Supplementary Information

Holstein-Peirls-Hubbard Trimer as a model for quadrupolar two-photon absorbing dyes

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TABLES

Table S-1. Expressions and energies of the complete (6 state) basis set. Symmetry of the eigenstates: ‘’g’’ stands for gerade and ‘’u’’ stands for ungerade.

Basis State	Energy	Eigenstate	Symmetry
$\lvert S_1\rangle = \hat{a}^+_{2\uparrow}\hat{a}^+_{2\downarrow}\lvert 0\rangle$	U_d	$\lvert 1\rangle$	g
$\lvert S_2\rangle = \frac{1}{\sqrt{2}}\left[\hat{a}^+_{1\uparrow}\hat{a}^+_{2\downarrow} + \hat{a}^+_{2\uparrow}\hat{a}^+_{1\downarrow}\right]\lvert 0\rangle$	ε	$\lvert 2\rangle$	u
$\lvert S_3\rangle = \frac{1}{\sqrt{2}}\left[\hat{a}^+_{3\uparrow}\hat{a}^+_{2\downarrow} + \hat{a}^+_{2\uparrow}\hat{a}^+_{3\downarrow}\right]\lvert 0\rangle$	ε	$\lvert 3\rangle$	g
$\lvert S_4\rangle = \frac{1}{\sqrt{2}}\left[\hat{a}^+_{1\uparrow}\hat{a}^+_{3\downarrow} + \hat{a}^+_{3\uparrow}\hat{a}^+_{1\downarrow}\right]\lvert 0\rangle$	2ε	$\lvert 4\rangle$	g
$\lvert S_5\rangle = \hat{a}^+_{3\uparrow}\hat{a}^+_{3\downarrow}\lvert 0\rangle$	$2\varepsilon + U_a$	$\lvert 5\rangle$	u
$\lvert S_6\rangle = \hat{a}^+_{1\uparrow}\hat{a}^+_{1\downarrow}\lvert 0\rangle$	$2\varepsilon + U_a$	$\lvert 6\rangle$	g

Table S-2. Exact eigenvalues and eigenvectors of the reduced Hamiltonian Eq. (5).

Eigenvector[a]	Eigenvalue[b]	Transition Energy[b]
$\lvert 1\rangle = \sum_i a_i \lvert S_i\rangle$	$E_1 = \frac{(U_d + \varepsilon) - \sqrt{\Delta^2 + 16t^2}}{2}$	$E_{21} = \frac{\Delta + \sqrt{\Delta^2 + 16t^2}}{2}$
$\lvert 2\rangle = \sum_i b_i \lvert S_i\rangle$	$E_2 = \varepsilon$	$E_{32} = \frac{-\Delta + \sqrt{\Delta^2 + 16t^2}}{2}$
$\lvert 3\rangle = \sum_i c_i \lvert S_i\rangle$	$E_3 = \frac{(U_d + \varepsilon) + \sqrt{\Delta^2 + 16t^2}}{2}$	$E_{31} = \sqrt{\Delta^2 + 16t^2}$

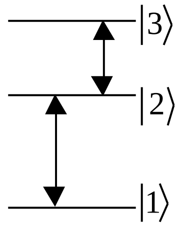
[a]Eigenvectors coefficients:

$$a_1 = \frac{E_{21}}{\sqrt{E_{21}^2 + 4t^2}} \qquad b_1 = 0 \qquad c_1 = \frac{-E_{32}}{\sqrt{E_{32}^2 + 4t^2}}$$

$$a_2 = a_3 = \frac{\sqrt{2}t}{\sqrt{E_{21}^2 + 4t^2}} \qquad b_2 = -b_3 = \frac{1}{\sqrt{2}} \qquad c_2 = c_3 = \frac{\sqrt{2}t}{\sqrt{E_{32}^2 + 4t^2}}$$

[b]$\Delta = \varepsilon - U_d$

Table S-3. Analytical expression of $\alpha(-\omega_1;+\omega_1)$ for the dimer and the trimer without electron-phonon coupling. Data concerning the dimer are from Ref. 32.

	DIMER	TRIMER
Level Diagram		
Expression for α	$\alpha(-\omega_1;\omega_1)=\frac{-2}{\varepsilon_0}\frac{R_{12}^2 E_{21}^2}{(\hbar\omega_1+i\Gamma)^2-E_{21}^2}$	
Transition Dipoles	$R_{12}^2=(edc_1)^2$	$R_{12}^2=(eda_2b_2)^2$
Transition energies	$E_{21}=\frac{U+\sqrt{U^2+16t^2}}{2}$	$E_{21}=\frac{\Delta+\sqrt{\Delta^2+16t^2}}{2}$
	$E_{32}=\frac{-U+\sqrt{U^2+16t^2}}{2}$	$E_{32}=\frac{-\Delta+\sqrt{\Delta^2+16t^2}}{2}$
Coefficient Expressions	$c_1=\frac{E_{32}}{\sqrt{E_{32}^2+4t^2}}$	$a_2b_2=\frac{t}{\sqrt{E_{21}^2+4t^2}}$

FIGURES

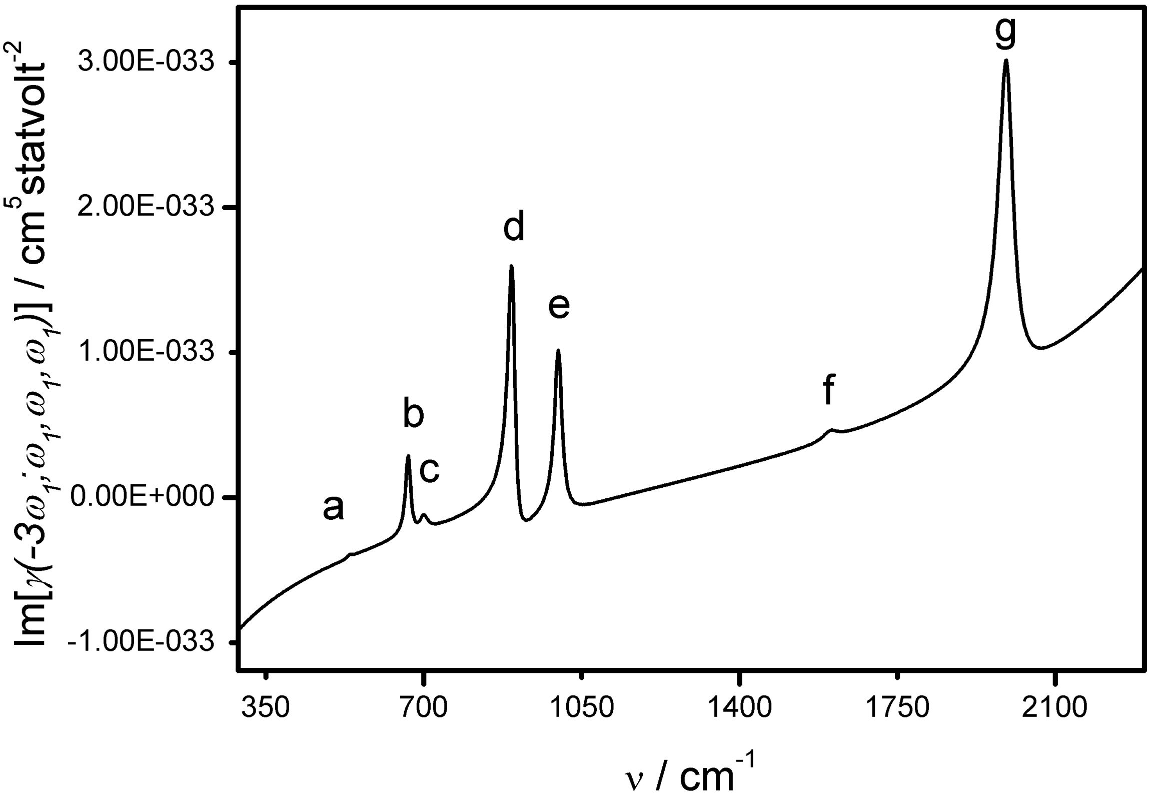


Fig. S-1. Enlargment of $\mathrm{Im}[\gamma(-3\omega_1;\omega_1,\omega_1,\omega_1)]$ in the vibrational region.

APPENDIXES

APPENDIX 1

Definition of the BOV modes

We recognise four BOV modes in the system under investigation (3N-5, N=3), but we are only interested in the symmetric and antisymmetric stretching modes which modulate the distance between A and D. The modes are respectively written as follows:

$$Q_S^{BOV} = \frac{1}{\sqrt{2}}\left(q_3 - q_1\right) \qquad Q_{AS}^{BOV} = \frac{1}{\sqrt{2m}}\left(\sqrt{m_1}q_3 - 2\sqrt{m_2}q_2 + \sqrt{m_1}q_1\right) \qquad \text{(A1-1)}$$

where m_i is the mass of the i-site, $m = 2m_1 + m_2$ and q_i are the spectroscopic mass-weighted coordinates. The subscripts "S" and "AS" to Q^e specify if the coordinate is symmetric or antisymetric with respect to the exchange of the sites 1 and 3. The BOV modes can also be treated as in-phase and out-of-phase combinations of a "left" and a "right" coordinate:

$$Q_S^{BOV} = \frac{1}{\sqrt{2}}\left(Q_L^{BOV} + Q_R^{BOV}\right) \qquad Q_{AS}^{BOV} = \frac{1}{\sqrt{2}}\sqrt{\frac{m_1}{m}}\left(Q_L^{BOV} - Q_R^{BOV}\right) \qquad \text{(A1-2)}$$

where $Q_L^{BOV} = \sqrt{\frac{m_2}{m_1}}q_2 - q_1$ and $Q_R^{BOV} = q_3 - \sqrt{\frac{m_2}{m_1}}q_2$: the former affects only the distance between the sites 1 and 2 and the latter between the sites 2 and 3. In terms of dimensionless modes we finally have

$$u_+ \equiv u_S = \frac{1}{\sqrt{2}}\left(u_L + u_R\right) \qquad u_- \equiv u_{AS} = \frac{1}{\sqrt{2}}R_m\left(u_L - u_R\right) \qquad \text{(A1-3)}$$

$$u_{L,R} = \sqrt{\frac{2\omega_+}{\hbar}}Q_{L,R}^{BOV} \qquad R_m = \sqrt{\frac{\omega_-}{\omega_+}}\sqrt{\frac{m_1}{m}} \qquad \text{(A1-4)}$$

Derivation of the vibronic coupling Hamiltonian H_{EMV}

The vibronic coupling Hamiltonian can be derived by considering the site-energies as linearly dependent on the SEV modes: to perform this expansion, Eq. (5) needs recasting in a more useful way, so that all site-energies are shown explicitly:

$$\begin{aligned}\hat{H}_H = {} & \varepsilon_{LUMO}^{Acceptor\,1}\hat{n}_1 + \varepsilon_{LUMO}^{Acceptor\,3}\hat{n}_3 + \varepsilon_{HOMO}^{Donor}\hat{n}_2 \\ & + U_d\hat{n}_{2\uparrow}\hat{n}_{2\downarrow} + U_a\left(\hat{n}_{1\uparrow}\hat{n}_{1\downarrow} + \hat{n}_{3\uparrow}\hat{n}_{3\downarrow}\right) \\ & - t_{AD}\hat{T}_{AD} - t_{DA}\hat{T}_{DA}\end{aligned} \quad \text{(A1-5)}$$

The first row is equivalent to the term $\varepsilon(\hat{n}_1 + \hat{n}_3)$ since $\varepsilon_{LUMO}^{Acceptor\,1} = \varepsilon_{LUMO}^{Acceptor\,3}$ and $\varepsilon_{HOMO}^{Donor}$ can be set to zero (as considered in the main text) without loss of generality. All site-energies are therefore developed in power series as a function of the corresponding SEV modes up to the first order:

$$\varepsilon_{LUMO}^{Acceptor\,1} = \left(\varepsilon_{LUMO}^{Acceptor\,1}\right)^0 + \sum_i \left(\frac{\partial \varepsilon_{LUMO}^{Acceptor\,1}}{\partial Q_{i1}}\right)_0 Q_{i1} \quad \text{(A1-6)}$$

$$\varepsilon_{LUMO}^{Acceptor\,3} = \left(\varepsilon_{LUMO}^{Acceptor\,3}\right)^0 + \sum_i \left(\frac{\partial \varepsilon_{LUMO}^{Acceptor\,3}}{\partial Q_{i3}}\right)_0 Q_{i3} \quad \text{(A1-7)}$$

$$\varepsilon_{HOMO}^{Donor} = \left(\varepsilon_{HOMO}^{Donor}\right)^0 + \sum_i \left(\frac{\partial \varepsilon_D}{Q_{i2}}\right) Q_{i2} \quad \text{(A1-8)}$$

Considering only the first row in (A1-5) and inserting the previous expressions, the following equation is obtained:

$$\begin{aligned}&\varepsilon_{LUMO}^{Acceptor\,1}\hat{n}_1 + \varepsilon_{LUMO}^{Acceptor\,3}\hat{n}_3 + \varepsilon_{HOMO}^{Donor}\hat{n}_2 = \\ &\left(\left(\varepsilon_{LUMO}^{Acceptor\,1}\right)^0 + \sum_i \left(\frac{\partial \varepsilon_{LUMO}^{Acceptor\,1}}{\partial Q_{i1}}\right)_0 Q_{i1}\right)\hat{n}_1 + \left(\left(\varepsilon_{LUMO}^{Acceptor\,3}\right)^0 + \sum_i \left(\frac{\partial \varepsilon_{LUMO}^{Acceptor\,3}}{\partial Q_{i3}}\right)_0 Q_{i3}\right)\hat{n}_3 + \left(\left(\varepsilon_{HOMO}^{Donor}\right)^0 + \sum_i \left(\frac{\partial \varepsilon_D}{Q_{iD}}\right) Q_{i2}\right)\hat{n}_2\end{aligned} \quad \text{(A1-9)}$$

On the right hand side we then set $\left(\varepsilon_{HOMO}^{Donor}\right)^0 = 0$ and define $\left(\varepsilon_{LUMO}^{Acceptor1}\right)^0 - \left(\varepsilon_{HOMO}^{Donor}\right)^0 = \varepsilon$, so that we obtain:

$$\begin{aligned}&\varepsilon_{LUMO}^{Acceptor\,1}\hat{n}_1 + \varepsilon_{LUMO}^{Acceptor\,3}\hat{n}_3 + \varepsilon_{HOMO}^{Donor}\hat{n}_2 = \\ &\quad \varepsilon(\hat{n}_1 + \hat{n}_3) + \hat{n}_1 \sum_i \left(\frac{\partial \varepsilon_{LUMO}^{Acceptor\,1}}{\partial Q_{i1}}\right)_0 Q_{i1} + \hat{n}_3 \sum_i \left(\frac{\partial \varepsilon_{LUMO}^{Acceptor\,3}}{\partial Q_{i3}}\right)_0 Q_{i3} + \hat{n}_2 \sum_i \left(\frac{\partial \varepsilon_{HOMO}^{Donor}}{Q_{iD}}\right) Q_{i2}\end{aligned} \quad \text{(A1-10)}$$

Making use of the definitions in Eq. (10) and (13), the following equation can be written down:

$$\varepsilon_{LUMO}^{Acceptor\,1}\hat{n}_1 + \varepsilon_{LUMO}^{Acceptor\,3}\hat{n}_3 + \varepsilon_{HOMO}^{Donor}\hat{n}_2 = \varepsilon(\hat{n}_1 + \hat{n}_3) + \sum_i \left\{\frac{g_{iA}}{\sqrt{2}}\left[R_{i+}\hat{N}^+ + R_{i-}\hat{N}^-\right] + g_{iD}Q_{i2}\hat{n}_2\right\} \quad \text{(A1-11)}$$

where $\sum_i \left\{ \frac{g_{iA}}{\sqrt{2}} \left[R_{i+} \hat{N}^{+} + R_{i-} \hat{N}^{-} \right] + g_{iD} Q_{i2} \hat{n}_2 \right\}$ is the definition of $\hat{H}_{EMV}$ in Eq. (6).

Derivation of the vibrational coupling Hamiltonian H_{EIP}

In this case we develop the charge transfer integrals (in the last two terms in Eq. (5) or in the last row in Eq. (A1-5)) in power series as a function of the BOV modes:

$$t'_{AD} = t_{AD} + \left(\frac{\partial t_{AD}}{\partial u_L} \right)_0 u_L \text{ and } t'_{DA} = t_{DA} + \left(\frac{\partial t_{DA}}{\partial u_R} \right)_0 u_R \qquad \text{(A1-12)}$$

Notice that in the electronic Hamiltonian $\hat{H}_H$ the charge transfer integrals indicated with t are considered to be "unperturbed": once the vibronic coupling is introduced, the unperturbed ones are still named t and the coupled ones are named t'.

The term $t_{AD}\hat{T}_{AD} + t_{DA}\hat{T}_{DA}$ in Eq. (5) can be rewritten including the expansion (A1-12) and making use of the definitions (A1-3), (11) and (13):

$$t'_{AD}\hat{T}_{AD} + t'_{DA}\hat{T}_{DA} = t_{AD}\hat{T}_{AD} + t_{DA}\hat{T}_{DA} - \frac{g}{\sqrt{2}} \left[u_+ \hat{T}^{+} + R_m u_- \hat{T}^{-} \right] \qquad \text{(A1-13)}$$

where $\frac{g}{\sqrt{2}} \left[u_+ \hat{T}^{+} + R_m u_- \hat{T}^{-} \right]$ is the definition of $\hat{H}_{EIP}$ in Eq. (7).

Derivation of the vibronic Hamiltonian H_V

Starting from the vibrational Hamiltonian:

$$\hat{H}_V = \sum_i \left\{ \frac{\hbar\omega_{iA}}{4} \left[\left(Q_{i1}^2 + P_{i1}^2 \right) + \left(Q_{i3}^2 + P_{i3}^2 \right) \right] + \frac{\hbar\omega_{iD}}{4} \left[P_{i2}^2 + Q_{i2}^2 \right] \right\} \qquad \text{(A1-14)}$$

It can be easily rewritten in the form of Eq. (8), by using the Eq. (10)-(12).

APPENDIX 2

The expressions for the vibrational operators can be worked out by solving the Heisenberg equation of the motion:

$$i\hbar\frac{d\hat{A}^{H}(t)}{dt}=\left[\hat{A}^{H}(t),\hat{H}^{H}(t)\right] \tag{A2-1}$$

The superscript H specifies that the operator is in the Heisenberg picture; $\hat{A}^{H}(t)$ represents any of the vibrational operators or the corresponding momenta. $\hat{H}^{H}(t)$ is the Heisenberg representation of the total Hamiltonian defined in Eq. (1). As an example, the equation of motion for $\hat{R}^{H}_{i+}(t)$ is worked out in the following: Eq. (A2-1) is solved for $\hat{A}^{H}_{i+}(t)=\hat{S}^{H}_{i+}(t)$ providing:

$$i\hbar\frac{d\hat{S}^{H}_{i+}(t)}{dt}=\left[\hat{S}^{H}_{i+}(t),\hat{H}^{H}(t)\right]=\left[\hat{S}^{H}_{i+}(t),\hat{H}^{H}_{EMV}(t)\right]+\left[\hat{S}^{H}_{i+}(t),\hat{H}^{H}_{V}(t)\right] \tag{A2-2}$$

By substituting the expressions for $\hat{H}^{H}_{EMV}(t)$ and $\hat{H}^{H}_{V}(t)$ we have:

$$\hbar\frac{d\hat{S}^{H}_{i+}(t)}{dt}=-\sqrt{2}g_{iA}\left[\hat{N}^{+H}(t)\right]-\hbar\omega_{iA}\hat{R}^{H}_{i+}(t) \tag{A2-3}$$

The relation $\left[\left(\hat{R}^{H}_{i+}(t)\right)^{2},\hat{S}^{H}_{i+}(t)\right]=4i\hat{R}^{H}_{i+}(t)$ has been used. Finally, considering the expression $\frac{1}{\omega_{iA}}\frac{d\hat{R}^{H}_{i+}(t)}{dt}=\hat{R}^{H}_{i+}(t)$, we achieve in the time domain:

$$\ddot{\hat{R}}^{H}_{i+}(t)+\omega^{2}_{iA}\hat{R}^{H}_{i+}(t)=\frac{-\sqrt{2}g_{iA}\omega_{iA}}{\hbar}\hat{N}^{+H}(t) \tag{A2-4}$$

In the frequency domain (i.e. performing a Fourier transform on the previous equation) we have:

$$\hat{R}^{H}_{i+}(\omega)=D^{i}_{A}(\omega)\hat{N}^{+H}(\omega) \tag{A2-5}$$

Where $D^{i}_{A}(\omega)=\frac{-\sqrt{2}g_{iA}\omega_{iA}}{\hbar\left[\omega^{2}_{iA}-(\omega+i\gamma_{A})^{2}\right]}$.

The calculation outlined above, can be repeated for all vibrational operators: in the following the expressions for all of them are summarized:

$$\hat{R}^{H}_{i+}(\omega) = D^{i}_{A}(\omega)\hat{N}^{+H}(\omega) \qquad \hat{Q}^{H}_{i2}(\omega) = D^{i}_{D}(\omega)\hat{n}^{H}_{2}(\omega) \tag{A2-6}$$

$$\hat{R}^{H}_{i+}(\omega) = D^{i}_{A}(\omega)\hat{N}^{+H}(\omega) \qquad \hat{R}^{H}_{i-}(\omega) = D^{i}_{A}(\omega)\hat{N}^{-H}(\omega) \tag{A2-7}$$

$$\hat{u}^{H}_{-}(\omega) = F_{-}(\omega)\hat{\Gamma}^{-H}(\omega) + G_{-}(\omega)\Im\{E(t)\hat{N}^{+H}(t)\} \tag{A2-8}$$

$$\hat{u}^{H}_{+}(\omega) = F_{+}(\omega)\hat{\Gamma}^{+H}(\omega) + G_{+}(\omega)\Im\{E(t)\hat{N}^{-H}(t)\} \tag{A2-9}$$

where

$$D^{i}_{D}(\omega) = \frac{-2g_{iD}\omega_{iD}}{\hbar\left[\omega_{iD}^{2} - (\omega + i\gamma_{D})^{2}\right]} \qquad D^{i}_{A}(\omega) = \frac{-\sqrt{2}g_{iA}\omega_{iA}}{\hbar\left[\omega_{iA}^{2} - (\omega + i\gamma_{A})^{2}\right]} \tag{A2-10}$$

$$F_{-}(\omega) = \frac{R_{m}\sqrt{2}g\omega_{-}}{\hbar\left[\omega_{-}^{2} - (\omega + i\gamma)^{2}\right]} \qquad F_{+}(\omega) = \frac{\sqrt{2}g\omega_{+}}{\hbar\left[\omega_{+}^{2} - (\omega + i\gamma)^{2}\right]} \tag{A2-11}$$

$$G_{-}(\omega) = \frac{-e\sqrt{2}\,h_{Z}\,\omega_{-}R_{m}}{\hbar\left[\omega_{-}^{2} - (\omega + i\gamma)^{2}\right]} \qquad G_{+}(\omega) = \frac{e\sqrt{2}\,h_{Z}\,\omega_{+}}{\hbar\left[\omega_{+}^{2} - (\omega + i\gamma)^{2}\right]} \tag{A2-12}$$

$$D_{D}(\omega) = \sum_{i} g_{iD} D^{i}_{D}(\omega) \qquad D_{A}(\omega) = \sum_{i} \frac{g_{iA}}{\sqrt{2}} D^{i}_{A}(\omega) \tag{A2-13}$$

$\Im\{f(t)\}$ is the Fourier transform of f(t); γ are the damping parameters for the vibrational transitions. The Fourier transform and its inverse have been respectively performed with the relations

$$z(\omega) = \Im\{z(t)\} = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} z(t)e^{i\omega t}dt \tag{A2-14a}$$

and

$$z(t) = \Im^{-1}\{z(\omega)\} = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} z(\omega)e^{-i\omega t}\,d\omega \qquad \text{(A2-14b)}$$

The quantities F(ω), G(ω) and D(ω) are usually called propagators: the first and the second are respectively originated by the dependence of t and d on the BOV coordinates, whereas D(ω) derives from the dependence of the site energies on the SEV modes. The subscripts of D(ω), A and D, specify if it has been expanded the Donor or the Acceptor site energy; the subscripts of F(ω) and G(ω), + and –, indicate that we are dealing with the coupling with u_+ and u_-.

Random phase approximation

The RPA requires that vibrational operators are replaced by their expectation values. The expression for the expectation values in the time and in the frequency domain are:

$$\left\langle \hat{Q}_{i2}(\omega) \right\rangle = D_D^i(\omega)\left\langle \hat{n}_2(\omega) \right\rangle \qquad \text{(A2-15)}$$

$$\left\langle \hat{R}_{i+}(\omega) \right\rangle = D_A^i(\omega)\left\langle \hat{N}^+(\omega) \right\rangle \qquad \left\langle \hat{R}_{i-}(\omega) \right\rangle = D_A^i(\omega)\left\langle \hat{N}^-(\omega) \right\rangle \qquad \text{(A2-16)}$$

$$\left\langle \hat{u}_-(\omega) \right\rangle = F_-(\omega)\left\langle \hat{T}^-(\omega) \right\rangle + G_-(\omega)\Im\left\{E(t)\left\langle \hat{N}^+(t) \right\rangle\right\} \qquad \text{(A2-17)}$$

$$\left\langle \hat{u}_+(\omega) \right\rangle = F_+(\omega)\left\langle \hat{T}^+(\omega) \right\rangle + G_+(\omega)\Im\left\{E(t)\left\langle \hat{N}^-(t) \right\rangle\right\} \qquad \text{(A2-18)}$$

$$\left\langle \hat{Q}_{i2}(t) \right\rangle = \Im^{-1}\left\{D_D^i(\omega)\left\langle \hat{n}_2(\omega) \right\rangle\right\} \qquad \text{(A2-19)}$$

$$\left\langle \hat{R}_{i+}(t) \right\rangle = \Im^{-1}\left\{D_A^i(\omega)\left\langle \hat{N}^+(\omega) \right\rangle\right\} \qquad \left\langle \hat{R}_{i-}(t) \right\rangle = \Im^{-1}\left\{D_A^i(\omega)\left\langle \hat{N}^-(\omega) \right\rangle\right\} \qquad \text{(A2-20)}$$

$$\left\langle \hat{u}_-(t) \right\rangle = \Im^{-1}\left\{F_-(\omega)\left\langle \hat{T}^+(\omega) \right\rangle\right\} + \Im^{-1}\left\{G_-(\omega)\Im\left\{E(t)\left\langle \hat{N}^-(t) \right\rangle\right\}\right\} \qquad \text{(A2-21)}$$

$$\left\langle \hat{u}_+(t) \right\rangle = \Im^{-1}\left\{F_+(\omega)\left\langle \hat{T}^+(\omega) \right\rangle\right\} + \Im^{-1}\left\{G_+(\omega)\Im\left\{E(t)\left\langle \hat{N}^-(t) \right\rangle\right\}\right\} \qquad \text{(A2-22)}$$

APPENDIX 3

We are interested in comparing $\hat{h}_T^{(0)}$ and $\hat{h}_H$; considering the six level system the expressions are the following

$$\hat{h}_H = \varepsilon(\hat{n}_1 + \hat{n}_3) + U_d \hat{n}_{2\uparrow}\hat{n}_{2\downarrow} + U_a(\hat{n}_{1\uparrow}\hat{n}_{1\downarrow} + \hat{n}_{3\uparrow}\hat{n}_{3\downarrow}) - t\ \hat{T}^+ \qquad \text{(A3-1)}$$

$$\begin{aligned}\hat{h}_T^{(0)} &= \hat{h}_H + \hat{h}_{EMV}^{(0)} + \hat{h}_{EIP}^{(0)} = \\ &\left[\varepsilon + \sum_i \frac{g_{iA}}{\sqrt{2}}\left\langle \hat{R}_{i+}\right\rangle^{(0)}\right]\hat{N}^+ + \sum_i g_{iD}\left\langle \hat{Q}_{i2}\right\rangle^{(0)}\hat{n}_2 + \left[-t - \frac{g}{\sqrt{2}}\left\langle \hat{u}_+\right\rangle^{(0)}\right]\hat{T}^+ + \\ &U_d \hat{n}_{2\uparrow}\hat{n}_{2\downarrow} + U_a(\hat{n}_{1\uparrow}\hat{n}_{1\downarrow} + \hat{n}_{3\uparrow}\hat{n}_{3\downarrow})\end{aligned} \qquad \text{(A3-2)}$$

It is now clear that $\hat{h}_T^{(0)}$ is different from $\hat{h}_H$ and then their eigenvectors are not the same. However, exploiting the relation $\hat{N}^+ + \hat{n}_2 = \hat{n}_1 + \hat{n}_2 + \hat{n}_3 = 2$ the equation (A3-2) can be recast in the form

$$\hat{h}_T^{(0)} = \hat{h}_H + \hat{h}_{EMV}^{(0)} + \hat{h}_{EIP}^{(0)} = \varepsilon' \hat{N}^+ - t' \hat{T}^+ + U_d \hat{n}_{2\uparrow}\hat{n}_{2\downarrow} + U_a(\hat{n}_{1\uparrow}\hat{n}_{1\downarrow} + \hat{n}_{3\uparrow}\hat{n}_{3\downarrow}) \qquad \text{(A3-3)}$$

where

$$\varepsilon' = \varepsilon + \sum_i \frac{4g_{iD}^2}{\hbar\omega_{iD}} - \left(\frac{g_{iA}^2}{\hbar\omega_{iA}} + \frac{2g_{iD}^2}{\hbar\omega_{iD}}\right)\left\langle \hat{N}^+\right\rangle \qquad t' = t + \frac{g^2}{\hbar\omega_+}\left\langle \hat{T}^+\right\rangle^{(0)} \qquad \text{(A3-4)}$$

Thus, the eigenvectors (and the eigenvalues) of $\hat{h}_T^{(0)}$ can be formally derived from that ones of $\hat{h}_H$ by swapping the parameters ε and t with ε' and t'.

APPENDIX 4

First of all, it is worth working out some relations in the time and frequency domain for a general function z(t) which depends on the electrical field **E**(t). The power series expansion of z(t) results

$$z(t) = z^{(1)}(t) + z^{(2)}(t) + z^{(3)}(t) \ldots \quad \text{(A4-1)}$$

where $z^{(n)}(t)$ depends on $\mathbf{E}^{(n)}(t)$.

Choosing a monochromatic electrical field as

$$\mathbf{E}(t) = \frac{1}{2}\left[\mathbf{E}_{\omega_1} e^{-i\omega_1 t} + \mathbf{E}_{-\omega_1} e^{i\omega_1 t}\right] \quad \text{(A4-2)}$$

where $\mathbf{E}_{\omega_1} = \mathbf{E}^*_{-\omega_1} = \mathbf{E}_1$, the following expressions are achieved at the first three orders

TIME DOMAIN

$$z^{(1)}(t) = \frac{1}{\sqrt{2\pi}}\left[\tilde{z}^{(1)}(-\omega_1;+\omega_1)e^{-i\omega_1 t} + \tilde{z}^{(1)}(\omega_1;-\omega_1)e^{i\omega_1 t}\right] \quad \text{(A4-3)}$$

$$z^{(2)}(t) = \frac{1}{\sqrt{2\pi}}\left[\tilde{z}^{(2)}(-2\omega_1;\omega_1,\omega_1)e^{-i2\omega_1 t} + \tilde{z}^{(2)}(0;\omega_1,-\omega_1) + \tilde{z}^{(2)}(+2\omega_1;-\omega_1,-\omega_1)e^{i2\omega_1 t}\right] \quad \text{(A4-4)}$$

$$\begin{aligned} z^{(3)}(t) = \frac{1}{\sqrt{2\pi}}\Big[&\tilde{z}^{(3)}(-3\omega_1;\omega_1,\omega_1,\omega_1)e^{-3i\omega_1 t} + \tilde{z}^{(3)}(-\omega_1;\omega_1,\omega_1,-\omega_1)e^{-i\omega_1 t} + \\ &+\tilde{z}^{(3)}(\omega_1;-\omega_1,-\omega_1,\omega_1)e^{i\omega_1 t} + \tilde{z}^{(3)}(+3\omega_1;-\omega_1,-\omega_1,-\omega_1)e^{3i\omega_1 t}\Big] \end{aligned} \quad \text{(A4-5)}$$

FREQUENCY DOMAIN

$$z^{(1)}(\omega) = \tilde{z}^{(1)}(-\omega_1;\omega_1)\delta(\omega-\omega_1) + \tilde{z}^{(1)}(\omega_1;-\omega_1)\delta(\omega+\omega_1) \quad \text{(A4-6)}$$

$$\begin{aligned} z^{(2)}(\omega) = &\tilde{z}^{(2)}(-2\omega_1;\omega_1,\omega_1)\delta(\omega-2\omega_1) + \tilde{z}^{(2)}(0;\omega_1,-\omega_1)\delta(\omega) \\ &+ \tilde{z}^{(2)}(+2\omega_1;-\omega_1,-\omega_1)\delta(\omega+2\omega_1) \end{aligned} \quad \text{(A4-7)}$$

$$\begin{aligned} z^{(3)}(\omega) = &\tilde{z}^{(3)}(-3\omega_1;\omega_1,\omega_1,\omega_1)\delta(\omega-3\omega_1) + \tilde{z}^{(3)}(-\omega_1;\omega_1,\omega_1,-\omega_1)\delta(\omega-\omega_1) \\ &+\tilde{z}^{(3)}(\omega_1;-\omega_1,-\omega_1,\omega_1)\delta(\omega+\omega_1) + \tilde{z}^{(3)}(+3\omega_1;-\omega_1,-\omega_1,-\omega_1)\delta(\omega+3\omega_1) \end{aligned} \quad \text{(A4-8)}$$

The Fourier transform and its inverse have been defined in Eq. (A2-14).

The solution of the equation of motion for the density operator, Eq. (19)

Let's first recast $\hat{h}_T(t)$ in Eq. 19 as the sum of two components:

$$\hat{h}_T(t) = \hat{h}(t) + \hat{f}(t) \tag{A4-9}$$

where $\hat{h}(t)$ collects all the terms that do not show any explicit dependence on the electrical field and $\hat{f}(t)$ collects the others.

Eq. (19) is solved in a perturbative way by expanding the density matrix in a power series of **E**:

$$\hat{\rho}(t) = \hat{\rho}^{(0)} + \hat{\rho}^{(1)}(t) + \hat{\rho}^{(2)}(t) + \dots \tag{A4-10}$$

The Hamiltonian $\hat{h}_T(t)$ contains $\hat{\rho}(t)$ in the expectation values of the vibrational operators which are consequently expanded in power series:

$$\left\langle \hat{O} \right\rangle = \left\langle \hat{O} \right\rangle^{(0)} + \left\langle \hat{O} \right\rangle^{(1)} + \left\langle \hat{O} \right\rangle^{(2)} + \dots \tag{A4-11}$$

where $\left\langle \hat{O} \right\rangle^{(n)} = \mathrm{Tr}\left[\hat{O}\hat{\rho}^{(n)}\right]$ and $\hat{O}$ is any of the vibrational operators.

Working in the Liouville space instead of the Hilbert one, and substituting the expansions in the electrical field of Eq. (A4-9) into the equation of motion, Eq. (19), the following expressions for the first three orders are obtained:

$$i\hbar\dot{\hat{\rho}}^{(1)}(t) = \mathsf{L}\hat{\rho}^{(1)}(t) + \left[\hat{f}^{(1)}(t), \hat{\rho}^{(0)}\right] \tag{A4-12}$$

$$i\hbar\dot{\hat{\rho}}^{(2)}(t) = \mathsf{L}\hat{\rho}^{(2)}(t) + \left[\hat{h}^{(1)}(t) + \hat{f}^{(1)}(t), \hat{\rho}^{(1)}(t)\right] + \left[\hat{f}^{(2)}(t), \hat{\rho}^{(0)}\right] \tag{A4-13}$$

$$\begin{aligned} i\hbar\dot{\hat{\rho}}^{(3)}(t) = \mathsf{L}\hat{\rho}^{(3)}(t) &+ \left[\hat{h}^{(1)}(t) + \hat{f}^{(1)}(t), \hat{\rho}^{(2)}\right] \\ &+ \left[\hat{h}^{(2)}(t) + \hat{f}^{(2)}(t), \hat{\rho}^{(1)}\right] + \left[\hat{f}^{(3)}(t), \hat{\rho}^{(0)}\right] \end{aligned} \tag{A4-14}$$

Solution of Eq. (A4-12) provides $\hat{\rho}^{(1)}$ and consequently any first order term: inserting it into Eq. (A4-13), second order quantities can be worked out and so on. Further detail is given in Ref. 32: here we just remind that to solve previous Equations we need to perform a Fourier transform and therefore we get as a solution the density operator in the frequency domain. [32] We remind that the superscript in round brackets at the top of operators and expectation values correspond to the order in electrical field.

L is the Liouville operator and it is defined, in the frequency domain, as

$$\sum_{nm} L_{ij,nm}(\omega)\rho_{nm}^{(n)}(\omega) = \left[\hat{h}^{(n)}(\omega), \hat{\rho}^{(0)}\right]_{ij} + \left[\hat{h}^{(0)}, \hat{\rho}^{(n)}(\omega)\right]_{ij} \qquad \text{(A4-15)}$$

The expression of h_T at the first three orders.

Here we show the Fourier components for $\hat{h}(t)$ and $\hat{f}(t)$ up to the third order. The ones belonging to $\hat{h}_T(t)$ can be calculated from Eq. (A4-9). $\hat{h}_T$ in the frequency and time domain can be reconstructed from Eq. (A4-3)-(A4-5) and Eq. (A4-6)-(A4-8) respectively.

$$\tilde{\hat{h}}^{(1)}(\pm\omega_1;\mp\omega_1) = D_A(\mp\omega_1)\left\langle \hat{N}^-(\pm\omega_1;\mp\omega_1)\right\rangle^{(1)}\hat{N}^- - \frac{gR_m}{\sqrt{2}}F_-(\mp\omega_1)\left\langle \hat{T}^-(\pm\omega_1;\mp\omega_1)\right\rangle^{(1)}\hat{T}^- \qquad \text{(A4-16)}$$

$$\begin{aligned}\tilde{\hat{h}}^{(2)}(\pm 2\omega_1;\mp\omega_1,\mp\omega_1) = {} & D_A(\mp 2\omega_1)\left\langle \hat{N}^+(\pm 2\omega_1;\mp\omega_1,\mp\omega_1)\right\rangle^{(2)}\hat{N}^+ \\ & + D_D(\mp 2\omega_1)\left\langle \hat{n}_2(\pm 2\omega_1;\mp\omega_1,\mp\omega_1)\right\rangle^{(2)}\hat{n}_2 \\ & - \frac{g}{\sqrt{2}}F_+(\mp 2\omega_1)\left\langle \hat{T}^+(\pm 2\omega_1;\mp\omega_1,\mp\omega_1)\right\rangle^{(2)}\hat{T}^+\end{aligned} \qquad \text{(A4-17)}$$

$$\begin{aligned}\tilde{\hat{h}}^{(2)}(0;\mp\omega_1,\pm\omega_1) = {} & D_A(0)\left\langle \hat{N}^+(0;\mp\omega_1,\pm\omega_1)\right\rangle^{(2)}\hat{N}^+ + D_D(0)\left\langle \hat{n}_2(0;\mp\omega_1,\pm\omega_1)\right\rangle^{(2)}\hat{n}_2 \\ & - \frac{g}{\sqrt{2}}F_+(0)\left\langle \hat{T}^+(0;\mp\omega_1,\pm\omega_1)\right\rangle^{(2)}\hat{T}^+\end{aligned} \qquad \text{(A4-18)}$$

$$\begin{aligned}\tilde{\hat{h}}^{(3)}(\pm 3\omega_1;\mp\omega_1,\mp\omega_1,\mp\omega_1) = {} & D_A(\mp 3\omega_1)\left\langle \hat{N}^-(\pm 3\omega_1;\mp\omega_1,\mp\omega_1,\mp\omega_1)\right\rangle^{(3)}\hat{N}^- \\ & - \frac{gR_m}{\sqrt{2}}F_-(\mp 3\omega_1)\left\langle \hat{T}^-(\pm 3\omega_1;\mp\omega_1,\mp\omega_1,\mp\omega_1)\right\rangle^{(3)}\hat{T}^-\end{aligned} \qquad \text{(A4-19)}$$

$$\begin{aligned}\tilde{\hat{h}}^{(3)}(\pm\omega_1;\mp\omega_1,\mp\omega_1,\pm\omega_1) = {} & D_A(\mp\omega_1)\left\langle \hat{N}^-(\pm\omega_1;\mp\omega_1,\mp\omega_1,\pm\omega_1)\right\rangle^{(3)}\hat{N}^- \\ & - \frac{gR_m}{\sqrt{2}}F_-(\mp\omega_1)\left\langle \hat{T}^-(\pm\omega_1;\mp\omega_1,\mp\omega_1,\pm\omega_1)\right\rangle^{(3)}\hat{T}^-\end{aligned}$$

(A4-20)

$$\hat{\tilde{f}}^{(1)}(\pm\omega_1;\mp\omega_1) = -\frac{\sqrt{\pi} g R_m}{2} G_-(\mp\omega_1)\langle\hat{N}^+\rangle^{(0)} E_{\mp\omega_1}\hat{T}^- - e\sqrt{\frac{\pi}{2}}\left[\frac{d_0}{2} + \frac{h_z}{2} F_+(0)\langle\hat{T}^+\rangle^{(0)}\right] E_{\mp\omega_1}\hat{N}^- \quad \text{(A4-21)}$$

$$\hat{\tilde{f}}^{(2)}(\pm 2\omega_1;\pm\omega_1,\pm\omega_1) = -\frac{g}{2\sqrt{2}} G_+(\mp 2\omega_1) E_{\mp\omega_1}\langle\hat{N}^-(\pm\omega_1;\mp\omega_1)\rangle^{(1)}\hat{T}^+ + \frac{e h_z R_m}{2\sqrt{2}} E_{\mp\omega_1}\langle\hat{u}_-(\pm\omega_1;\mp\omega_1)\rangle^{(1)}\hat{N}^+ \quad \text{(A4-22)}$$

$$\hat{\tilde{f}}^{(2)}(0;\mp\omega_1,\pm\omega_1) = -\frac{g}{2\sqrt{2}} G_+(0) E_{\mp\omega_1}\left[E_{\mp\omega_1}\langle\hat{N}^-(\mp\omega_1;\pm\omega_1)\rangle^{(1)} + E_{\pm\omega_1}\langle\hat{N}^-(\pm\omega_1;\mp\omega_1)\rangle^{(1)}\right]\hat{T}^+ + \frac{e h_z R_m}{2\sqrt{2}}\left[E_{\mp\omega_1}\langle\hat{u}_-(\mp\omega_1;\pm\omega_1)\rangle^{(1)} + E_{\pm\omega_1}\langle\hat{u}_-(\pm\omega_1;\mp\omega_1)\rangle^{(1)}\right]\hat{N}^+$$

(A4-23)

$$\hat{\tilde{f}}^{(3)}(\pm 3\omega_1;\mp\omega_1,\mp\omega_1,\mp\omega_1) = -\frac{g R_m}{2\sqrt{2}} G_-(\mp 3\omega_1)\left[\langle\hat{N}^+(\pm 2\omega_1;\mp\omega_1,\mp\omega_1)\rangle^{(2)} E_{\mp\omega_1}\right]\hat{T}^- - \frac{e h_z}{2\sqrt{2}}\left[\langle\hat{u}^+(\pm 2\omega_1;\mp\omega_1,\mp\omega_1)\rangle^{(2)} E_{\mp\omega_1}\right]\hat{N}^-$$

(A4-24)

$$\begin{aligned}\hat{\tilde{f}}^{(3)}(\pm\omega_1;\mp\omega_1,\mp\omega_1,\pm\omega_1) = & -\frac{g R_m}{2\sqrt{2}} G_-(\mp\omega_1)\left[\langle\hat{N}^+(0;\mp\omega_1,\pm\omega_1)\rangle^{(2)} E_{\mp\omega_1} + \langle\hat{N}^+(\pm 2\omega_1;\mp\omega_1,\mp\omega_1)\rangle^{(2)} E_{\pm\omega_1}\right]\hat{T}^- \\ & -\frac{e h_z}{2\sqrt{2}}\left[\langle\hat{u}_+(0;\mp\omega_1,\pm\omega_1)\rangle^{(2)} E_{\mp\omega_1} + \langle\hat{u}_+(\pm 2\omega_1;\mp\omega_1,\mp\omega_1)\rangle^{(2)} E_{\pm\omega_1}\right]\hat{N}^-\end{aligned}$$

(A4-25)

In the following, the expectation values for the BOV vibrational operators in the frequency domain are shown, in explicit form, from the first to the third order in the electrical field:

$$\langle\hat{u}_-(\omega)\rangle^{(0)} = 0 \qquad \langle\hat{u}_+(\omega)\rangle^{(0)} = F_+(0)\langle\hat{T}^+\rangle^{(0)} \quad \text{(A4-26)}$$

$$\left\langle \hat{u}_-\left(\pm\omega_1;\mp\omega_1\right)\right\rangle^{(1)} = F_-\left(\mp\omega_1\right)\left\langle \hat{T}^-\left(\pm\omega_1;\mp\omega_1\right)\right\rangle^{(1)} + \sqrt{\frac{\pi}{2}}G_-\left(\mp\omega_1\right)E_{\mp\omega_1}\left\langle \hat{N}^+\right\rangle^{(0)}$$

(A4-27)

$$\left\langle \hat{u}_+\left(\omega\right)\right\rangle^{(1)} = 0 \qquad \text{(A4-28)}$$

$$\left\langle \hat{u}_-\left(\omega\right)\right\rangle^{(2)} = 0 \qquad \text{(A4-29)}$$

$$\begin{aligned}\left\langle \hat{u}_+\left(\pm 2\omega_1;\mp\omega_1,\mp\omega_1\right)\right\rangle^{(2)} &= F_+\left(\mp 2\omega_1\right)\left\langle \hat{T}^+\left(\pm 2\omega_1;\mp\omega_1,\mp\omega_1\right)\right\rangle^{(2)} \\ &+\frac{1}{2}G_+\left(\mp 2\omega_1\right)\left\langle \hat{N}^-\left(\pm\omega_1;\mp\omega_1\right)\right\rangle^{(1)}E_{\mp\omega_1}\end{aligned} \qquad \text{(A4-30)}$$

$$\begin{aligned}\left\langle \hat{u}_+\left(0;\mp\omega_1,\pm\omega_1\right)\right\rangle^{(2)} &= F_+\left(0\right)\left\langle \hat{T}^+\left(0;\mp\omega_1,\pm\omega_1\right)\right\rangle^{(2)} \\ &+\frac{1}{2}G_+\left(0\right)\left[\left\langle \hat{N}^-\left(\pm\omega_1;\mp\omega_1\right)\right\rangle^{(1)}E_{\pm\omega_1} + \left\langle \hat{N}^-\left(\mp\omega_1;\pm\omega_1\right)\right\rangle^{(1)}E_{\mp\omega_1}\right]\end{aligned}$$

(A4-31)

$$\begin{aligned}\left\langle \hat{u}_-\left(\pm 3\omega_1;\mp\omega_1,\mp\omega_1,\mp\omega_1\right)\right\rangle^{(3)} &= F_-\left(\mp 3\omega_1\right)\left\langle \hat{T}^+\left(\pm 3\omega_1;\mp\omega_1,\mp\omega_1,\mp\omega_1\right)\right\rangle^{(3)} \\ &+\frac{1}{2}G_-\left(\mp 3\omega_1\right)\left\langle \hat{N}^+\left(\pm 2\omega_1;\mp\omega_1,\mp\omega_1\right)\right\rangle^{(2)}E_{\mp\omega_1}\end{aligned}$$

(A4-32)

$$\left\langle \hat{u}_+\left(\omega\right)\right\rangle^{(3)} = 0 \qquad \text{(A4-33)}$$

$$\begin{aligned}\left\langle \hat{u}_-\left(\pm\omega_1;\mp\omega_1,\mp\omega_1,\pm\omega_1\right)\right\rangle^{(3)} &= F_-\left(\mp\omega_1\right)\left\langle \hat{T}^-\left(\pm\omega_1;\mp\omega_1,\mp\omega_1,\pm\omega_1\right)\right\rangle^{(3)} \\ &+\frac{1}{2}G_-\left(\mp\omega_1\right)\left[\left\langle \hat{N}^+\left(\pm 2\omega_1;\mp\omega_1,\mp\omega_1\right)\right\rangle^{(2)}E_{\pm\omega_1} + \left\langle \hat{N}^+\left(0_1;\omega_1,-\omega_1\right)\right\rangle^{(2)}E_{\mp\omega_1}\right]\end{aligned}$$

(A4-34)

APPENDIX 5

Making use of the response theory, the following expressions are achieved for the polarizabilities and hyperpolarizabilities[32]:

$$\alpha(\pm\omega_1;\mp\omega_1) = \frac{2}{\varepsilon_0\sqrt{2\pi}E_1}\left\langle \hat{R}(\pm\omega_1;\mp\omega_1)\right\rangle^{(1)} \tag{A5-1}$$

$$\gamma(\pm 3\omega_1;\mp\omega_1,\mp\omega_1,\mp\omega_1) = \frac{8}{\varepsilon_0\sqrt{2\pi}E_1^3}\left\langle \hat{R}(\pm 3\omega_1;\mp\omega_1,\mp\omega_1,\mp\omega_1)\right\rangle^{(3)} \tag{A5-2}$$

$$\gamma(\pm\omega_1;\mp\omega_1,\mp\omega_1,\pm\omega_1) = \frac{8}{3\varepsilon_0\sqrt{2\pi}E_1^3}\left\langle \hat{R}(\pm\omega_1;\mp\omega_1,\mp\omega_1,\pm\omega_1)\right\rangle^{(3)}. \tag{A5-3}$$

To write the expressions for the polarizabilities more than one convention is found in the literature. We followed the same convention as in the textbook by Butcher and Cotter.[35] The electrical field is defined in Eq. (A4-2).

The Fourier components of $\hat{R}(t)$ at the first and third order are:

$$\left\langle \hat{R}^{(1)}(\pm\omega_1;\mp\omega_1)\right\rangle = e\left[\frac{d_0}{2} + \frac{h_z}{\sqrt{2}}\left\langle u_+\right\rangle^{(0)}\right]\left\langle \hat{N}^-(\pm\omega_1;\mp\omega_1)\right\rangle^{(1)} - \frac{e\,h_z R_m}{\sqrt{2}}\left\langle \hat{u}_-(\pm\omega_1;\mp\omega_1)\right\rangle^{(1)}\left\langle \hat{N}^+\right\rangle^{(0)} \tag{A5-4}$$

$$\begin{aligned}\left\langle \hat{R}(\pm 3\omega_1;\mp\omega_1,\mp\omega_1,\mp\omega_1)\right\rangle^{(3)} &= e\left[\frac{d_0}{2} + \frac{h_z}{\sqrt{2}}\left\langle \hat{u}_+\right\rangle^{(0)}\right]\left\langle \hat{N}^-(\pm 3\omega_1;\mp\omega_1,\mp\omega_1,\mp\omega_1)\right\rangle^{(3)} \\ &- e\frac{h_z R_m}{\sqrt{2}}\left\langle \hat{N}^+\right\rangle^{(0)}\left\langle \hat{u}_-(\pm 3\omega_1;\mp\omega_1,\mp\omega_1,\mp\omega_1)\right\rangle^{(3)} \\ &+ e\frac{h_z}{\sqrt{2}}\left\langle \hat{u}_+(\pm 2\omega_1;\mp\omega_1,\mp\omega_1)\right\rangle^{(2)}\left\langle \hat{N}^-(\pm\omega_1;\mp\omega_1)\right\rangle^{(1)} \\ &- e\frac{h_z R_m}{\sqrt{2}}\left\langle \hat{N}^+(\pm 2\omega_1;\mp\omega_1,\mp\omega_1)\right\rangle^{(2)}\left\langle \hat{u}_-(\pm\omega_1;\mp\omega_1)\right\rangle^{(1)}\end{aligned} \tag{A5-5}$$

$$\left\langle \hat{R}\left(\pm\omega_1;\mp\omega_1,\mp\omega_1,\pm\omega_1\right)\right\rangle^{(3)} = e\left[\frac{d_0}{2} + \frac{h_z}{\sqrt{2}}\left\langle \hat{u}_+\right\rangle^{(0)}\right]\left\langle \hat{N}^-\left(\pm\omega_1;\mp\omega_1,\mp\omega_1,\pm\omega_1\right)\right\rangle^{(3)}$$
$$- e\frac{h_z R_m}{\sqrt{2}}\left\langle \hat{N}^+\right\rangle^{(0)}\left\langle \hat{u}_-\left(\pm\omega_1;\mp\omega_1,\mp\omega_1,\pm\omega_1\right)\right\rangle^{(3)}$$
$$+ e\frac{h_z}{\sqrt{2}}\left[\left\langle \hat{u}_+\left(0;\mp\omega_1,\pm\omega_1\right)\right\rangle^{(2)}\left\langle \hat{N}^-\left(\pm\omega_1;\mp\omega_1\right)\right\rangle^{(1)} + \left\langle \hat{u}_+\left(\pm 2\omega_1;\mp\omega_1,\mp\omega_1\right)\right\rangle^{(0)}\left\langle \hat{N}^-\left(\mp\omega_1;\pm\omega_1\right)\right\rangle^{(1)}\right]$$
$$- e\frac{h_z R_m}{\sqrt{2}}\left[\left\langle \hat{N}^+\left(0;\mp\omega_1,\pm\omega_1\right)\right\rangle^{(2)}\left\langle \hat{u}_-\left(\pm\omega_1;\mp\omega_1\right)\right\rangle^{(1)}\left\langle \hat{N}^+\left(\pm 2\omega_1;\mp\omega_1,\mp\omega_1\right)\right\rangle^{(2)}\left\langle \hat{u}_-\left(\mp\omega_1;\pm\omega_1\right)\right\rangle^{(1)}\right]$$

(A5-6)

APPENDIX 6

TPA is often expressed in terms of absorption cross section, σ_2:

$$\sigma_2 = \frac{\hbar\omega_1}{N} a_2 \qquad \text{(A6-1)}$$

where N is the number of molecules per unit volume and

$$a_2 = \frac{3\omega_1 \operatorname{Im}\chi^{(3)}(-\omega_1;\omega_1,\omega_1,-\omega_1)}{2\varepsilon_0 c^2 \eta_0^2} \qquad \text{(SI units)} \qquad \text{(A6-2)}$$

$$a_2 = \frac{24\pi^2\omega_1 \operatorname{Im}\chi^{(3)}(-\omega_1;\omega_1,\omega_1,-\omega_1)}{c^2 \eta_0^2} \qquad \text{(esu units)} \qquad \text{(A6-3)}$$

η_0 is the linear refractive index and c the speed of light.