulse

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

initial condition $\quad |\Psi(t << t_1(\Sigma))\rangle = e^{-iH(t - t_1(\Sigma))/\hbar} |X\rangle |\Psi_0\rangle .$

$|\Psi_0\rangle$ is the initial nuclear state of the combined intramolecular and medium degrees of freedom in the (solely occupied) electronic ground state (assumed to be pure without any loss of generality).*

Interaction picture $\quad |\tilde{\Psi}(t)\rangle = e^{iH(t - t_1(\Sigma))/\hbar} |\Psi(t)\rangle ;$

$$|\tilde{\Psi}(t << t_1(\Sigma))\rangle = |X\rangle |\Psi_0\rangle .$$

$$i\hbar \frac{\partial}{\partial t} |\tilde{\Psi}(t)\rangle = e^{iH(t - t_1(\Sigma))/\hbar} (-H + H + V(t)) |\Psi(t)\rangle$$

$$= \tilde{V}(t) |\tilde{\Psi}(t)\rangle ,$$

with $\quad \tilde{V}(t) = e^{iH(t - t_1(\Sigma))/\hbar} \, V(t) \, e^{-iH(t - t_1(\Sigma))/\hbar} .$

We introduce a square-bracket notation for the free molecular time-evolution operator:

$$[t] \equiv e^{-iHt/\hbar}$$

$$[t]_{xx} \equiv \langle X | [t] | X \rangle = e^{-iH_x t/\hbar} , \text{ etc.}$$

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* The initial reduced density operator of the intramolecular degrees) of freedom is $\sigma_0 = \mathrm{Tr}_{\text{medium}} |\Psi_0 X \Psi_0|$.

In this way of writing things,

$$|\tilde{\Psi}(t)\rangle = [-t+t_1(\Sigma)]\,|\Psi(t)\rangle$$

and $$\tilde{V}(t) = [-t+t_1(\Sigma)]\,V(t)\,[t-t_1(\Sigma)]\,.$$

Formal solution of Schrödinger equation in the Interaction Picture:

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

Iterating twice and reverting to the Schrödinger picture give

$$|\Psi(t)\rangle \cong [t-t_1(\Sigma)]\left\{1 + \frac{1}{i\hbar}\int_{-\infty}^{t} d\tau\, \tilde{V}(\tau) + \left(\frac{1}{i\hbar}\right)^2 \int_{-\infty}^{t} d\tau \int_{-\infty}^{\tau} d\tau'\, \tilde{V}(\tau)\,\tilde{V}(\tau')\right\}|X\rangle|\Psi_0\rangle$$

or

$$|\Psi(t)\rangle = \left\{[t-t_1(\Sigma)] + \sum_j [t-t_j(\Sigma)]\,P_j(t;\tau)\,[t_{j1}(\Sigma)] + \sum_{jk} [t-t_j(\Sigma)]\,P_j(t;\tau)\,[t_{jk}(\Sigma)]\,P_k(\tau;\tau')\,[t_{k1}(\Sigma)]\right\}|X\rangle|\Psi_0\rangle.$$

($t_{j1}(\Sigma) = t_j(\Sigma) - t_1(\Sigma)$)

We've introduced **pulse propagators**,

$$P_j(t;\tau) = \frac{i}{\hbar}\int_{-\infty}^{t} d\tau\, [-\tau+t_j(\Sigma)]\,\hat{\mu}\,[\tau-t_j(\Sigma)]\,E_j(t)\,.$$

We can also write

$$P_j(t;\tau) = im\,E_j\, e^{-i\varphi_j}\,|BXX|\,p_j^{(BX)}(t;\tau) + im\,E_j\, e^{i\varphi_j}\,|XXB|\,p_j^{(XB)}(t;\tau) + im'\,E_j\, e^{-i\varphi_j}\,|EXB)\,p_j^{(EB)}(t;\tau) + im'\,E_j\, e^{i\varphi_j}\,|BXE|\,p_j^{(BE)}(t;\tau)\,,$$

with reduced pulse propagators, given for example by

$$p_j^{(BX)}(t;\tau) \cong \frac{1}{2\pi}\int_{-\infty}^{+} d\tau\,[-\tau+t_j(t)]_{BB}\,[\tau-t_j(t)]_{XX}\,f_j(t-t_j(t))\,e^{-i\Omega_j(\tau-t_j(t))}$$

We've made the usual "rotating-wave approximation" by neglecting the ineffectual counter-rotating term in the integrand. We have also

$$p_j^{(XB)}(t;\tau) = \left(p_j^{(BX)}(t;\tau)\right)^{\dagger}.$$

Segale and Apkarian choose center frequencies Ω_1 and Ω_2 within the $B \leftarrow X$ absorption band and Ω_3 within the resonant range for $E \leftrightarrow B$. Accordingly, $p_1^{(BX)}$, $p_2^{(BX)}$, and $p_3^{(EB)}$ are nonvanishing, whereas $p_1^{(EB)}$, $p_2^{(EB)}$, and $p_3^{(BX)}$ are negligibly small.

With only multilinear terms retained, the state (p. (3)) takes the form

$$|\Psi(t)\rangle = [t - t_1(\Sigma)]\,|X\rangle|\Psi_0\rangle + |\Psi_1\rangle + |\Psi_2\rangle + |\Psi_3\rangle$$

$$+ |\Psi_{12}\rangle + |\Psi_{13}\rangle + |\Psi_{23}\rangle + |\Psi_{123}\rangle .$$

$|\Psi_3\rangle$ and $|\Psi_{123}\rangle$ vanish because of pulse-3's nonresonance with $B \leftarrow X$.* $[t - t_1(\Sigma)]\,|X\rangle|\Psi_0\rangle$ and $|\Psi_{12}\rangle$ are X-state amplitudes and are therefore irrelevant for the trilinear contribution to the expectation value of the dipole moment operator (see below) due to the absence of trilinear and pulse-3 amplitudes in the B state, respectively. For our purposes then,

$$|\Psi(t)\rangle = |\Psi_1\rangle + |\Psi_2\rangle + |\Psi_{13}\rangle + |\Psi_{23}\rangle .$$

$$|\Psi(t)\rangle = |B\rangle|\Psi_1(t)\rangle + |B\rangle|\Psi_2(t)\rangle + |E\rangle|\Psi_{13}(t)\rangle + |E\rangle|\Psi_{23}(t)\rangle .$$

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* The perturbation theory expansion of $|\Psi(t)\rangle$ on p. (3) was truncated at second order in anticipation of $|\Psi_{123}\rangle$'s negligibility.

Now there's a word with a truly impressive number of alternating i's.

Here are the explicit expressions for the one- and two-pulse nuclear kets:

$$|\psi_1(t)\rangle = im E_1 e^{-i\varphi_1} \cdot [t - t_1(\Sigma)]_{BB} \, p_1^{(BX)}(t;\bar{\tau}) |\psi_0\rangle$$

$$|\psi_2(t)\rangle = im E_2 e^{-i\varphi_2} [t - t_2(\Sigma)]_{BB} \, p_2^{(BX)}(t;\bar{\tau}) \, [t_{21}(\Sigma)]_{xx} |\psi_0\rangle$$

$$|\psi_{13}(t)\rangle = -mm' E_1 E_3 e^{-i\varphi_1 - i\varphi_3} [t - t_3(\Sigma)]_{EE} \, p_3^{(EB)}(t;\tau)$$

$$\hookrightarrow [t_{31}(\Sigma)]_{BB} \, p_1^{(BX)}(\tau;\tau') |\psi_0\rangle$$

$$|\psi_{23}(t)\rangle = -mm' E_2 E_3 e^{-i\varphi_2 - i\varphi_3} [t - t_3(\Sigma)]_{EE} \, p_3^{(EB)}(t;\tau)$$

$$\hookrightarrow [t_{32}(\Sigma)]_{BB} \, p_2^{(BX)}(\tau;\tau') |\psi_0\rangle .$$

Using these expressions, along with the form for $|\Psi(t)\rangle$ given on p. (5), we can isolate the trilinear contributions to the dipole moment expectation value $\langle \Psi(t)|\hat{\mu}|\Psi|t)\rangle$ (see next page).

$$\mu_{123}(t) = 2\,\mathrm{Re}\left\{\langle\psi_2(t)|\langle B|\hat{\mu}|E\rangle|\psi_{13}(t)\rangle + \langle\psi_1(t)|\langle B|\hat{\mu}|E\rangle|\psi_{23}(t)\rangle\right\}$$

($\hat{\mu}$ in each term: m')

$$= 2m'\,\mathrm{Re}\left\{\langle\psi_2(t)|\psi_{13}(t)\rangle + \langle\psi_1(t)|\psi_{23}(t)\rangle\right\}$$

$$\mu_{123}(t) = -2m^2m'^2E_1E_2E_3\,\mathrm{Im}\,e^{i\varphi_{21}-i\varphi_3}$$

$$\rightarrow \langle\psi_0|[-t_{21}(\Sigma)]_{XX}\,P_2^{(XB)}(t;\bar{\tau})\,[-t+t_2(\Sigma)]_{BB}$$

$$\rightarrow [t-t_3(\Sigma)]_{EE}\,P_3^{(EB)}(t;\tau)\,[t_{31}(\Sigma)]_{BB}\,P_1^{(BX)}(\tau;\tau')|\psi_0\rangle$$

$$-2m^2m'^2E_1E_2E_3\,\mathrm{Im}\,e^{-i\varphi_{21}-i\varphi_3}$$

$$\rightarrow \langle\psi_0|\,P_1^{(XB)}(t;\bar{\tau})\,[-t+t_1(\Sigma)]_{BB}$$

$$\rightarrow [t-t_3(\Sigma)]_{EE}\,P_3^{(EB)}(t;\tau)\,[t_{32}(\Sigma)]_{BB}\,P_2^{(BX)}(\tau;\tau')\,[t_{21}(\Sigma)]_{XX}\,|\psi_0\rangle$$

The two contributing terms are those illustrated by the time-circuit diagrams in Figure 1 of Segale and Aptkarian.

A significant simplification of the basic formula for $u_{123}(t)$ can be made for the choices of pulse center-frequency adopted by Segale and Aptkarian. Because their values of Ω_1 and Ω_2 on one hand, and Ω_3 on the other, are locally resonant, respectively, with $B \leftarrow X$ near the inner turning point of B-state motion and with $E \leftarrow B$ near the outer turning point of B-state motion, an interval of half a vibrational period or more must elapse between the generation of nuclear amplitude in the B state (by pulse 1 or 2) and its nonnegligible transfer to state E (by pulse 3). Accordingly, the wave-packet overlaps constituting $u_{123}(t)$ are both vanishingly small unless t and τ (the integration variable for the pulse-3 reduced pulse propagator and the upper limit for $p_1^{(BX)}$ [first overlap] and $p_2^{(BX)}$ [second overlap] take values of half a vibrational period or larger, well in excess of the duration of the first and second pulses. It is therefore appropriate to neglect the nesting of the pulse that acts first on $|\Psi_0\rangle$ within the $p_3^{(EB)}$ integral and push the

upper limit of integration in all pulse-1 and pulse-2 reduced propagators to plus infinity, writing, for example,

$$\rho_1^{(BX)}(\tau;\tau') \longrightarrow \rho_1^{(BX)}(\infty;\tau') \equiv \rho_1^{(BX)}$$

and

$$\rho_2^{(XB)}(t;\bar{\tau}) \longrightarrow \rho_2^{(XB)}(\infty;\bar{\tau}) \equiv \rho_2^{(XB)} .$$

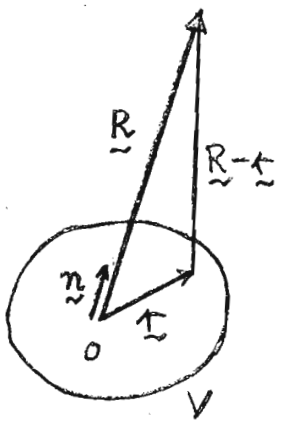
These mathematical simplifications correspond to the physical observation that, with Segale and Aptekarian's choice of center frequencies, the turn-on of the trilinear molecular dipole is unaffected by the precise form of the pulse-1 and pulse-2 electric-field envelopes, but is governed instead by the temporal envelope of pulse 3.

The molecules distributed with density ρ within the illuminated sample volume V | of cross-sectional area $\pi(d/2)^2$, where d is the diameter of the focused (laser spots) give rise to a trilinear electric field

$$E_{123}(t) = -\frac{\rho}{c^2 R}\int_V d^3r\ \ddot{\mu}_{123}\left(t - \frac{R}{c} + \frac{\underline{n}\cdot\underline{r}}{c}\right)$$

$$\cong \frac{\rho \Omega_3^2}{c^2 R}\int_V d^3r\ \mu_{123}\left(t - \frac{R}{c} + \frac{\underline{n}\cdot\underline{r}}{c}\right)$$

at a point $\underline{R}$ far from the sample. The electric field at time t is determined by the trilinear dipoles at times earlier by the travel-time of a light wave from their location $\underline{r}$ to the field point $\underline{R} = R\underline{n}$ (i.e. $|\underline{R}-\underline{r}|/c \cong R/c - \underline{n}\cdot\underline{r}/c$).



The free molecular evolution operators appearing in $U_{123}(t - R/c + \underset{\sim}{n}\cdot\underset{\sim}{r}/c)$ are for time intervals such as

$$t_{jk}(\underset{\sim}{r}) = t_{jk} + \underset{\sim}{n}_{jk}\cdot\underset{\sim}{r}/c$$

(t_{jk}: interpulse delay reckoned at the sample origin)

($\underset{\sim}{n}_{jk} \equiv \underset{\sim}{n}_j - \underset{\sim}{n}_k$; not a unit vector)

and

$$t - R/c + (\underset{\sim}{n} - \underset{\sim}{n}_j)\cdot\underset{\sim}{r}/c \quad .$$

We assume that the angle $\delta\theta_{jk}$ between beams j and k is small enough that

$$|\underset{\sim}{n}_{jk}\cdot\underset{\sim}{r}/c| < |n_{jk}|\, d/c \cong \sqrt{(\underset{\sim}{n}_j - \underset{\sim}{n}_k)^2}\, d/c = \sqrt{2 - 2\cos\delta\theta_{jk}}$$

$$\cong \delta\theta_{jk}\, d/c$$

is **much shorter than the vibrational timescale**, and also anticipate that the trilinear signal field will be nonnegligible only in some directions very similar to the incident directions, so that $\sqrt{(\underset{\sim}{n} - \underset{\sim}{n}_j)^2}\, d/c$ is similarly short on the vibrational timescale. It follows

That $[-t_{z1}(\underline{\Sigma})]_{xx} = [-t_{z1}]_{xx}[-\underline{n}_{z1}\cdot\underline{\Sigma}/c]_{xx}$

$\cong [-t_{z1}]_{xx}$,

$[-t + R/c - \underline{n}\cdot\underline{\Sigma}/c + t_2(\underline{\Sigma})]_{BB} = [-t + \frac{R}{c} + t_2]_{BB}[-(\underline{n}-\underline{n}_2)\cdot\underline{\Sigma}/c]_{BB}$

$\cong e^{i\Omega_2(\underline{n}-\underline{n}_2)\cdot\underline{\Sigma}/c}[-t+\frac{R}{c}+t_2]_{BB}$,

$[t - t_3(\underline{\Sigma})]_{EE} \cong e^{-i(\Omega_2+\Omega_3)(\underline{n}-\underline{n}_3)\cdot\underline{\Sigma}/c}[t + R/c - t_3]_{EE}$,

and so forth. We took advantage of the fact that the resonantly accessed states in the X, B, and E manifolds have energies of rough size 0, $\hbar\Omega_{1,2}$, and $\hbar(\Omega_2+\Omega_3)$, respectively. In accounting for the location dependence of the pulse-3 propagator, we proceed as follows.

$$p_3^{(EB)}(t-\tfrac{R}{c}+\tfrac{\underline{n}\cdot\underline{\Sigma}}{c};\tau) = \int_{-\infty}^{t-\frac{R}{c}+\frac{\underline{n}\cdot\underline{\Sigma}}{c}} d\tau\; g(\tau - t_3 - \tfrac{\underline{n}_3\cdot\underline{\Sigma}}{c})$$

(see p. 4 for the form of the integrand)

let $\tau' = \tau - \underline{n}\cdot\underline{\Sigma}/c$

$$= \int_{-\infty}^{t-\frac{R}{c}} d\tau'\; g(\tau' - t_3 + \underbrace{(\underline{n}-\underline{n}_3)\cdot\underline{\Sigma}/c}_{\text{negligible}}) \cong p_3^{(EB)}(t-\tfrac{R}{c};\tau,\underline{\Sigma}=0) .$$

For the last quantity we write simply $p_3^{(EB)}(t-\frac{R}{c};\tau)$, with the understanding that, henceforward, it and all the pulse propagators are those for a **molecule at the sample origin.**

With this understanding, we obtain a new working expression for the trilinear dipole moment,

$$\mu_{123}\left(t-\frac{R}{c}+\frac{\underset{\sim}{n}\cdot\underset{\sim}{r}}{c}\right) \cong -2m^2m'^3 E_1E_2E_3 \,\mathrm{Im}\, e^{i\varphi_{21}-i\varphi_3-i(\Omega_3\underset{\sim}{n}+\Omega_2\underset{\sim}{n}_2-\Omega_3\underset{\sim}{n}_3-\Omega_2\underset{\sim}{n}_1)\cdot\frac{\underset{\sim}{r}}{c}}$$

$$\rightarrow \langle\psi_0|[-t_{21}]_{XX}\, p_2^{(XB)}\,[-t+\tfrac{R}{c}+t_2]_{BB}\,[t-\tfrac{R}{c}-t_3]_{EE}\, p_3^{(EB)}(t-\tfrac{R}{c};\tau)\,[t_{31}]_{BB}\, p_1^{(BX)}|\psi_0\rangle$$

$$-2m^2m'^2 E_1E_2E_3 \,\mathrm{Im}\, e^{-i\varphi_{21}-i\varphi_3-i(\underset{\sim}{n}\Omega_3+\underset{\sim}{n}_1\Omega_1-\underset{\sim}{n}_2\Omega_1-\underset{\sim}{n}_3\Omega_3)\cdot\underset{\sim}{r}/c}$$

$$\rightarrow \langle\psi_0|p_1^{(XB)}\,[-t+\tfrac{R}{c}+t_1]_{BB}\,[t-\tfrac{R}{c}-t_3]_{EE}\, p_3^{(EB)}(t-\tfrac{R}{c};\tau)\,[t_{32}]_{BB}\, p_2^{(BX)}\,[t_{21}]_{XX}|\psi_0\rangle\ .$$

In evaluating the spatial integral over u_{123}, we can write

$$\frac{1}{c}\left(\Omega_3 \underset{\sim}{n} + \Omega_2 \underset{\sim}{n}_2 - \Omega_3 \underset{\sim}{n}_3 - \Omega_2 \underset{\sim}{n}_1\right) \cong \underset{\sim}{k} + \underset{\sim}{k}_2 - \underset{\sim}{k}_3 - \underset{\sim}{k}_1$$

with wave vectors

$\underset{\sim}{k} = \frac{\Omega_3}{c}\underset{\sim}{n}$ (ignoring any small difference in center frequency between pulse 3 and the signal beam)

$\underset{\sim}{k}_1 = \frac{\Omega_1}{c}\underset{\sim}{n}_1$ (ignoring the small difference between Ω_2 and Ω_1)

$\underset{\sim}{k}_2 = \frac{\Omega_2}{c}\underset{\sim}{n}_2$

$\underset{\sim}{k}_3 = \frac{\Omega_3}{c}\underset{\sim}{n}_3$.

Similarly,

$$\frac{1}{c}\left(\Omega_3 \underset{\sim}{n} + \Omega_1 \underset{\sim}{n}_1 - \Omega_1 \underset{\sim}{n}_2 - \Omega_3 \underset{\sim}{n}_3\right) \cong \underset{\sim}{k} + \underset{\sim}{k}_1 - \underset{\sim}{k}_2 - \underset{\sim}{k}_3 .$$

We define $\delta_V(\underset{\sim}{\kappa}) = \int_V d^3r\, e^{-i\kappa\cdot r}$ (with $\delta_V(\underset{\sim}{0}) = V$).

Then

$$\mathbf{E}_{123}(t) = -2m^2 m'^2 E_1 E_2 E_3 \frac{\rho \Omega_3^2}{c^2 R} \operatorname{Im} e^{i\varphi_{21} - i\varphi_3} \delta_V(\underset{\sim}{k} - \underset{\sim}{k}_3 + \underset{\sim}{k}_2 - \underset{\sim}{k}_1)$$

$$\hookrightarrow \langle \psi_0 | [-t_{21}]_{XX} \mathcal{P}_2^{(XB)} \left[-t + \tfrac{R}{c} + t_2\right]_{BB} \left[t - \tfrac{R}{c} - t_3\right]_{EE} \mathcal{P}_3^{(EB)}\left(t - \tfrac{R}{c}; \tau\right) [t_{31}]_{BB} \mathcal{P}_1^{(BX)} | \psi_0 \rangle$$

$$- 2m^2 m'^2 E_1 E_2 E_3 \frac{\rho \Omega_3^2}{c^2 R} \operatorname{Im} e^{-i\varphi_{21} - i\varphi_3} \delta_V(\underset{\sim}{k} - \underset{\sim}{k}_3 - \underset{\sim}{k}_2 + \underset{\sim}{k}_1)$$

$$\hookrightarrow \langle \psi_0 | \mathcal{P}_1^{(XB)} \left[-t + \tfrac{R}{c} + t_1\right]_{BB} \left[t - \tfrac{R}{c} - t_3\right]_{EE} \mathcal{P}_3^{(EB)}\left(t - \tfrac{R}{c}; \tau\right) [t_{32}]_{BB} \mathcal{P}_2^{(BX)} [t_{21}]_{XX} | \psi_0 \rangle .$$

The δ_v-functions enforce **wave-vector matching**, such that the signal field of phase signature $\varphi_{21} - \varphi_3$ (referred to by S & A as the "anti-Stokes signal" because their $\Omega_2 < \Omega_1$) propagates in the direction of $\underline{k} = \underline{k}_3 - \underline{k}_2 + \underline{k}_1$, and the signal with signature $-\varphi_{21} - \varphi_3$ (the "Stokes signal") propagates in the direction of $\underline{k} = \underline{k}_3 + \underline{k}_2 - \underline{k}_1$.

Segale and Apkarian do not control the relative optical phase of their pulses, nor heterodyne-detect the signal field with a phase-controlled local-oscillator pulse. Instead, they determine the intensity ($\propto E_1^2 E_2^2 E_3^2$) of the frequency-resolved signal field $\tilde{E}_{123}(\omega)$; for this homodyne-detected signal the inter-pulse optical phase-shifts become irrelevant and need not be actively stabilized.

Because wave-packet evolution in the B- and E-states involves distinct phase-space trajectories of large-amplitude intramolecular motion coupled differently to the medium, we may anticipate (and Segale & Apkarian's results confirm) the the E/B overlaps will be maximal at some short time after the 3-pulse and very short-lived. We let $t = t_m + \frac{R}{c} + \delta t$ (with $t_m \gtrsim t_3$, a function of t_{21}, being the **time of maximal electronic coherence**).

Evaluation of

$$\tilde{E}_{123}(\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t} E_{123}(t) = e^{i\omega(t_m + \frac{R}{c})} \int_{-\infty}^{\infty} d(\delta t)\, e^{i\omega \delta t} E_{123}(t_m + \frac{R}{c} + \delta t)$$

Therefore involves the integral (anti-Stokes signal)

$$\int_{-\infty}^{\infty} d(\delta t)\, e^{i\omega\delta t} \left[-t_m - \frac{R}{c} - \delta t + \frac{R}{c} + t_2\right]_{BB} \left[t_m + \frac{R}{c} + \delta t - \frac{R}{c} - t_3\right]_{EE}$$

$$\hookrightarrow P_3^{(EB)}\left(t_m + \frac{R}{c} + \delta t - \frac{R}{c}; \tau\right)$$

$$= \left[-t_{m2}\right]_{BB} \int_{-\infty}^{\infty} d(\delta t)\, e^{i\omega\delta t} \left[-\delta t\right]_{BB} \left[\delta t\right]_{EE} P_3^{(EB)}(t_m + \delta t; \tau) \left[t_{m3}\right]_{EE}$$

$$\equiv \left[-t_{m2}\right]_{BB} W^{(EB)}(\omega; t_m) \left[t_{m3}\right]_{EE}$$

with t_m chosen to maximize the anti-Stokes signal

and the integral (Stokes signal)

$$\int_{-\infty}^{\infty} d(\delta t)\, e^{i\omega\delta t)} \left[-t_m - \delta t + t_1\right]_{BB} \left[t_m + \delta t - t_3\right]_{EE} P_3^{(EB)}(t_m + \delta t; \tau)$$

$$= \left[-t_{m1}\right]_{BB} W^{(EB)}(\omega; t_m) \left[t_{m3}\right]_{EE}$$

with t_m chosen to maximize the Stokes signal

A variety of approximations can be envisaged for $W^{(EB)}$ which are based on the fact that its integrand need be accurately represented only for values of δt that are short on the vibrational timescales.

By way of example, we choose $\underline{k} = \underline{k}_3 - \underline{k}_2 + \underline{k}_1$ (i.e. in the phase-matched direction of the anti-Stokes signal). In evaluating the Fourier transform, we specialize to $\omega > 0$ and, using $\mathrm{Im}(a+ib) = b = \frac{-i(a+ib) + i(a+ib)^*}{2}$, neglect the counter-rotating term to obtain the spectrally resolved **anti-Stokes signal field**,

$$\tilde{E}_{123}(\omega) = i m^2 m'^2 E_1 E_2 E_3 \frac{V_p \mathcal{N}_3^2}{c^2 R} e^{i\varphi_{21} - i\varphi_3 + i\omega(t_m + \frac{R}{c})}$$

$$\hookrightarrow \langle \psi_0 | [-t_{21}]_{XX} P_2^{(XB)} [-t_{m2}]_{BB} W^{(EB)}(\omega) [t_{m3}]_{EE} [t_{31}]_{BB} P_1^{(BX)} | \psi_0 \rangle ,$$

which we could readily imagine calculating in the **FVB/GB theory**, and the anti-Stokes four-wave-mixing signal is proportional to $|\tilde{E}_{123}(\omega)|^2$.

Similarly, we may take $\underline{k} = \underline{k}_3 + \underline{k}_2 - \underline{k}_1$ to obtain the spectrally resolved **Stokes signal field**,

$$\tilde{E}_{123}(\omega) = i m^2 m'^2 E_1 E_2 E_3 \frac{V_p \mathcal{N}_3^2}{c^2 R} e^{-i\varphi_{21} - i\varphi_3 + i\omega(t_m + \frac{R}{c})}$$

$$\hookrightarrow \langle \psi_0 | P_1^{(XB)} [-t_{m1}]_{BB} W^{(EB)}(\omega) [t_{m3}]_{EE} [t_{32}]_{BB} P_2^{(BX)} [t_{21}]_{XX} | \psi_0 \rangle .$$

Using these expressions and working from multidimensional potentials for the molecule and medium in the X-, B-, and E-states, it should be possible to generate from first principles the signals measured by Segale and Apkarian, and to test quantitatively the quantities and concepts considered in their interpretation.