Supplementary Information

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

Robertino Pilot[a] and Renato Bozio*[a]

[a] Dr. Robertino Pilot
Consorzio INSTM, UdR Padova
Department of Chemical Sciences
Via Marzolo 1, 35131 Padova (Italy)
Fax: +39 049 827 5135
E-Mail: roberto.pilot@unipd.it

Prof. Renato Bozio
Consorzio INSTM, UdR Padova
Department of Chemical Sciences
Via Marzolo 1, 35131 Padova (Italy)
Fax: +39 049 827 5135
E-Mail: renato.bozio@unipd.it
### 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.

<table>
<thead>
<tr>
<th>Basis State</th>
<th>Energy</th>
<th>Eigenstate</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td>S_1\rangle = \hat{a}<em>{2\uparrow}^\dagger \hat{a}</em>{2\downarrow}^\dagger</td>
<td>0\rangle$</td>
<td>$U_d$</td>
</tr>
<tr>
<td>$</td>
<td>S_2\rangle = \frac{1}{\sqrt{2}} \left[ \hat{a}<em>{1\uparrow}^\dagger \hat{a}</em>{2\downarrow}^\dagger + \hat{a}<em>{2\uparrow}^\dagger \hat{a}</em>{1\downarrow}^\dagger \right]</td>
<td>0\rangle$</td>
<td>$\epsilon$</td>
</tr>
<tr>
<td>$</td>
<td>S_3\rangle = \frac{1}{\sqrt{2}} \left[ \hat{a}<em>{3\uparrow}^\dagger \hat{a}</em>{2\downarrow}^\dagger + \hat{a}<em>{2\uparrow}^\dagger \hat{a}</em>{3\downarrow}^\dagger \right]</td>
<td>0\rangle$</td>
<td>$\epsilon$</td>
</tr>
<tr>
<td>$</td>
<td>S_4\rangle = \frac{1}{\sqrt{2}} \left[ \hat{a}<em>{1\uparrow}^\dagger \hat{a}</em>{3\downarrow}^\dagger + \hat{a}<em>{3\uparrow}^\dagger \hat{a}</em>{1\downarrow}^\dagger \right]</td>
<td>0\rangle$</td>
<td>$2\epsilon$</td>
</tr>
<tr>
<td>$</td>
<td>S_5\rangle = \hat{a}<em>{3\uparrow}^\dagger \hat{a}</em>{3\downarrow}^\dagger</td>
<td>0\rangle$</td>
<td>$2\epsilon + U_a$</td>
</tr>
<tr>
<td>$</td>
<td>S_6\rangle = \hat{a}<em>{1\uparrow}^\dagger \hat{a}</em>{1\downarrow}^\dagger</td>
<td>0\rangle$</td>
<td>$2\epsilon + U_a$</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Eigenvector$^a$</th>
<th>Eigenvalue$^b$</th>
<th>Transition Energy$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$</td>
<td>1\rangle = \sum_i a_i</td>
<td>S_i\rangle$</td>
</tr>
<tr>
<td>$</td>
<td>2\rangle = \sum_i b_i</td>
<td>S_i\rangle$</td>
</tr>
<tr>
<td>$</td>
<td>3\rangle = \sum_i c_i</td>
<td>S_i\rangle$</td>
</tr>
</tbody>
</table>

$^a$Eigenvectors coefficients:

- $a_1 = \frac{E_{21}}{\sqrt{E_{21}^2 + 4t^2}}$
- $b_1 = 0$
- $c_1 = \frac{-E_{32}}{\sqrt{E_{32}^2 + 4t^2}}$
- $a_2 = a_3 = \frac{\sqrt{2t}}{\sqrt{E_{21}^2 + 4t^2}}$
- $b_2 = -b_3 = \frac{1}{\sqrt{2}}$
- $c_2 = c_3 = \frac{\sqrt{2t}}{\sqrt{E_{32}^2 + 4t^2}}$

$^b\Delta = \epsilon - U_d$
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.

<table>
<thead>
<tr>
<th>DIMER</th>
<th>TRIMER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level Diagram</td>
<td>$\begin{array}{c} \uparrow \rightarrow</td>
</tr>
</tbody>
</table>

Expression for $\alpha$

$$\alpha(-\omega_1;+\omega_1) = -2 \frac{R_{12}^2 E_{21}^2}{\epsilon_0 \left(\hbar \omega_1 + i\Gamma\right)^2 - E_{21}^2}$$

Transition Dipoles

$$R_{12}^2 = (edc_1)^2 \quad R_{12}^2 = (eda_2 b_2)^2$$

Transition energies

$$E_{21} = \frac{U + \sqrt{U^2 + 16t^2}}{2} \quad E_{21} = \frac{\Delta + \sqrt{\Delta^2 + 16t^2}}{2}$$

$$E_{32} = \frac{-U + \sqrt{U^2 + 16t^2}}{2} \quad E_{32} = \frac{-\Delta + \sqrt{\Delta^2 + 16t^2}}{2}$$

Coefficient Expressions

$$c_1 = \frac{E_{32}}{\sqrt{E_{32}^2 + 4t^2}} \quad a_2 b_2 = \frac{t}{\sqrt{E_{21}^2 + 4t^2}}$$
**Fig. S-1.** Enlargement of $\text{Im}[\gamma(-3\omega_1;\omega_q,\omega_q,\omega_q)]$ 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:

\[
Q_{S}^{\text{BOV}} = \frac{1}{\sqrt{2}} (q_3 - q_1) \\
Q_{AS}^{\text{BOV}} = \frac{1}{\sqrt{2m}} \left( \sqrt{m_1} q_3 - 2\sqrt{m_2} q_2 + \sqrt{m_1} q_1 \right)
\] (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 antisymmetric 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:

\[
Q_{S}^{\text{BOV}} = \frac{1}{\sqrt{2}} (Q_{L}^{\text{BOV}} + Q_{R}^{\text{BOV}}) \\
Q_{AS}^{\text{BOV}} = \frac{1}{\sqrt{2}} \sqrt{\frac{m_1}{m}} (Q_{L}^{\text{BOV}} - Q_{R}^{\text{BOV}})
\] (A1-2)

where \(Q_{L}^{\text{BOV}} = \sqrt{\frac{m_2}{m_1}} q_2 - q_1\) and \(Q_{R}^{\text{BOV}} = q_3 - \sqrt{\frac{m_2}{m_1}} q_2\): 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

\[
u_+ = u_s = \frac{1}{\sqrt{2}} (u_L + u_R) \\
u_- = u_{AS} = \frac{1}{\sqrt{2}} R_m (u_L - u_R)
\] (A1-3)

\[
u_{L,R} = \frac{2\omega_x}{\hbar} Q_{L,R}^{\text{BOV}} \\
R_m = \sqrt{\frac{\omega_-}{\omega_+}} \sqrt{\frac{m_1}{m}}
\] (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:

$$\hat{H}_H = \epsilon_{\text{LUMO}} \hat{n}_1 + \epsilon_{\text{LUMO}} \hat{n}_3 + \epsilon_{\text{HOMO}} \hat{n}_2 + U_d \hat{n}_2 \hat{n}_3 + U_a \left( \hat{n}_1 \hat{n}_1 + \hat{n}_3 \hat{n}_3 \right)$$

$$-t_{AD} \hat{T}_{AD} - t_{DA} \hat{T}_{DA}$$

(A1-5)

The first row is equivalent to the term $\epsilon(\hat{n}_1 + \hat{n}_3)$ since $\epsilon_{\text{LUMO}}^1 = \epsilon_{\text{LUMO}}^3$ and $\epsilon_{\text{HOMO}}$ 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:

$$\epsilon_{\text{LUMO}}^1 = \left( \epsilon_{\text{LUMO}}^1 \right)^0 + \sum_i \left( \frac{\partial \epsilon_{\text{LUMO}}^1}{\partial Q_i} \right) Q_{i1}$$

(A1-6)

$$\epsilon_{\text{LUMO}}^3 = \left( \epsilon_{\text{LUMO}}^3 \right)^0 + \sum_i \left( \frac{\partial \epsilon_{\text{LUMO}}^3}{\partial Q_i} \right) Q_{i3}$$

(A1-7)

$$\epsilon_{\text{HOMO}} = \left( \epsilon_{\text{HOMO}} \right)^0 + \sum_i \left( \frac{\partial \epsilon_{\text{HOMO}}}{\partial Q_{i2}} \right) Q_{i2}$$

(A1-8)

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

$$\epsilon_{\text{LUMO}}^1 \hat{n}_1 + \epsilon_{\text{LUMO}}^3 \hat{n}_3 + \epsilon_{\text{HOMO}} \hat{n}_2 =$$

$$(\epsilon_{\text{LUMO}}^1)^0 + \sum_i \left( \frac{\partial \epsilon_{\text{LUMO}}^1}{\partial Q_{i1}} \right) Q_{i1} \hat{n}_1 + (\epsilon_{\text{LUMO}}^3)^0 + \sum_i \left( \frac{\partial \epsilon_{\text{LUMO}}^3}{\partial Q_{i3}} \right) Q_{i3} \hat{n}_3 + (\epsilon_{\text{HOMO}})^0 + \sum_i \left( \frac{\partial \epsilon_{\text{HOMO}}}{\partial Q_{i2}} \right) Q_{i2} \hat{n}_2$$

(A1-9)

On the right hand side we then set $(\epsilon_{\text{HOMO}})^0 = 0$ and define $(\epsilon_{\text{LUMO}}^1)^0 - (\epsilon_{\text{HOMO}})^0 = \epsilon$, so that we obtain:

$$\epsilon_{\text{LUMO}}^1 \hat{n}_1 + \epsilon_{\text{LUMO}}^3 \hat{n}_3 + \epsilon_{\text{HOMO}} \hat{n}_2 =$$

$$\epsilon(\hat{n}_1 + \hat{n}_3) + \hat{n}_1 \sum_i \left( \frac{\partial \epsilon_{\text{LUMO}}^1}{\partial Q_{i1}} \right) Q_{i1} + \hat{n}_3 \sum_i \left( \frac{\partial \epsilon_{\text{LUMO}}^3}{\partial Q_{i3}} \right) Q_{i3} + \hat{n}_2 \sum_i \left( \frac{\partial \epsilon_{\text{HOMO}}}{\partial Q_{i2}} \right) Q_{i2}$$

(A1-10)

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

$$\epsilon_{\text{LUMO}}^1 \hat{n}_1 + \epsilon_{\text{LUMO}}^3 \hat{n}_3 + \epsilon_{\text{HOMO}} \hat{n}_2 = \epsilon(\hat{n}_1 + \hat{n}_3) + \sum_i \frac{g_{iA}}{\sqrt{2}} \left[ \hat{R}_{i1} \hat{N}^+ + \hat{R}_{i1} \hat{N}^- + g_{iD} Q_{i2} \hat{n}_2 \right]$$

(A1-11)
where \[ \sum_{i} \left\{ \frac{g_{iA}}{\sqrt{2}} \left[ R_{i}^{+} \hat{N}_{i} + R_{i}^{-} \hat{N}_{i} \right] + g_{iD} Q_{i2} \hat{n}_{i} \right\} \] is the definition of \( \hat{H}_{\text{ESVB}} \) in Eq. (6).

**Derivation of the vibrational coupling Hamiltonian \( H_{\text{EIP}} \)**

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:

\[
t'_{\text{AD}} = t_{\text{AD}} + \left( \frac{\partial t_{\text{AD}}}{\partial u_{L}} \right)_{0} u_{L} \quad \text{and} \quad t'_{\text{DA}} = t_{\text{DA}} + \left( \frac{\partial t_{\text{DA}}}{\partial u_{R}} \right)_{0} u_{R}
\]

(A1-12)

Notice that in the electronic Hamiltonian \( \hat{H}_{\text{H}} \) 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 \( t_{\text{AD}} \hat{T}_{\text{AD}} + t_{\text{DA}} \hat{T}_{\text{DA}} \) in Eq. (5) can be rewritten including the expansion (A1-12) and making use of the definitions (A1-3), (11) and (13):

\[
t'_{\text{AD}} \hat{T}_{\text{AD}} + t'_{\text{DA}} \hat{T}_{\text{DA}} = t_{\text{AD}} \hat{T}_{\text{AD}} + t_{\text{DA}} \hat{T}_{\text{DA}} - \frac{g}{\sqrt{2}} \left[ u_{+} ^{+} \hat{T}^{+} + R_{m} u_{-} \hat{T}^{-} \right]
\]

(A1-13)

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

**Derivation of the vibronic Hamiltonian \( H_{\text{V}} \)**

Starting from the vibrational Hamiltonian:

\[
\hat{H}_{\text{V}} = \sum_{i} \left\{ \frac{\hbar \omega_{i}}{4} \left[ (Q_{i1}^{2} + P_{i1}^{2}) + (Q_{i3}^{2} + P_{i3}^{2}) \right] + \frac{\hbar \omega_{p}}{4} \left[ P_{i2}^{2} + Q_{i2}^{2} \right] \right\}
\]

(A1-14)

It can be easily rewritten in the form of Eq. (8), by using the Eq. (10)-(12).
The expressions for the vibrational operators can be worked out by solving the Heisenberg equation of the motion:

\[
\frac{\text{i}\hbar}{\text{d}t} \hat{A}_H(t) = \left[ \hat{A}_H(t), \hat{H}_H(t) \right]
\]  

(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 \( \hat{R}_{i\alpha}^H(t) \) is worked out in the following: Eq. (A2-1) is solved for \( \hat{A}_i^H(t) = \hat{S}_i^H(t) \) providing:

\[
\frac{\text{i}\hbar}{\text{d}t} \hat{S}_i^H(t) = \left[ \hat{S}_i^H(t), \hat{H}_H(t) \right] = \left[ \hat{S}_i^H(t), \hat{H}_{\text{EMV}}^H(t) \right] + \left[ \hat{S}_i^H(t), \hat{H}_V^H(t) \right]
\]  

(A2-2)

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

\[
\frac{\hbar}{\text{d}t} \hat{S}_i^H(t) = -\sqrt{2}g_{i\alpha} \left[ \hat{N}^H(t) \right] - \hbar \omega_{i\alpha} \hat{R}_{i\alpha}^H(t)
\]  

(A2-3)

The relation \( \left[ \left( \hat{R}_{i\alpha}^H(t) \right)^2, \hat{S}_i^H(t) \right] = 4\text{i} \hat{R}_{i\alpha}^H(t) \) has been used. Finally, considering the expression

\[
\frac{1}{\omega_{i\alpha}} \frac{\text{d}\hat{R}_{i\alpha}^H(t)}{\text{d}t} = \hat{R}_{i\alpha}^H(t), \text{ we achieve in the time domain:}
\]

\[
\hat{R}_{i\alpha}^H(t)\text{+}\omega_{i\alpha}^2\hat{R}_{i\alpha}^H(t) = -\frac{\sqrt{2}g_{i\alpha} \omega_{i\alpha}}{\hbar} \hat{N}^H(t)
\]  

(A2-4)

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

\[
\hat{R}_{i\alpha}^H(\omega) = D_{\alpha}^j(\omega) \hat{N}^H(\omega)
\]  

(A2-5)

Where \( D_{\alpha}^j(\omega) = \frac{-\sqrt{2}g_{i\alpha} \omega_{i\alpha}}{\hbar \left[ \omega_{i\alpha}^2 - (\omega + i\gamma_{\alpha})^2 \right]} \).

The calculation outlined above, can be repeated for all vibrational operators: in the following the expressions for all of them are summarized:
\[ \hat{R}_i^H(\omega) = D_i^A(\omega) \hat{N}_i^H(\omega) \]
\[ \hat{Q}_i^H(\omega) = D_i^D(\omega) \hat{n}_2^H(\omega) \] (A2-6)

\[ \hat{R}_i^H(\omega) = D_i^A(\omega) \hat{N}_i^H(\omega) \]
\[ \hat{R}_i^H(\omega) = D_i^A(\omega) \hat{n}_2^H(\omega) \] (A2-7)

\[ \hat{u}_i^H(\omega) = F_-(\omega) \hat{T}_i^H(\omega) + G_-(\omega) \mathcal{F}[E(t) \hat{N}_i^H(t)] \] (A2-8)

\[ \hat{u}_i^H(\omega) = F_+(\omega) \hat{T}_i^H(\omega) + G_+(\omega) \mathcal{F}[E(t) \hat{N}_i^H(t)] \] (A2-9)

where

\[ D_i^D(\omega) = \frac{-2g_{iD} \omega_{iD}}{\hbar \left[ \omega_{iD}^2 - (\omega + i\gamma_D)^2 \right]} \]
\[ D_i^A(\omega) = \frac{-\sqrt{2}g_{IA} \omega_{IA}}{\hbar \left[ \omega_{IA}^2 - (\omega + i\gamma_A)^2 \right]} \] (A2-10)

\[ F_-(\omega) = \frac{R_m \sqrt{2} \omega}{\hbar \left[ \omega^2 - (\omega + i\gamma)^2 \right]} \]
\[ F_+(\omega) = \frac{\sqrt{2} \omega}{\hbar \left[ \omega^2 - (\omega + i\gamma)^2 \right]} \] (A2-11)

\[ G_-(\omega) = \frac{-e\sqrt{2} h_z \omega - R_m}{\hbar \left[ \omega^2 - (\omega + i\gamma)^2 \right]} \]
\[ G_+(\omega) = \frac{e\sqrt{2} h_z \omega}{\hbar \left[ \omega^2 - (\omega + i\gamma)^2 \right]} \] (A2-12)

\[ D_D(\omega) = \sum_i g_{iD} D_i^D(\omega) \]
\[ D_A(\omega) = \sum_i \frac{g_{IA}}{\sqrt{2}} D_i^A(\omega) \] (A2-13)

\[ \mathcal{F}[f(t)] \] is the Fourier transform of \( f(t) \); \( \gamma \) are the damping parameters for the vibrational transitions.

The Fourier transform and its inverse have been respectively performed with the relations

\[ z(\omega) = \mathcal{F}[z(t)] = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} z(t) e^{i\omega t} dt \] (A2-14a)

and
The quantities $F(\omega)$, $G(\omega)$ and $D(\omega)$ are usually called propagators: the first and the second are respectively originated by the dependence of $t$ and $d$ on the BOV coordinates, whereas $D(\omega)$ derives from the dependence of the site energies on the SEV modes. The subscripts of $D(\omega)$, $A$ and $D$, specify if it has been expanded the Donor or the Acceptor site energy; the subscripts of $F(\omega)$ and $G(\omega)$, $+$ 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:

\[
\langle \hat{Q}_{12}(\omega) \rangle = D_{11}(\omega) \langle \hat{n}_{12}(\omega) \rangle 
\]

\[
\langle \hat{R}_{1+}(\omega) \rangle = D_A^+(\omega) \langle \hat{N}^+(\omega) \rangle \quad \langle \hat{R}_{1-}(\omega) \rangle = D_A^-(\omega) \langle \hat{N}^-(\omega) \rangle 
\]

\[
\langle \hat{u}_{-}(\omega) \rangle = F_-(\omega) \langle \hat{T}^-(\omega) \rangle + G_-(\omega) \delta(t) \langle \hat{N}^+(t) \rangle 
\]

\[
\langle \hat{u}_{+}(\omega) \rangle = F_+(\omega) \langle \hat{T}^+(\omega) \rangle + G_+(\omega) \delta(t) \langle \hat{N}^-(t) \rangle 
\]

\[
\langle \hat{Q}_{12}(t) \rangle = \mathcal{Z}^{-1} \{ D_{11}(\omega) \langle \hat{n}_{12}(\omega) \rangle \} 
\]

\[
\langle \hat{R}_{1+}(t) \rangle = \mathcal{Z}^{-1} \{ D_A^+(\omega) \langle \hat{N}^+(\omega) \rangle \} \quad \langle \hat{R}_{1-}(t) \rangle = \mathcal{Z}^{-1} \{ D_A^-(\omega) \langle \hat{N}^-(\omega) \rangle \} 
\]

\[
\langle \hat{u}_{-}(t) \rangle = \mathcal{Z}^{-1} \{ F_-(\omega) \langle \hat{T}^-(\omega) \rangle \} + \mathcal{Z}^{-1} \{ G_-(\omega) \delta(t) \langle \hat{N}^+(t) \rangle \} 
\]

\[
\langle \hat{u}_{+}(t) \rangle = \mathcal{Z}^{-1} \{ F_+(\omega) \langle \hat{T}^+(\omega) \rangle \} + \mathcal{Z}^{-1} \{ G_+(\omega) \delta(t) \langle \hat{N}^-(t) \rangle \} 
\]
We are interested in comparing \( \hat{h}_T^{(0)} \) and \( \hat{h}_H^{(0)} \); considering the six level system the expressions are the following

\[
\hat{h}_H = \varepsilon (\hat{n}_1 + \hat{n}_3) + U_d \hat{n}_{2\uparrow} \hat{n}_{2\downarrow} + U_u (\hat{n}_{1\uparrow} \hat{n}_{1\downarrow} + \hat{n}_{3\uparrow} \hat{n}_{3\downarrow}) - t \hat{T}^+ \tag{A3-1}
\]

\[
\hat{h}_T^{(0)} = \hat{h}_H + \hat{h}^{(0)}_{\text{EMV}} + \hat{h}^{(0)}_{\text{EP}} = \\
\varepsilon + \sum_i \frac{g_{IA}}{\sqrt{2}} \langle \hat{R}_i^+ \rangle^{(0)} \hat{N}^+ + \sum_i \frac{g_{ID}}{\sqrt{2}} \langle \hat{Q}_{i2} \rangle^{(0)} \hat{n}_2 + \left[ -t - \frac{g}{\sqrt{2}} \langle \hat{u}_+ \rangle^{(0)} \right] \hat{T}^+ + \\
U_d \hat{n}_{2\uparrow} \hat{n}_{2\downarrow} + U_u (\hat{n}_{1\uparrow} \hat{n}_{1\downarrow} + \hat{n}_{3\uparrow} \hat{n}_{3\downarrow})
\tag{A3-2}
\]

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

\[
\hat{h}_T^{(0)} = \hat{h}_H + \hat{h}^{(0)}_{\text{EMV}} + \hat{h}^{(0)}_{\text{EP}} = \varepsilon' \hat{N}^+ - t' \hat{T}^+ + U_d \hat{n}_{2\uparrow} \hat{n}_{2\downarrow} + U_u (\hat{n}_{1\uparrow} \hat{n}_{1\downarrow} + \hat{n}_{3\uparrow} \hat{n}_{3\downarrow}) \tag{A3-3}
\]

where

\[
\varepsilon' = \varepsilon + \sum_i \frac{4g_{ID}^2}{\hbar \omega_{iD}} - \left( \frac{g_{IA}^2}{\hbar \omega_{iA}} + \frac{2g_{ID}^2}{\hbar \omega_{iD}} \right) \langle \hat{N}^+ \rangle \\
t' = t + \frac{g^2}{\hbar \omega_u} \langle \hat{T}^+ \rangle^{(0)} \tag{A3-4}
\]

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 \( \varepsilon \) and \( t \) with \( \varepsilon' \) 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

\[
z(t) = z^{(1)}(t) + z^{(2)}(t) + z^{(3)}(t) + \ldots
\]  
(A4-1)

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

Choosing a monochromatic electrical field as

\[
E(t) = {1 \over 2} \left[ E_{o+} e^{-i\omega t} + E^{-} e^{i\omega t} \right]
\]  
(A4-2)

where \( E_{o+} = E^* - E_0 = E_1 \), the following expressions are achieved at the first three orders

**TIME DOMAIN**

\[
z^{(1)}(t) = \frac{1}{\sqrt{2\pi}} \left[ \tilde{z}^{(1)}(-\omega_1;+\omega_2) e^{-i\omega t} + \tilde{z}^{(1)}(\omega_1;-\omega_2) e^{i\omega t} \right]
\]  
(A4-3)

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

\[
z^{(3)}(t) = \frac{1}{\sqrt{2\pi}} \left[ \tilde{z}^{(3)}(-3\omega_1;\omega_1,\omega_1,\omega_1) e^{-3i\omega t} + \tilde{z}^{(3)}(-\omega_1;\omega_1,\omega_1,-\omega_1) e^{-i\omega t} + \tilde{z}^{(3)}(3\omega_1;\omega_1,-\omega_1,-\omega_1) e^{3i\omega t} \right]
\]  
(A4-5)

**FREQUENCY DOMAIN**

\[
z^{(1)}(\omega) = \tilde{z}^{(1)}(-\omega_1;\omega_1) \delta(\omega - \omega_1) + \tilde{z}^{(1)}(\omega_1;-\omega_1) \delta(\omega + \omega_1)
\]  
(A4-6)

\[
z^{(2)}(\omega) = \tilde{z}^{(2)}(-2\omega_1;\omega_1,\omega_1) \delta(\omega - 2\omega_1) + \tilde{z}^{(2)}(0;\omega_1,-\omega_1) \delta(\omega) + \tilde{z}^{(2)}(2\omega_1;\omega_1,\omega_1,\omega_1) \delta(\omega + 2\omega_1)
\]  
(A4-7)

\[
z^{(3)}(\omega) = \tilde{z}^{(3)}(-3\omega_1;\omega_1,\omega_1,\omega_1) \delta(\omega - 3\omega_1) + \tilde{z}^{(3)}(-\omega_1;\omega_1,\omega_1,-\omega_1) \delta(\omega - \omega_1) + \tilde{z}^{(3)}(3\omega_1;\omega_1,-\omega_1,-\omega_1) \delta(\omega + 3\omega_1)
\]  
(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 \( E \):

\[
\hat{\rho}(t) = \hat{\rho}^{(0)} + \hat{\rho}^{(1)}(t) + \hat{\rho}^{(2)}(t) + \ldots \tag{A4-10}
\]

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:

\[
\langle \hat{O} \rangle = \langle \hat{O} \rangle^{(0)} + \langle \hat{O} \rangle^{(1)} + \langle \hat{O} \rangle^{(2)} + \ldots \tag{A4-11}
\]

where \( \langle \hat{O} \rangle^{(n)} = \text{Tr}[\hat{\rho}^{(n)}] \) 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:

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

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

\[
i\hbar\hat{\rho}^{(3)}(t) = \mathbf{L}\hat{\rho}^{(3)}(t) + \left[ \hat{h}^{(1)}(t) + \hat{f}^{(1)}(t), \hat{\rho}^{(2)}(t) \right] + \left[ \hat{h}^{(2)}(t) + \hat{f}^{(2)}(t), \hat{\rho}^{(1)}(t) \right] + \left[ \hat{f}^{(3)}(t), \hat{\rho}^{(0)} \right] \tag{A4-14}
\]

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

$$\sum_{n,m} L_{n,m}(\omega)\rho^{(n)}_{n,m}(\omega) = \left[ \hat{h}^{(n)}(\omega), \hat{\rho}^{(0)} \right]_{\hat{}} + \left[ \hat{h}^{(0)}, \hat{\rho}^{(n)}(\omega) \right]_{\hat{}}$$  \hspace{1cm} (A4-15)

The expression of $h_\tau$ 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 $\hat{h}_\tau(t)$ can be calculated from Eq. (A4-9). $\hat{h}_\tau$ in the frequency and time domain can be reconstructed from Eq. (A4-3)-(A4-5) and Eq. (A4-6)-(A4-8) respectively.

$$\hat{h}^{(1)}(\pm \omega_i;\mp \omega_i) = D_\Lambda (\mp \omega_i) \left( \hat{N}^- (\pm \omega_i;\mp \omega_i) \right)^{(1)} \hat{N}^- - \frac{gR_m}{\sqrt{2}} F_\lambda (\mp \omega_i) \left( \hat{T}^- (\pm \omega_i;\mp \omega_i) \right)^{(1)} \hat{T}^-$$  \hspace{1cm} (A4-16)

$$\hat{h}^{(2)}(\pm 2\omega_i;\mp \omega_i,\pm \omega_i) = D_\Lambda (\mp 2\omega_i) \left( \hat{N}^+ (\pm 2\omega_i;\mp \omega_i,\pm \omega_i) \right)^{(2)} \hat{N}^+ + D_D (\mp 2\omega_i) \left( \hat{n}_2 (\pm 2\omega_i;\mp \omega_i,\pm \omega_i) \right)^{(2)} \hat{n}_2$$
$$- \frac{g}{\sqrt{2}} F_\epsilon (\mp 2\omega_i) \left( \hat{T}^+ (\pm 2\omega_i;\mp \omega_i,\pm \omega_i) \right)^{(2)} \hat{T}^+$$  \hspace{1cm} (A4-17)

$$\hat{h}^{(2)}(0;\mp \omega_i,\pm \omega_i) = D_\Lambda (0) \left( \hat{N}^+ (0;\mp \omega_i,\pm \omega_i) \right)^{(2)} \hat{N}^+ + D_D (0) \left( \hat{n}_2 (0;\mp \omega_i,\pm \omega_i) \right)^{(2)} \hat{n}_2$$
$$- \frac{g}{\sqrt{2}} F_\epsilon (0) \left( \hat{T}^+ (0;\mp \omega_i,\pm \omega_i) \right)^{(2)} \hat{T}^+$$  \hspace{1cm} (A4-18)

$$\hat{h}^{(3)}(\pm 3\omega_i;\mp \omega_i,\mp \omega_i,\pm \omega_i) = D_\Lambda (\mp 3\omega_i) \left( \hat{N}^- (\pm 3\omega_i;\mp \omega_i,\mp \omega_i,\pm \omega_i) \right)^{(3)} \hat{N}^-$$
$$- \frac{gR_m}{\sqrt{2}} F_\lambda (\mp 3\omega_i) \left( \hat{T}^- (\pm 3\omega_i;\mp \omega_i,\mp \omega_i,\pm \omega_i) \right)^{(3)} \hat{T}^-$$  \hspace{1cm} (A4-19)

$$\hat{h}^{(3)}(\pm \omega_i;\mp \omega_i,\mp \omega_i,\pm \omega_i) = D_\Lambda (\mp \omega_i) \left( \hat{N}^- (\pm \omega_i;\mp \omega_i,\mp \omega_i,\pm \omega_i) \right)^{(3)} \hat{N}^-$$
$$- \frac{gR_m}{\sqrt{2}} F_\lambda (\mp \omega_i) \left( \hat{T}^- (\pm \omega_i;\mp \omega_i,\mp \omega_i,\pm \omega_i) \right)^{(3)} \hat{T}^-$$  \hspace{1cm} (A4-19)
\[ \hat{f}^{(1)}(\pm \omega_i; \mp \omega_i) = \frac{\sqrt{\pi g R_m}}{2} G_-(\mp \omega_i) \langle \hat{N}^+ \rangle^{(0)} E_{\mp \omega_i} \hat{T}^- \]
\[ -e \sqrt{\pi} \left[ \frac{d_0}{2} + \frac{h_z}{2} F_+(0) \langle \hat{T}^+ \rangle^{(0)} \right] E_{\mp \omega_i} \hat{N}^- \]  

(A4-20)

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

(A4-22)

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

(A4-23)

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

(A4-24)

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

(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:

\[ \langle \hat{u}_- (\omega) \rangle^{(0)} = 0 \quad \langle \hat{u}_+ (\omega) \rangle^{(0)} = F_+(0) \langle \hat{T}^+ \rangle^{(0)} \]  

(A4-26)
\[ \langle \hat{u}_+ (\pm \omega_1; \mp \omega_1) \rangle^{(1)} = F_+ (\pm \omega_1) \langle \hat{T}^- (\pm \omega_1; \mp \omega_1) \rangle^{(1)} + \frac{\sqrt{2}}{\pi} G_+ (\pm \omega_1) E_{\tau_{\omega_1}} \langle \hat{N}^+ \rangle^{(0)} \]  
\[ \langle \hat{u}_+ (\omega) \rangle^{(1)} = 0 \]  
\[ \langle \hat{u}_- (\omega) \rangle^{(2)} = 0 \]  
\[ \langle \hat{u}_+ (\pm 2 \omega_1; \pm \omega_1) \rangle^{(2)} = F_+ (\pm 2 \omega_1) \langle \hat{T}^- (\pm 2 \omega_1; \pm \omega_1) \rangle^{(2)} + \frac{1}{\pi} G_+ (\pm 2 \omega_1) \langle \hat{N}^- (\pm \omega_1; \pm \omega_1) \rangle^{(1)} E_{\tau_{\omega_1}} \]  
\[ \langle \hat{u}_+ (0; \pm \omega_1, \pm \omega_1) \rangle^{(2)} = F_+ (0) \langle \hat{T}^- (0; \pm \omega_1, \pm \omega_1) \rangle^{(2)} + \frac{1}{\pi} G_+ (0) \left[ \langle \hat{N}^- (\pm \omega_1; \pm \omega_1) \rangle^{(1)} E_{\tau_{\omega_1}} + \langle \hat{N}^- (\mp \omega_1; \mp \omega_1) \rangle^{(1)} E_{\tau_{\omega_1}} \right] \]  
\[ \langle \hat{u}_+ (\pm 3 \omega_1; \pm \omega_1, \pm \omega_1, \mp \omega_1) \rangle^{(3)} = F_+ (\pm 3 \omega_1) \langle \hat{T}^- (\pm 3 \omega_1; \pm \omega_1, \mp \omega_1, \mp \omega_1) \rangle^{(3)} + \frac{1}{\pi} G_+ (\pm 3 \omega_1) \langle \hat{N}^- (\pm 2 \omega_1; \pm \omega_1, \mp \omega_1) \rangle^{(2)} E_{\tau_{\omega_1}} \]  
\[ \langle \hat{u}_+ (\omega) \rangle^{(3)} = 0 \]  
\[ \langle \hat{u}_- (\pm \omega_1; \pm \omega_1, \pm \omega_1, \pm \omega_1) \rangle^{(3)} = F_+ (\pm \omega_1) \langle \hat{T}^- (\pm \omega_1; \pm \omega_1, \mp \omega_1, \pm \omega_1) \rangle^{(3)} + \frac{1}{\pi} G_+ (\pm \omega_1) \left[ \langle \hat{N}^- (\pm 2 \omega_1; \pm \omega_1, \mp \omega_1) \rangle^{(2)} E_{\tau_{\omega_1}} + \langle \hat{N}^- (0; \omega_1, \mp \omega_1) \rangle^{(2)} E_{\tau_{\omega_1}} \right] \]  
(A4-27)  
(A4-28)  
(A4-29)  
(A4-30)  
(A4-31)  
(A4-32)  
(A4-33)  
(A4-34)
APPENDIX 5

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

\[ \alpha(\pm \omega_i; \mp \omega_i) = \frac{2}{\varepsilon_0 \sqrt{2\pi} E_1} \langle \hat{\mathbf{R}}(\pm \omega_i; \mp \omega_i) \rangle^{(1)} \]  \hspace{1cm} (A5-1)

\[ \gamma(\pm 3\omega_i; \mp \omega_i, \mp \omega_i, \pm \omega_i) = \frac{8}{\varepsilon_0 \sqrt{2\pi} E_1^3} \langle \hat{\mathbf{R}}(\pm 3\omega_i; \mp \omega_i, \mp \omega_i, \pm \omega_i) \rangle^{(1)} \]  \hspace{1cm} (A5-2)

\[ \gamma(\pm \omega_i; \mp \omega_i, \mp \omega_i, \pm \omega_i) = \frac{8}{3\varepsilon_0 \sqrt{2\pi} E_1^3} \langle \hat{\mathbf{R}}(\pm \omega_i; \mp \omega_i, \mp \omega_i, \pm \omega_i) \rangle^{(1)} \]  \hspace{1cm} (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. The electrical field is defined in Eq. (A4-2).

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

\[ \langle \hat{\mathbf{R}}^{(1)}(\pm \omega_i; \mp \omega_i) \rangle = \mathbf{e} \left[ \frac{d_0}{2} + \frac{h_x}{\sqrt{2}} \langle \mathbf{u}^{(0)} \rangle \right] \langle \hat{\mathbf{N}}^{(1)}(\pm \omega_i; \mp \omega_i) \rangle - \mathbf{e} \frac{h_x R_m}{\sqrt{2}} \langle \hat{\mathbf{u}}^{(0)}(\pm \omega_i; \mp \omega_i) \rangle \langle \hat{\mathbf{N}}^{(1)} \rangle \]  \hspace{1cm} (A5-4)

\[ \langle \hat{\mathbf{R}}^{(3)}(\pm 3\omega_i; \mp \omega_i, \mp \omega_i, \pm \omega_i) \rangle = \mathbf{e} \left[ \frac{d_0}{2} + \frac{h_x}{\sqrt{2}} \langle \mathbf{u}^{(0)} \rangle \right] \langle \hat{\mathbf{N}}^{(3)}(\pm 3\omega_i; \mp \omega_i, \mp \omega_i, \pm \omega_i) \rangle - \mathbf{e} \frac{h_x R_m}{\sqrt{2}} \langle \hat{\mathbf{u}}^{(0)}(\pm 3\omega_i; \mp \omega_i, \mp \omega_i, \pm \omega_i) \rangle \langle \hat{\mathbf{N}}^{(3)} \rangle \]  \hspace{1cm} (A5-5)
\[
\left\langle \hat{R}(\pm \omega_1; \mp \omega_1, \mp \omega_1, \pm \omega_1) \right\rangle^{(0)} = e \left[ \frac{d_0}{2} + \frac{h_z}{\sqrt{2}} \langle \hat{u}_+ \rangle^{(0)} \right] \left\langle \hat{N}^{-}(\pm \omega_1; \mp \omega_1, \pm \omega_1, \pm \omega_1) \right\rangle^{(0)} \\
- e \frac{h_z}{\sqrt{2}} R_m \left\langle \hat{N}^{+}\right\rangle^{(0)} \langle \hat{u}_- (\pm \omega_1; \mp \omega_1, \mp \omega_1, \pm \omega_1) \rangle^{(0)} \\
+ e \frac{h_z}{\sqrt{2}} \left[ \langle \hat{u}_- (0; \mp \omega_1, \pm \omega_1) \rangle^{(2)} \left\langle \hat{N}^{-}(\pm \omega_1; \mp \omega_1) \right\rangle^{(0)} + \langle \hat{u}_- (\pm 2 \omega_1; \mp \omega_1, \mp \omega_1) \rangle^{(0)} \left\langle \hat{N}^{-}(\mp \omega_1; \pm \omega_1) \right\rangle^{(0)} \right] \\
- e \frac{h_z R_m}{\sqrt{2}} \left[ \langle \hat{N}^{+}(0; \mp \omega_1, \pm \omega_1) \rangle^{(2)} \langle \hat{u}_- (\pm \omega_1; \mp \omega_1) \rangle^{(0)} \left\langle \hat{N}^{-}(\pm 2 \omega_1; \mp \omega_1, \mp \omega_1) \right\rangle \langle \hat{u}_- (\mp \omega_1; \pm \omega_1) \rangle^{(0)} \right]
\]

\text{(A5-6)}
TPA is often expressed in terms of absorption cross section, $\sigma_2$:

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

where $N$ is the number of molecules per unit volume and

$$a_2 = \frac{3 \omega_1 \text{Im} \chi^{(3)}(-\omega_1; \omega_1, \omega_1, -\omega_1)}{2 \varepsilon_0 c^2 \eta_0^2}$$  \hspace{1cm} (SI units)  \hspace{1cm} (A6-2)

$$a_2 = \frac{24 \pi^2 \omega_1 \text{Im} \chi^{(3)}(-\omega_1; \omega_1, \omega_1, -\omega_1)}{c^2 \eta_0^2}$$  \hspace{1cm} (esu units)  \hspace{1cm} (A6-3)

$\eta_0$ is the linear refractive index and $c$ the speed of light.