Eq 2 is derived from the expression of the third order susceptibility $\chi^{(3)}$ obtained under the Sum Over States (SOS) formalism for a simple isotropic three level system. Only the two terms completely resonant in a TPA process are considered among the 48 terms of the whole expression for $\chi^{(3)}$. Under these approximations, the expression obtained is:

$$
\chi^{(3)}(\omega_b; \omega_a, -\omega_a, \omega_b) \propto \left[ \frac{|\mu_{10}|^2 |\mu_{21}|^2}{(\omega_{20} - \omega_a - \omega_b - i\Gamma_{20})^2} \right] \times \left\{ \begin{array}{c}
\frac{1}{(\omega_{10} - \omega_b - i\Gamma_{10})(\omega_{10} - \omega_a - i\Gamma_{10})^2} \\
+ \frac{1}{(\omega_{10} - \omega_b - i\Gamma_{10})^2} \\
- \frac{1}{(\omega_{21} - \omega_b - i\Gamma_{21})(\omega_{10} - \omega_a - i\Gamma_{10})} \\
- \frac{1}{(\omega_{21} - \omega_b - i\Gamma_{21})(\omega_{10} - \omega_b - i\Gamma_{10})}
\end{array} \right\}
$$

(S .1)

where the subscripts 0, 1, 2 refer to the ground state, a one-photon allowed state and a two-photon allowed state respectively; $\mu_{ij}$, $\omega_{ij}$, $\Gamma_{ij}$ are the transition dipole moment, the transition frequency and the HWHM relative to transition between states $i$ and $j$; $\omega_a$ and $\omega_b$ are the frequencies of the applied fields: the pump and the probe respectively. For the system considered, it is always true that $\omega_{21} = \omega_{20} - \omega_{10}$. If one assumes that: (i) both the frequencies of the pump and probe beams are chosen far enough from the one-photon resonance transition frequency, so that $(\omega_{10} - \omega_a) >> (\omega_{10} - \omega_b)$ and $(\omega_{10} - \omega_a) >> [\omega_{20} - (\omega_a + \omega_b)]$ and (ii) the HWHMs satisfy the conditions: $(\omega_{10} - \omega_b) >> \Gamma_{10}$ and $\Gamma_{21} \approx \Gamma_{10}$, the imaginary part of eq S .1 becomes:
\[ \text{Im}[\chi^{(3)}(\omega_b)] \propto \frac{|\mu_{10}|^2}{(\omega_{10} - \omega_b)^2} \cdot \frac{|\mu_{12}|^2 \Gamma_{20}}{[(\omega_{20} - \omega_b - \omega_a)^2 + \Gamma_{20}^2]} \]  

(S.2)

Since it is recognized that, at the third order of the perturbative approach, the two photon absorption cross section is proportional to the imaginary part of the third order non linear susceptibility, then:

\[ \sigma_{TPA}(\omega_b) \propto \frac{|\mu_{10}|^2}{(\omega_{10} - \omega_b)^2} \cdot \frac{|\mu_{12}|^2 \Gamma_{20}}{[(\omega_{20} - \omega_b - \omega_a)^2 + \Gamma_{20}^2]} \]  

(S.3)

Rebane et al.\textsuperscript{S1,S2} obtained a similar expression for the degenerate case, i.e. when \(\omega_a = \omega_b\), like in two-photon induced fluorescence experiments.
