Supporting Information File

Solvent Induced Channel Interference in Two-Photon Absorption Process - A theoretical study with generalized few-states-model in three dimensions

Md. Mehboob Alam,[a] **Mausumi Chattopadhyaya,**[a] **and Swapan Chakrabarti**[*a]

[a]Department of Chemsitry, University of Calcutta, 92 A.P.C Road, Kolkata - 700009

Contents

1 Derivation of Generalized Few-States Model formula

The TPA tensor elements $S_{\alpha\beta}$ is given by -

$$S_{\alpha\beta} = \sum_i \left(\frac{\mu_\alpha^{0i}\mu_\beta^{if}}{\Delta E_i} + \frac{\mu_\beta^{0i}\mu_\alpha^{if}}{\Delta E_i} \right) (\alpha, \beta = x, y, z)$$

Where $\Delta E_i = \omega_i - \frac{\omega_f}{2}$, ω_m = excitation energy for excitation from ground $\langle 0|$ to excited state $|m\rangle$. In the above summation the sum runs over all the states including ground state.If we consider that the involved states are $i, j, k, \ldots, n$ then the explicit expression of $S_{\alpha\beta}$ becomes -

$$S_{xx} = \frac{2\mu_x^{0i}\mu_x^{if}}{\Delta E_i} + \frac{2\mu_x^{0j}\mu_x^{jf}}{\Delta E_j} + \ldots + \frac{2\mu_x^{0n}\mu_x^{nf}}{\Delta E_n}$$

$$S_{yy} = \frac{2\mu_y^{0i}\mu_y^{if}}{\Delta E_i} + \frac{2\mu_y^{0j}\mu_y^{jf}}{\Delta E_j} + \ldots + \frac{2\mu_y^{0n}\mu_y^{nf}}{\Delta E_n}$$

$$S_{zz} = \frac{2\mu_z^{0i}\mu_z^{if}}{\Delta E_i} + \frac{2\mu_z^{0j}\mu_z^{jf}}{\Delta E_j} + \ldots + \frac{2\mu_z^{0n}\mu_z^{nf}}{\Delta E_n}$$

$$S_{xy} = \frac{\mu_x^{0i}\mu_y^{if} + \mu_y^{0i}\mu_x^{if}}{\Delta E_i} + \frac{\mu_x^{0j}\mu_y^{jf} + \mu_y^{0j}\mu_x^{jf}}{\Delta E_j} + \ldots + \frac{\mu_x^{0n}\mu_y^{nf} + \mu_y^{0n}\mu_x^{nf}}{\Delta E_n}$$

$$S_{yz} = \frac{\mu_y^{0i}\mu_z^{if} + \mu_z^{0i}\mu_y^{if}}{\Delta E_i} + \frac{\mu_y^{0j}\mu_z^{jf} + \mu_z^{0j}\mu_y^{jf}}{\Delta E_j} + \ldots + \frac{\mu_y^{0n}\mu_z^{nf} + \mu_z^{0n}\mu_y^{nf}}{\Delta E_n}$$

$$S_{xz} = \frac{\mu_x^{0i}\mu_z^{if} + \mu_z^{0i}\mu_x^{if}}{\Delta E_i} + \frac{\mu_x^{0j}\mu_z^{jf} + \mu_z^{0j}\mu_x^{jf}}{\Delta E_j} + \ldots + \frac{\mu_x^{0n}\mu_z^{nf} + \mu_z^{0n}\mu_x^{nf}}{\Delta E_n}$$

For a monochromatic linearly polarized light beam the TPA transition probability (in a.u.) is given by the expression -

$$\delta_{TP} = 6\left(S_{xx}^2 + S_{yy}^2 + S_{zz}^2\right) + 8\left(S_{xy}^2 + S_{yz}^2 + S_{xz}^2\right) + 4\left(S_{xx}S_{yy} + S_{yy}S_{zz} + S_{xx}S_{zz}\right)$$

$$\begin{aligned}
\delta_{TP} &= 6\left(\frac{2\mu_x^{0i}\mu_x^{if}}{\Delta E_i} + \frac{2\mu_x^{0j}\mu_x^{jf}}{\Delta E_j} + \ldots + \frac{2\mu_x^{0n}\mu_x^{nf}}{\Delta E_n}\right)^2 + 6\left(\frac{2\mu_y^{0i}\mu_y^{if}}{\Delta E_i} + \frac{2\mu_y^{0j}\mu_y^{jf}}{\Delta E_j} + \ldots + \frac{2\mu_y^{0n}\mu_y^{nf}}{\Delta E_n}\right)^2 \\
&+ 6\left(\frac{2\mu_z^{0i}\mu_z^{if}}{\Delta E_i} + \frac{2\mu_z^{0j}\mu_z^{jf}}{\Delta E_j} + \ldots + \frac{2\mu_z^{0n}\mu_z^{nf}}{\Delta E_n}\right)^2 \\
&+ 8\left(\frac{\mu_x^{0i}\mu_y^{if} + \mu_y^{0i}\mu_x^{if}}{\Delta E_i} + \frac{\mu_x^{0j}\mu_y^{jf} + \mu_y^{0j}\mu_x^{jf}}{\Delta E_j} + \ldots + \frac{\mu_x^{0n}\mu_y^{nf} + \mu_y^{0n}\mu_x^{nf}}{\Delta E_n}\right)^2 \\
&+ 8\left(\frac{\mu_y^{0i}\mu_z^{if} + \mu_z^{0i}\mu_y^{if}}{\Delta E_i} + \frac{\mu_y^{0j}\mu_z^{jf} + \mu_z^{0j}\mu_y^{jf}}{\Delta E_j} + \ldots + \frac{\mu_y^{0n}\mu_z^{nf} + \mu_z^{0n}\mu_y^{nf}}{\Delta E_n}\right)^2 \\
&+ 8\left(\frac{\mu_x^{0i}\mu_z^{if} + \mu_z^{0i}\mu_x^{if}}{\Delta E_i} + \frac{\mu_x^{0j}\mu_z^{jf} + \mu_z^{0j}\mu_x^{jf}}{\Delta E_j} + \ldots + \frac{\mu_x^{0n}\mu_z^{nf} + \mu_z^{0n}\mu_x^{nf}}{\Delta E_n}\right)^2 \\
&+ 4\left(\frac{2\mu_x^{0i}\mu_x^{if}}{\Delta E_i} + \frac{2\mu_x^{0j}\mu_x^{jf}}{\Delta E_j} + \ldots + \frac{2\mu_x^{0n}\mu_x^{nf}}{\Delta E_n}\right)\left(\frac{2\mu_y^{0i}\mu_y^{if}}{\Delta E_i} + \frac{2\mu_y^{0j}\mu_y^{jf}}{\Delta E_j} + \ldots + \frac{2\mu_y^{0n}\mu_y^{nf}}{\Delta E_n}\right) \\
&+ 4\left(\frac{2\mu_y^{0i}\mu_y^{if}}{\Delta E_i} + \frac{2\mu_y^{0j}\mu_y^{jf}}{\Delta E_j} + \ldots + \frac{2\mu_y^{0n}\mu_y^{nf}}{\Delta E_n}\right)\left(\frac{2\mu_z^{0i}\mu_z^{if}}{\Delta E_i} + \frac{2\mu_z^{0j}\mu_z^{jf}}{\Delta E_j} + \ldots + \frac{2\mu_z^{0n}\mu_z^{nf}}{\Delta E_n}\right) \\
&+ 4\left(\frac{2\mu_x^{0i}\mu_x^{if}}{\Delta E_i} + \frac{2\mu_x^{0j}\mu_x^{jf}}{\Delta E_j} + \ldots + \frac{2\mu_x^{0n}\mu_x^{nf}}{\Delta E_n}\right)\left(\frac{2\mu_z^{0i}\mu_z^{if}}{\Delta E_i} + \frac{2\mu_z^{0j}\mu_z^{jf}}{\Delta E_j} + \ldots + \frac{2\mu_z^{0n}\mu_z^{nf}}{\Delta E_n}\right)
\end{aligned}$$

$$
\begin{aligned}
\delta_{TP} = 6\sum_{i}^{n} & \left[\left(\frac{2\mu_x^{0i}\mu_x^{if}}{\Delta E_i} \right)^2 + \left(\frac{2\mu_y^{0i}\mu_y^{if}}{\Delta E_i} \right)^2 + \left(\frac{2\mu_z^{0i}\mu_z^{if}}{\Delta E_i} \right)^2 \right] \\
& + 8\sum_{i}^{n} \left[\left(\frac{\mu_x^{0i}\mu_y^{if} + \mu_y^{0i}\mu_x^{if}}{\Delta E_i} \right)^2 + \left(\frac{\mu_y^{0i}\mu_z^{if} + \mu_z^{0i}\mu_y^{if}}{\Delta E_i} \right)^2 + \left(\frac{\mu_x^{0i}\mu_z^{if} + \mu_z^{0i}\mu_x^{if}}{\Delta E_i} \right)^2 \right] \\
& + 4\sum_{i}^{n} \left[\left(\frac{2\mu_x^{0i}\mu_x^{if}}{\Delta E_i} \times \frac{2\mu_y^{0i}\mu_y^{if}}{\Delta E_i} \right) + \left(\frac{2\mu_y^{0i}\mu_y^{if}}{\Delta E_i} \times \frac{2\mu_z^{0i}\mu_z^{if}}{\Delta E_i} \right) + \left(\frac{2\mu_x^{0i}\mu_x^{if}}{\Delta E_i} \times \frac{2\mu_z^{0i}\mu_z^{if}}{\Delta E_i} \right) \right] \\
& + 6\left(\frac{8\mu_x^{0i}\mu_x^{if}\mu_x^{0j}\mu_x^{jf}}{\Delta E_i \Delta E_j} + \frac{8\mu_x^{0i}\mu_x^{if}\mu_x^{0k}\mu_x^{kf}}{\Delta E_i \Delta E_k} + \ldots + \frac{8\mu_x^{0i}\mu_x^{if}\mu_x^{0n}\mu_x^{nf}}{\Delta E_i \Delta E_n} \right) \\
& + 6\left(\frac{8\mu_x^{0j}\mu_x^{jf}\mu_x^{0k}\mu_x^{kf}}{\Delta E_j \Delta E_k} + \frac{8\mu_x^{0j}\mu_x^{jf}\mu_x^{0l}\mu_x^{lf}}{\Delta E_j \Delta E_l} + \ldots + \frac{8\mu_x^{0j}\mu_x^{jf}\mu_x^{0n}\mu_x^{nf}}{\Delta E_j \Delta E_n} \right) + \ldots\ldots\ldots \\
& + 6\left(\frac{8\mu_y^{0i}\mu_y^{if}\mu_y^{0j}\mu_y^{jf}}{\Delta E_i \Delta E_j} + \frac{8\mu_y^{0i}\mu_y^{if}\mu_y^{0k}\mu_y^{kf}}{\Delta E_i \Delta E_k} + \ldots + \frac{8\mu_y^{0i}\mu_y^{if}\mu_y^{0n}\mu_y^{nf}}{\Delta E_i \Delta E_n} \right) \\
& + 6\left(\frac{8\mu_y^{0j}\mu_y^{jf}\mu_y^{0k}\mu_y^{kf}}{\Delta E_j \Delta E_k} + \frac{8\mu_y^{0j}\mu_y^{jf}\mu_y^{0l}\mu_y^{lf}}{\Delta E_j \Delta E_l} + \ldots + \frac{8\mu_y^{0j}\mu_y^{jf}\mu_y^{0n}\mu_y^{nf}}{\Delta E_j \Delta E_n} \right) + \ldots\ldots\ldots \\
& + 6\left(\frac{8\mu_z^{0i}\mu_z^{if}\mu_z^{0j}\mu_z^{jf}}{\Delta E_i \Delta E_j} + \frac{8\mu_z^{0i}\mu_z^{if}\mu_z^{0k}\mu_z^{kf}}{\Delta E_i \Delta E_k} + \ldots + \frac{8\mu_z^{0i}\mu_z^{if}\mu_z^{0n}\mu_z^{nf}}{\Delta E_i \Delta E_n} \right) \\
& + 6\left(\frac{8\mu_z^{0j}\mu_z^{jf}\mu_z^{0k}\mu_z^{kf}}{\Delta E_j \Delta E_k} + \frac{8\mu_z^{0j}\mu_z^{jf}\mu_z^{0l}\mu_z^{lf}}{\Delta E_j \Delta E_l} + \ldots + \frac{8\mu_z^{0j}\mu_z^{jf}\mu_z^{0n}\mu_z^{nf}}{\Delta E_j \Delta E_n} \right) + \ldots\ldots\ldots \\
& + 8\left(\frac{2(\mu_x^{0i}\mu_y^{if} + \mu_y^{0i}\mu_x^{if})(\mu_x^{0j}\mu_y^{jf} + \mu_y^{0j}\mu_x^{jf})}{\Delta E_i \Delta E_j} + \frac{2(\mu_x^{0i}\mu_y^{if} + \mu_y^{0i}\mu_x^{if})(\mu_x^{0k}\mu_y^{kf} + \mu_y^{0k}\mu_x^{kf})}{\Delta E_i \Delta E_k} + \ldots \right. \\
& \qquad \left. \ldots + \frac{2(\mu_x^{0i}\mu_y^{if} + \mu_y^{0i}\mu_x^{if})(\mu_x^{0n}\mu_y^{nf} + \mu_y^{0n}\mu_x^{nf})}{\Delta E_i \Delta E_n} \right) \\
& + 8\left(\frac{2(\mu_x^{0j}\mu_y^{jf} + \mu_y^{0j}\mu_x^{jf})(\mu_x^{0k}\mu_y^{kf} + \mu_y^{0k}\mu_x^{kf})}{\Delta E_j \Delta E_k} + \frac{2(\mu_x^{0j}\mu_y^{jf} + \mu_y^{0j}\mu_x^{jf})(\mu_x^{0l}\mu_y^{lf} + \mu_y^{0l}\mu_x^{lf})}{\Delta E_j \Delta E_l} + \ldots \right. \\
& \qquad \left. \ldots + \frac{2(\mu_x^{0j}\mu_y^{jf} + \mu_y^{0j}\mu_x^{jf})(\mu_x^{0n}\mu_y^{nf} + \mu_y^{0n}\mu_x^{nf})}{\Delta E_j \Delta E_n} \right) + \ldots \\
& + 8\left(\frac{2(\mu_y^{0i}\mu_z^{if} + \mu_z^{0i}\mu_y^{if})(\mu_y^{0j}\mu_z^{jf} + \mu_z^{0j}\mu_y^{jf})}{\Delta E_i \Delta E_j} + \frac{2(\mu_y^{0i}\mu_z^{if} + \mu_z^{0i}\mu_y^{if})(\mu_y^{0k}\mu_z^{kf} + \mu_z^{0k}\mu_y^{kf})}{\Delta E_i \Delta E_k} + \ldots \right. \\
& \qquad \left. \ldots + \frac{2(\mu_y^{0i}\mu_z^{if} + \mu_z^{0i}\mu_y^{if})(\mu_y^{0n}\mu_z^{nf} + \mu_z^{0n}\mu_y^{nf})}{\Delta E_i \Delta E_n} \right) \\
& + 8\left(\frac{2(\mu_y^{0j}\mu_z^{jf} + \mu_z^{0j}\mu_y^{jf})(\mu_y^{0k}\mu_z^{kf} + \mu_z^{0k}\mu_y^{kf})}{\Delta E_j \Delta E_k} + \frac{2(\mu_y^{0j}\mu_z^{jf} + \mu_z^{0j}\mu_y^{jf})(\mu_y^{0l}\mu_z^{lf} + \mu_z^{0l}\mu_y^{lf})}{\Delta E_j \Delta E_l} + \ldots \right. \\
& \qquad \left. \ldots + \frac{2(\mu_y^{0j}\mu_z^{jf} + \mu_z^{0j}\mu_y^{jf})(\mu_y^{0n}\mu_z^{nf} + \mu_z^{0n}\mu_y^{nf})}{\Delta E_j \Delta E_n} \right) + \ldots
\end{aligned}
$$

$$+8\left(\frac{2(\mu_x^{0i}\mu_z^{if}+\mu_z^{0i}\mu_x^{if})(\mu_x^{0j}\mu_z^{jf}+\mu_z^{0j}\mu_x^{jf})}{\Delta E_i\Delta E_j}+\frac{2(\mu_x^{0i}\mu_z^{if}+\mu_z^{0i}\mu_x^{if})(\mu_x^{0k}\mu_z^{kf}+\mu_z^{0k}\mu_x^{kf})}{\Delta E_i\Delta E_k}+\dots\right.$$
$$\left.\dots+\frac{2(\mu_x^{0i}\mu_z^{if}+\mu_z^{0i}\mu_x^{if})(\mu_x^{0n}\mu_z^{nf}+\mu_z^{0n}\mu_x^{nf})}{\Delta E_i\Delta E_n}\right)$$
$$+8\left(\frac{2(\mu_x^{0j}\mu_z^{jf}+\mu_z^{0j}\mu_x^{jf})(\mu_x^{0k}\mu_z^{kf}+\mu_z^{0k}\mu_x^{kf})}{\Delta E_j\Delta E_k}+\frac{2(\mu_x^{0j}\mu_z^{jf}+\mu_z^{0j}\mu_x^{jf})(\mu_x^{0l}\mu_z^{lf}+\mu_z^{0l}\mu_x^{lf})}{\Delta E_j\Delta E_l}+\dots\right.$$
$$\left.\dots+\frac{2(\mu_x^{0j}\mu_z^{jf}+\mu_z^{0j}\mu_x^{jf})(\mu_x^{0n}\mu_z^{nf}+\mu_z^{0n}\mu_x^{nf})}{\Delta E_j\Delta E_n}\right)+\dots$$
$$+4\sum_{i,j(\neq i)}^{n}\left(\frac{4\mu_x^{0i}\mu_x^{if}\mu_y^{0j}\mu_y^{jf}}{\Delta E_i\Delta E_j}+\frac{4\mu_y^{0i}\mu_y^{if}\mu_z^{0j}\mu_z^{jf}}{\Delta E_i\Delta E_j}+\frac{4\mu_x^{0i}\mu_x^{if}\mu_z^{0j}\mu_z^{jf}}{\Delta E_i\Delta E_j}\right)$$

The first three terms constitute the three-state model (3SM) formula δ_{TP}^{ii} whereas the remaining terms constitute the interference terms δ_{TP}^{ij}. Therefore the overall δ_{TP} can be written as -

$$\delta_{TP}=\sum_{i}^{n}\delta_{TP}^{ii}+\sum_{i,j(\neq i)}^{n}\delta_{TP}^{ij}$$

Let us first derive the 3SM formula - for this we shall consider the excitation from ground $\langle 0|$ to final state $|f\rangle$ via the intermediate state $|i\rangle$. Therefore, for this case the δ_{TP}^{3SM} may be written as -

$$\delta_{TP}^{3SM}=6\left[\left(\frac{2\mu_x^{0i}\mu_x^{if}}{\Delta E_i}\right)^2+\left(\frac{2\mu_y^{0i}\mu_y^{if}}{\Delta E_i}\right)^2+\left(\frac{2\mu_z^{0i}\mu_z^{if}}{\Delta E_i}\right)^2\right]$$
$$+8\left[\left(\frac{\mu_x^{0i}\mu_y^{if}+\mu_y^{0i}\mu_x^{if}}{\Delta E_i}\right)^2+\left(\frac{\mu_y^{0i}\mu_z^{if}+\mu_z^{0i}\mu_y^{if}}{\Delta E_i}\right)^2+\left(\frac{\mu_x^{0i}\mu_z^{if}+\mu_z^{0i}\mu_x^{if}}{\Delta E_i}\right)^2\right]$$
$$+4\left[\left(\frac{2\mu_x^{0i}\mu_x^{if}}{\Delta E_i}\times\frac{2\mu_y^{0i}\mu_y^{if}}{\Delta E_i}\right)+\left(\frac{2\mu_y^{0i}\mu_y^{if}}{\Delta E_i}\times\frac{2\mu_z^{0i}\mu_z^{if}}{\Delta E_i}\right)+\left(\frac{2\mu_x^{0i}\mu_x^{if}}{\Delta E_i}\times\frac{2\mu_z^{0i}\mu_z^{if}}{\Delta E_i}\right)\right]$$

$$\delta_{TP}^{3SM}=\frac{8}{\Delta E_i^2}\Big[3\{(\mu_x^{0i}\mu_x^{if})^2+(\mu_y^{0i}\mu_y^{if})^2+(\mu_z^{0i}\mu_z^{if})^2\}+(\mu_x^{0i}\mu_y^{if})^2+(\mu_y^{0i}\mu_x^{if})^2+2\mu_x^{0i}\mu_x^{if}\mu_y^{0i}\mu_y^{if}$$
$$+(\mu_x^{0i}\mu_z^{if})^2+(\mu_z^{0i}\mu_x^{if})^2+2\mu_x^{0i}\mu_z^{if}\mu_z^{0i}\mu_x^{if}+(\mu_y^{0i}\mu_z^{if})^2+(\mu_z^{0i}\mu_y^{if})^2+2\mu_y^{0i}\mu_z^{if}\mu_z^{0i}\mu_y^{if}$$
$$+2\mu_x^{0i}\mu_x^{if}\mu_y^{0i}\mu_y^{if}+2\mu_x^{0i}\mu_x^{if}\mu_z^{0i}\mu_z^{if}+2\mu_y^{0i}\mu_y^{if}\mu_z^{0i}\mu_z^{if}\Big]$$

$$\delta_{TP}^{3SM} = \frac{8}{\Delta E_i^2}\Big[4(\mu_x^{0i}\mu_x^{if}\mu_y^{0i}\mu_y^{if} + \mu_x^{0i}\mu_x^{if}\mu_z^{0i}\mu_z^{if} + \mu_y^{0i}\mu_y^{if}\mu_z^{0i}\mu_z^{if}) + 2\{(\mu_x^{0i}\mu_x^{if})^2 + (\mu_y^{0i}\mu_y^{if})^2 + (\mu_z^{0i}\mu_z^{if})^2\}$$
$$+ (\mu_x^{0i})^2\{(\mu_x^{if})^2 + (\mu_y^{if})^2 + (\mu_z^{if})^2\} + (\mu_y^{0i})^2\{(\mu_x^{if})^2 + (\mu_y^{if})^2 + (\mu_z^{if})^2\}$$
$$+ (\mu_z^{0i})^2\{(\mu_x^{if})^2 + (\mu_y^{if})^2 + (\mu_z^{if})^2\}\Big]$$

$$\delta_{TP}^{3SM} = \frac{8}{\Delta E_i^2}\Big[2(\mu_x^{0i}\mu_x^{if} + \mu_y^{0i}\mu_y^{if} + \mu_z^{0i}\mu_z^{if})^2 + \{(\mu_x^{if})^2 + (\mu_y^{if})^2 + (\mu_z^{if})^2\}\{(\mu_x^{0i})^2 + (\mu_y^{0i})^2 + (\mu_z^{0i})^2\}\Big]$$

$$\delta_{TP}^{3SM} = \frac{8}{\Delta E_i^2}\left[2\left(\overrightarrow{\mu^{0i}} \cdot \overrightarrow{\mu^{if}}\right)^2 + |\mu^{0i}|^2|\mu^{if}|^2\right]$$

$$\delta_{TP}^{3SM} = \frac{8|\mu^{0i}|^2|\mu^{if}|^2}{\Delta E_i^2}\left[2\left(\frac{\overrightarrow{\mu^{0i}} \cdot \overrightarrow{\mu^{if}}}{|\mu^{0i}||\mu^{if}|}\right)^2 + 1\right]$$

$$\delta_{TP}^{3SM} = \frac{8|\mu^{0i}|^2|\mu^{if}|^2}{\Delta E_i^2}\left(2cos^2\theta_{0i}^{if} + 1\right)$$

Next we shall consider the interference terms, δ_{TP}^{ij}.

$$\delta_{TP}^{cross} = 48\left(\frac{\mu_x^{0i}\mu_x^{if}\mu_x^{0j}\mu_x^{jf}}{\Delta E_i \Delta E_j} + \frac{\mu_y^{0i}\mu_y^{if}\mu_y^{0j}\mu_y^{jf}}{\Delta E_i \Delta E_j} + \frac{\mu_z^{0i}\mu_z^{if}\mu_z^{0j}\mu_z^{jf}}{\Delta E_i \Delta E_j}\right)$$
$$+16\left(\frac{\mu_x^{0i}\mu_y^{if} + \mu_y^{0i}\mu_x^{if}}{\Delta E_i} \times \frac{\mu_x^{0j}\mu_y^{jf} + \mu_y^{0j}\mu_x^{jf}}{\Delta E_j}\right) + 16\left(\frac{\mu_y^{0i}\mu_z^{if} + \mu_z^{0i}\mu_y^{if}}{\Delta E_i} \times \frac{\mu_y^{0j}\mu_z^{jf} + \mu_z^{0j}\mu_y^{jf}}{\Delta E_j}\right)$$
$$+16\left(\frac{\mu_x^{0i}\mu_z^{if} + \mu_z^{0i}\mu_x^{if}}{\Delta E_i} \times \frac{\mu_x^{0j}\mu_z^{jf} + \mu_z^{0j}\mu_x^{jf}}{\Delta E_j}\right) + 16\left(\frac{\mu_x^{0i}\mu_x^{if}\mu_y^{0j}\mu_y^{jf} + \mu_y^{0i}\mu_y^{if}\mu_z^{0j}\mu_z^{jf} + \mu_x^{0i}\mu_x^{if}\mu_z^{0j}\mu_z^{jf}}{\Delta E_i \Delta E_j}\right)$$
$$+16\left(\frac{\mu_x^{0j}\mu_x^{jf}\mu_y^{0i}\mu_y^{if} + \mu_y^{0j}\mu_y^{jf}\mu_z^{0i}\mu_z^{if} + \mu_x^{0j}\mu_x^{jf}\mu_z^{0i}\mu_z^{if}}{\Delta E_i \Delta E_j}\right)$$

$$\delta_{TP}^{cross} = \frac{16}{\Delta E_i \Delta E_j}\{3(\mu_x^{0i}\mu_x^{if}\mu_x^{0j}\mu_x^{jf} + \mu_y^{0i}\mu_y^{if}\mu_y^{0j}\mu_y^{jf} + \mu_z^{0i}\mu_z^{if}\mu_z^{0j}\mu_z^{jf}) + \mu_x^{0i}\mu_y^{if}\mu_x^{0j}\mu_y^{jf} + \mu_y^{0i}\mu_x^{if}\mu_x^{0j}\mu_y^{jf}$$
$$+ \mu_x^{0i}\mu_y^{if}\mu_y^{0j}\mu_x^{jf} + \mu_y^{0i}\mu_x^{if}\mu_y^{0j}\mu_x^{jf} + \mu_y^{0i}\mu_z^{if}\mu_y^{0j}\mu_z^{jf} + \mu_z^{0i}\mu_y^{if}\mu_y^{0j}\mu_z^{jf}$$
$$+ \mu_y^{0i}\mu_z^{if}\mu_z^{0j}\mu_y^{jf} + \mu_z^{0i}\mu_y^{if}\mu_z^{0j}\mu_y^{jf} + \mu_x^{0i}\mu_z^{if}\mu_x^{0j}\mu_z^{jf} + \mu_z^{0i}\mu_x^{if}\mu_x^{0j}\mu_z^{jf}$$
$$+ \mu_x^{0i}\mu_z^{if}\mu_z^{0j}\mu_x^{jf} + \mu_z^{0i}\mu_x^{if}\mu_z^{0j}\mu_x^{jf} + \mu_y^{0i}\mu_y^{if}\mu_x^{0j}\mu_x^{jf} + \mu_x^{0i}\mu_x^{if}\mu_y^{0j}\mu_y^{jf}$$
$$+ \mu_z^{0i}\mu_z^{if}\mu_y^{0j}\mu_y^{jf} + \mu_y^{0i}\mu_y^{if}\mu_z^{0j}\mu_z^{jf} + \mu_z^{0i}\mu_z^{if}\mu_x^{0j}\mu_x^{jf} + \mu_x^{0i}\mu_x^{if}\mu_z^{0j}\mu_z^{jf}\}$$

$$
\begin{aligned}
\delta_{TP}^{cross} = {} & \frac{16}{\Delta E_i \Delta E_j}\left[3(\mu_x^{0i}\mu_x^{if}+\mu_y^{0i}\mu_y^{if}+\mu_z^{0i}\mu_z^{if})(\mu_x^{0j}\mu_x^{jf}+\mu_y^{0j}\mu_y^{jf}+\mu_z^{0j}\mu_z^{jf})\right] \\
& + \frac{16}{\Delta E_i \Delta E_j}\{-3(\mu_x^{0i}\mu_x^{if}\mu_y^{0j}\mu_y^{jf}+\mu_x^{0i}\mu_x^{if}\mu_z^{0j}\mu_z^{jf}+\mu_y^{0i}\mu_y^{if}\mu_x^{0j}\mu_x^{jf}+\mu_y^{0i}\mu_y^{if}\mu_z^{0j}\mu_z^{jf} \\
& +\mu_z^{0i}\mu_z^{if}\mu_x^{0j}\mu_x^{jf}+\mu_z^{0i}\mu_z^{if}\mu_y^{0j}\mu_y^{jf})+\mu_x^{0i}\mu_y^{if}\mu_x^{0j}\mu_y^{jf}+\mu_y^{0i}\mu_x^{if}\mu_x^{0j}\mu_y^{jf} \\
& +\mu_x^{0i}\mu_y^{if}\mu_y^{0j}\mu_x^{jf}+\mu_y^{0i}\mu_x^{if}\mu_y^{0j}\mu_x^{jf}+\mu_y^{0i}\mu_z^{if}\mu_y^{0j}\mu_z^{jf}+\mu_z^{0i}\mu_y^{if}\mu_y^{0j}\mu_z^{jf} \\
& +\mu_y^{0i}\mu_z^{if}\mu_z^{0j}\mu_y^{jf}+\mu_z^{0i}\mu_y^{if}\mu_z^{0j}\mu_y^{jf}+\mu_x^{0i}\mu_z^{if}\mu_x^{0j}\mu_z^{jf}+\mu_z^{0i}\mu_x^{if}\mu_x^{0j}\mu_z^{jf} \\
& +\mu_x^{0i}\mu_z^{if}\mu_z^{0j}\mu_x^{jf}+\mu_z^{0i}\mu_x^{if}\mu_z^{0j}\mu_x^{jf}+\mu_y^{0i}\mu_y^{if}\mu_x^{0j}\mu_x^{jf}+\mu_x^{0i}\mu_x^{if}\mu_y^{0j}\mu_y^{jf} \\
& +\mu_z^{0i}\mu_z^{if}\mu_y^{0j}\mu_y^{jf}+\mu_y^{0i}\mu_y^{if}\mu_z^{0j}\mu_z^{jf}+\mu_z^{0i}\mu_z^{if}\mu_x^{0j}\mu_x^{jf}+\mu_x^{0i}\mu_x^{if}\mu_z^{0j}\mu_z^{jf}\}
\end{aligned}
$$

$$
\begin{aligned}
\delta_{TP}^{cross} = {} & \frac{16}{\Delta E_i \Delta E_j}\left[3(\overrightarrow{\mu^{0i}}\cdot\overrightarrow{\mu^{if}})(\overrightarrow{\mu^{0j}}\cdot\overrightarrow{\mu^{jf}})\right] \\
& + \frac{16}{\Delta E_i \Delta E_j}\{-2(\mu_x^{0i}\mu_x^{if}\mu_y^{0j}\mu_y^{jf}+\mu_x^{0i}\mu_x^{if}\mu_z^{0j}\mu_z^{jf}+\mu_y^{0i}\mu_y^{if}\mu_x^{0j}\mu_x^{jf}+\mu_y^{0i}\mu_y^{if}\mu_z^{0j}\mu_z^{jf} \\
& +\mu_z^{0i}\mu_z^{if}\mu_x^{0j}\mu_x^{jf}+\mu_z^{0i}\mu_z^{if}\mu_y^{0j}\mu_y^{jf})+\mu_x^{0i}\mu_y^{if}\mu_x^{0j}\mu_y^{jf}+\mu_y^{0i}\mu_x^{if}\mu_x^{0j}\mu_y^{jf}+\mu_x^{0i}\mu_y^{if}\mu_y^{0j}\mu_x^{jf} \\
& +\mu_y^{0i}\mu_x^{if}\mu_y^{0j}\mu_x^{jf}+\mu_y^{0i}\mu_z^{if}\mu_y^{0j}\mu_z^{jf}+\mu_z^{0i}\mu_y^{if}\mu_y^{0j}\mu_z^{jf}+\mu_y^{0i}\mu_z^{if}\mu_z^{0j}\mu_y^{jf}+\mu_z^{0i}\mu_y^{if}\mu_z^{0j}\mu_y^{jf} \\
& +\mu_x^{0i}\mu_z^{if}\mu_x^{0j}\mu_z^{jf}+\mu_z^{0i}\mu_x^{if}\mu_x^{0j}\mu_z^{jf}+\mu_x^{0i}\mu_z^{if}\mu_z^{0j}\mu_x^{jf}+\mu_z^{0i}\mu_x^{if}\mu_z^{0j}\mu_x^{jf}\}
\end{aligned}
$$

$$
\begin{aligned}
\delta_{TP}^{cross} = {} & \frac{16|\mu^{0i}||\mu^{if}||\mu^{0j}||\mu^{jf}|}{\Delta E_i \Delta E_j}\left[3\frac{\overrightarrow{\mu^{0i}}\cdot\overrightarrow{\mu^{if}}}{|\mu^{0i}||\mu^{if}|}\frac{\overrightarrow{\mu^{0j}}\cdot\overrightarrow{\mu^{jf}}}{|\mu^{0j}||\mu^{jf}|}\right] \\
& + \frac{16}{\Delta E_i \Delta E_j}\Big[\mu_x^{0i}\mu_x^{0j}(\mu_y^{if}\mu_y^{jf}+\mu_z^{if}\mu_z^{jf})+\mu_y^{0i}\mu_y^{0j}(\mu_x^{if}\mu_x^{jf}+\mu_z^{if}\mu_z^{jf})+\mu_z^{0i}\mu_z^{0j}(\mu_y^{if}\mu_y^{jf}+\mu_x^{if}\mu_x^{jf}) \\
& -2\{\mu_x^{0i}\mu_x^{if}(\mu_y^{0j}\mu_y^{jf}+\mu_z^{0j}\mu_z^{jf})+\mu_y^{0i}\mu_y^{if}(\mu_x^{0j}\mu_x^{jf}+\mu_z^{0j}\mu_z^{jf})+\mu_z^{0i}\mu_z^{if}(\mu_x^{0j}\mu_x^{jf}+\mu_y^{0j}\mu_y^{jf})\} \\
& +\mu_y^{0i}\mu_x^{if}\mu_x^{0j}\mu_y^{jf}+\mu_x^{0i}\mu_y^{if}\mu_y^{0j}\mu_x^{jf}+\mu_z^{0i}\mu_y^{if}\mu_y^{0j}\mu_z^{jf}+\mu_y^{0i}\mu_z^{if}\mu_z^{0j}\mu_y^{jf}+\mu_z^{0i}\mu_x^{if}\mu_x^{0j}\mu_z^{jf}+\mu_x^{0i}\mu_z^{if}\mu_z^{0j}\mu_x^{jf}\Big]
\end{aligned}
$$

$$
\begin{aligned}
\delta_{TP}^{cross} = {} & \frac{16|\mu^{0i}||\mu^{if}||\mu^{0j}||\mu^{jf}|}{\Delta E_i \Delta E_j}\left(3cos\theta_{0i}^{if}cos\theta_{0j}^{jf}\right) \\
& + \frac{16}{\Delta E_i \Delta E_j}\Big[(\mu_x^{0i}\mu_x^{0j}+\mu_y^{0i}\mu_y^{0j}+\mu_z^{0i}\mu_z^{0j})(\mu_x^{if}\mu_x^{jf}+\mu_y^{if}\mu_y^{jf}+\mu_z^{if}\mu_z^{jf}) \\
& -(\mu_x^{0i}\mu_x^{0j}\mu_x^{if}\mu_x^{jf}+\mu_y^{0i}\mu_y^{0j}\mu_y^{if}\mu_y^{jf}+\mu_z^{0i}\mu_z^{0j}\mu_z^{if}\mu_z^{jf}) \\
& -2(\mu_x^{0i}\mu_x^{if}+\mu_y^{0i}\mu_y^{if}+\mu_z^{0i}\mu_z^{if})(\mu_x^{0j}\mu_x^{jf}+\mu_y^{0j}\mu_y^{jf}+\mu_z^{0j}\mu_z^{jf}) \\
& +2(\mu_x^{0i}\mu_x^{0j}\mu_x^{if}\mu_x^{jf}+\mu_y^{0i}\mu_y^{0j}\mu_y^{if}\mu_y^{jf}+\mu_z^{0i}\mu_z^{0j}\mu_z^{if}\mu_z^{jf})+\mu_y^{0i}\mu_x^{0j}\mu_x^{if}\mu_y^{jf} \\
& +\mu_x^{0i}\mu_y^{0j}\mu_x^{jf}\mu_y^{if}+\mu_z^{0i}\mu_y^{0j}\mu_y^{if}\mu_z^{jf}+\mu_y^{0i}\mu_z^{0j}\mu_z^{if}\mu_y^{jf}+\mu_z^{0i}\mu_x^{0j}\mu_x^{if}\mu_z^{jf}+\mu_x^{0i}\mu_z^{0j}\mu_z^{if}\mu_x^{jf}+\Big]
\end{aligned}
$$

$$\delta_{TP}^{cross} = \frac{16|\mu^{0i}||\mu^{if}||\mu^{0j}||\mu^{jf}|}{\Delta E_i \Delta E_j}\left(3cos\theta_{0i}^{if}cos\theta_{0j}^{jf}\right)$$
$$+\frac{16}{\Delta E_i \Delta E_j}\left[\left(\overrightarrow{\mu^{0i}}\cdot\overrightarrow{\mu^{0j}}\right)\left(\overrightarrow{\mu^{if}}\cdot\overrightarrow{\mu^{jf}}\right)-2\left(\overrightarrow{\mu^{0i}}\cdot\overrightarrow{\mu^{if}}\right)\left(\overrightarrow{\mu^{0j}}\cdot\overrightarrow{\mu^{jf}}\right)\right.$$
$$+\mu_x^{0i}\mu_x^{0j}\mu_x^{if}\mu_x^{jf}+\mu_y^{0i}\mu_y^{0j}\mu_y^{if}\mu_y^{jf}+\mu_z^{0i}\mu_z^{0j}\mu_z^{if}\mu_z^{jf}+\mu_y^{0i}\mu_x^{if}\mu_x^{0j}\mu_y^{jf}+\mu_x^{0i}\mu_y^{if}\mu_y^{0j}\mu_x^{jf}$$
$$\left.+\mu_z^{0i}\mu_y^{if}\mu_y^{0j}\mu_z^{jf}+\mu_y^{0i}\mu_z^{if}\mu_z^{0j}\mu_y^{jf}+\mu_z^{0i}\mu_x^{if}\mu_x^{0j}\mu_z^{jf}+\mu_x^{0i}\mu_z^{if}\mu_z^{0j}\mu_x^{jf}\right]$$

$$\delta_{TP}^{cross} = \frac{16|\mu^{0i}||\mu^{if}||\mu^{0j}||\mu^{jf}|}{\Delta E_i \Delta E_j}\left(3cos\theta_{0i}^{if}cos\theta_{0j}^{jf}\right)$$
$$+\frac{16|\mu^{0i}||\mu^{if}||\mu^{0j}||\mu^{jf}|}{\Delta E_i \Delta E_j}\left[\frac{\overrightarrow{\mu^{0i}}\cdot\overrightarrow{\mu^{0j}}}{|\mu^{0i}||\mu^{0j}|}\frac{\overrightarrow{\mu^{if}}\cdot\overrightarrow{\mu^{jf}}}{|\mu^{if}||\mu^{jf}|}-2\frac{\overrightarrow{\mu^{0i}}\cdot\overrightarrow{\mu^{if}}}{|\mu^{0i}||\mu^{if}|}\frac{\left(\overrightarrow{\mu^{0j}}\cdot\overrightarrow{\mu^{jf}}\right)}{|\mu^{0j}||\mu^{jf}|}\right]$$
$$+\frac{16}{\Delta E_i \Delta E_j}\left[\mu_x^{0i}\mu_x^{jf}(\mu_x^{0j}\mu_x^{if}+\mu_y^{0j}\mu_y^{if}+\mu_z^{0j}\mu_z^{if})+\mu_y^{0i}\mu_y^{jf}(\mu_x^{0j}\mu_x^{if}+\mu_y^{0j}\mu_y^{if}+\mu_z^{0j}\mu_z^{if})\right.$$
$$\left.+\mu_z^{0i}\mu_z^{jf}(\mu_x^{0j}\mu_x^{if}+\mu_y^{0j}\mu_y^{if}+\mu_z^{0j}\mu_z^{if})\right]$$

$$\delta_{TP}^{cross} = \frac{16|\mu^{0i}||\mu^{if}||\mu^{0j}||\mu^{jf}|}{\Delta E_i \Delta E_j}\left(cos\theta_{0i}^{if}cos\theta_{0j}^{jf}+cos\theta_{0i}^{0j}cos\theta_{if}^{jf}\right)$$
$$+\frac{16}{\Delta E_i \Delta E_j}(\mu_x^{0j}\mu_x^{if}+\mu_y^{0j}\mu_y^{if}+\mu_z^{0j}\mu_z^{if})(\mu_x^{0i}\mu_x^{jf}+\mu_y^{0i}\mu_y^{jf}+\mu_z^{0i}\mu_z^{jf})$$

$$\delta_{TP}^{cross} = \frac{16|\mu^{0i}||\mu^{if}||\mu^{0j}||\mu^{jf}|}{\Delta E_i \Delta E_j}\left(cos\theta_{0i}^{if}cos\theta_{0j}^{jf}+cos\theta_{0i}^{0j}cos\theta_{if}^{jf}+\frac{\overrightarrow{\mu^{0j}}\cdot\overrightarrow{\mu^{if}}}{|\mu^{0j}||\mu^{if}|}\frac{\overrightarrow{\mu^{0i}}\cdot\overrightarrow{\mu^{jf}}}{|\mu^{0i}||\mu^{jf}|}\right)$$

$$\delta_{TP}^{cross} = \frac{16|\mu^{0i}||\mu^{0j}||\mu^{if}||\mu^{jf}|}{\Delta E_i \Delta E_j}(cos\theta_{0i}^{if}cos\theta_{0j}^{jf}+cos\theta_{0i}^{0j}cos\theta_{if}^{jf}+cos\theta_{0j}^{if}cos\theta_{0i}^{jf})$$

Here $\delta_{TP}^{ij} = \delta_{TP}^{ji}$. Therefore, $\delta_{TP}^{cross} = \delta_{TP}^{ij} + \delta_{TP}^{ji} = 2\delta_{TP}^{ij}$ This means -

$$\delta_{TP}^{ij} = \frac{8|\mu^{0i}||\mu^{0j}||\mu^{if}||\mu^{jf}|}{\Delta E_i \Delta E_j}(cos\theta_{0i}^{if}cos\theta_{0j}^{jf}+cos\theta_{0i}^{0j}cos\theta_{if}^{jf}+cos\theta_{0i}^{jf}cos\theta_{0j}^{if})$$

This expression can be reduced to 3SM formula by putting $i = j$. Therefore the overall δ_{TP} can be written as -

$$\delta_{TP} = \sum_i\sum_j \frac{8|\mu^{0i}||\mu^{0j}||\mu^{if}||\mu^{jf}|}{\Delta E_i \Delta E_j}(cos\theta_{0i}^{if}cos\theta_{0j}^{jf}+cos\theta_{0i}^{0j}cos\theta_{if}^{jf}+cos\theta_{0i}^{jf}cos\theta_{0j}^{if})$$

This is the required Generalized Few-State Model (GFSM) formula for TPA transition probability.

Table 1. a) Optimized geometry of ortho-betain in gas and water media at CAM-B3LYP/6-311++G(d,p) level of theory

Atom	Gas medium			Water medium		
	X	Y	Z	X	Y	Z
C	-1.44332	0.94470	0.49258	-1.43005	0.75887	0.79484
C	-2.82159	0.99344	0.44507	-2.80516	0.82108	0.78842
C	-3.54203	-0.08957	-0.02474	-3.52323	-0.08289	0.01855
C	-2.84367	-1.20979	-0.46185	-2.83893	-1.02735	-0.73460
C	-1.47263	-1.21034	-0.42397	-1.46351	-1.04107	-0.70513
N	-0.77534	-0.15624	0.07080	-0.78112	-0.16603	0.06082
H	-4.62340	-0.06361	-0.06180	-4.61004	-0.05159	0.00449
H	-0.82175	1.75902	0.82962	-0.80815	1.42050	1.38564
H	-3.31516	1.89090	0.79218	-3.30238	1.57145	1.39539
H	-3.35534	-2.07543	-0.85979	-3.36151	-1.74811	-1.35595
H	-0.87915	-2.02649	-0.80413	-0.86628	-1.73386	-1.28956
C	0.65218	-0.18498	0.10460	0.66556	-0.19164	0.07848
C	1.30425	-1.39672	0.35877	1.30894	-1.37125	0.42579
C	1.36010	1.04013	-0.18496	1.34725	1.00753	-0.29399
C	2.67360	-1.47913	0.30682	2.69191	-1.43489	0.42405
H	0.72653	-2.27046	0.64201	0.71673	-2.23899	0.71005
C	2.78659	0.87240	-0.26664	2.76894	0.88311	-0.28397
C	3.40580	-0.32141	-0.02526	3.40877	-0.28882	0.06225
H	3.17786	-2.40840	0.53547	3.20220	-2.35036	0.70331
H	3.35401	1.76192	-0.51201	3.34336	1.76156	-0.56727
H	4.48796	-0.37750	-0.07810	4.49628	-0.31945	0.05381
O	0.79002	2.14391	-0.36269	0.73434	2.08187	-0.61422

Table 1. b) Optimized geometry of ortho-betain in acetonitrile and THF media at CAM-B3LYP/6-311++G(d,p) level of theory

Atom	Acetonitrile medium			THF medium		
	X	Y	Z	X	Y	Z
C	-1.42975	0.76557	0.78607	-1.43126	0.84308	0.67663
C	-2.80500	0.82837	0.77745	-2.80714	0.90485	0.65784
C	-3.52297	-0.08305	0.01666	-3.52640	-0.08454	0.00675
C	-2.83830	-1.03565	-0.72595	-2.84094	-1.11465	-0.62347
C	-1.46302	-1.04905	-0.69550	-1.46698	-1.12373	-0.59285
N	-0.78050	-0.16742	0.06278	-0.77977	-0.16596	0.06452
H	-4.60958	-0.05118	0.00104	-4.60799	-0.05322	-0.01409
H	-0.80883	1.43316	1.37041	-0.81030	1.57326	1.16822
H	-3.30217	1.58568	1.37553	-3.30085	1.72354	1.16195
H	-3.36039	-1.76220	-1.34070	-3.36074	-1.90032	-1.15315
H	-0.86643	-1.74688	-1.27399	-0.87199	-1.87275	-1.09298
C	0.66569	-0.19239	0.08034	0.66280	-0.19112	0.08622
C	1.31090	-1.37166	0.42605	1.30990	-1.37899	0.40565
C	1.34555	1.00836	-0.29253	1.34764	1.01945	-0.26448
C	2.69370	-1.43393	0.42207	2.68973	-1.44758	0.38921
H	0.72131	-2.24023	0.71260	0.72410	-2.24756	0.68802
C	2.76779	0.88432	-0.28590	2.77212	0.88218	-0.27774
C	3.40888	-0.28695	0.05866	3.40788	-0.29632	0.03771
H	3.20540	-2.34860	0.70096	3.19874	-2.36550	0.65154
H	3.34057	1.76352	-0.56975	3.34310	1.76339	-0.54817
H	4.49632	-0.31669	0.04850	4.49226	-0.33243	0.01769
O	0.73081	2.08146	-0.60858	0.74348	2.09970	-0.54244

Table 2. a) Optimized geometry of Para-betain in Gas and Water media at CAM-B3LYP/6-311++G(d,p) level of theory

Atom	Gas medium			Water medium		
	X	Y	Z	X	Y	Z
C	-1.78270	-1.11850	-0.34556	-1.78287	-1.06619	-0.48198
C	-3.15527	-1.14221	-0.32663	-3.15753	-1.09633	-0.47598
C	-3.87433	0.00005	0.00004	-3.86171	0.00003	0.00004
C	-3.15519	1.14227	0.32668	-3.15748	1.09636	0.47603
C	-1.78262	1.11847	0.34555	-1.78282	1.06618	0.48198
N	-1.07952	-0.00004	-0.00001	-1.10857	-0.00001	-0.00002
H	-4.95559	0.00008	0.00006	-4.94361	0.00004	0.00006
H	-1.19263	-1.95914	-0.67189	-1.18051	-1.86690	-0.88266
H	-3.65535	-2.05977	-0.60678	-3.66322	-1.96837	-0.86548
H	-3.65520	2.05986	0.60683	-3.66313	1.96843	0.86555
H	-1.19248	1.95908	0.67184	-1.18042	1.86688	0.88262
C	0.32399	-0.00005	-0.00005	0.33347	-0.00003	-0.00005
C	1.04293	-1.17527	0.31840	1.03249	-1.11407	0.46407
C	1.04290	1.17523	-0.31837	1.03248	1.11405	-0.46409
C	2.40236	-1.18162	0.32726	2.40891	-1.11632	0.46562
H	0.50917	-2.06930	0.62306	0.49313	-1.97212	0.85053
C	2.40232	1.18160	-0.32734	2.40890	1.11628	-0.46570
H	0.50909	2.06932	-0.62280	0.49312	1.97216	-0.85041
C	3.18751	-0.00011	-0.00044	3.17808	-0.00011	-0.00026
H	2.95180	-2.06996	0.61327	2.94575	-1.97955	0.84254
H	2.95172	2.07005	-0.61306	2.94574	1.97961	-0.84241
O	4.42184	0.00011	0.00029	4.45019	0.00009	0.00021

Table 2. b) Optimized geometry of Para-betain in acetonitrile and THF media at CAM-B3LYP/6-311++G(d,p) level of theory

Atom	Acetonitrile medium			THF medium		
	X	Y	Z	X	Y	Z
C	-1.78119	-1.05587	-0.50708	-1.78260	-1.07435	-0.46239
C	-3.15651	-1.08528	-0.50278	-3.15733	-1.10499	-0.45319
C	-3.86037	0.00000	0.00002	-3.86314	0.00002	0.00003
C	-3.15652	1.08529	0.50282	-3.15729	1.10501	0.45322
C	-1.78119	1.05586	0.50709	-1.78256	1.07434	0.46239
N	-1.10893	-0.00001	0.00000	-1.10518	-0.00001	-0.00001
H	-4.94744	0.00000	0.00001	-4.94505	0.00003	0.00005
H	-1.17868	-1.85301	-0.92903	-1.18071	-1.87983	-0.85384
H	-3.66480	-1.95159	-0.91506	-3.66247	-1.98475	-0.82625
H	-3.66479	1.95161	0.91510	-3.66240	1.98479	0.82630
H	-1.17867	1.85300	0.92902	-1.18065	1.87981	0.85381
C	0.33489	0.00000	0.00000	0.33257	-0.00002	-0.00003
C	1.03086	-1.10288	0.49063	1.03407	-1.12461	0.44204
C	1.03086	1.10288	-0.49063	1.03406	1.12460	-0.44205
C	2.40878	-1.10447	0.49175	2.40780	-1.12740	0.44526
H	0.48895	-1.95534	0.89500	0.49522	-1.98882	0.81611
C	2.40877	1.10448	-0.49176	2.40779	1.12738	-0.44532
H	0.48894	1.95535	-0.89498	0.49520	1.98885	-0.81601
C	3.17332	-0.00001	-0.00004	3.18074	-0.00008	-0.00021
H	2.94777	-1.96074	0.88807	2.94696	-1.99473	0.80842
H	2.94776	1.96076	-0.88806	2.94694	1.99477	-0.80832
O	4.45167	0.00001	-0.00001	4.44483	0.00007	0.00016

Table 3. Excited-Excited states transition moments of ortho- and para-betain in gas, THF, CH3CN and water medium (calculated at CAMB3LYP/aug-cc-pVDZ level of theory)

System	Solvents	μ^{11} in (a.u.)				μ^{12} in (a.u.)			
		x	y	z	Total	x	y	z	Total
ortho-betain	Gas	2.1340	-0.1300	-1.1020	2.4050	0.1030	0.0410	-0.2310	0.2560
		-0.1030	-0.0410	0.2310	0.2560	1.8920	-0.1410	-1.7940	2.6110
	THF	3.5570	-0.0800	-1.7510	3.9650	-0.0060	-0.2380	-0.1690	0.2920
		0.0060	0.2380	0.1690	0.2920	3.9200	-0.0920	-2.0670	4.4330
	CH_3CN	3.9090	-0.0430	-1.9190	4.3550	-0.0460	0.2650	0.1240	0.2960
		0.0460	-0.2650	-0.1240	0.2960	4.2220	-0.0640	-2.1320	4.7300
	Water	3.9320	-0.0320	-1.9390	4.3840	-0.0530	0.2670	0.1200	0.2970
		0.0530	-0.2670	-0.1200	0.2970	4.2370	-0.0530	-2.1400	4.7470
para-betain	Gas	0.0000	0.0000	-0.9900	0.9900	0.0830	-0.2560	0.0000	0.2690
		-0.0830	0.2560	0.0000	0.2690	0.0000	0.0000	-2.7590	2.7590
	THF	0.0000	0.0000	-3.8790	3.8790	0.2230	-0.1950	0.0000	0.2970
		-0.2240	0.1950	0.0000	0.2970	0.0000	0.0000	-5.2150	5.2150
	CH_3CN	0.0000	0.0000	-4.5830	4.5830	0.2270	0.1830	0.0000	0.2920
		-0.2270	-0.1830	0.0000	0.2920	0.0000	0.0000	-5.5590	5.5590
	Water	0.0000	0.0000	-4.3720	4.3720	0.2400	-0.1720	0.0000	0.2950
		-0.2400	0.1720	0.0000	0.2950	0.0000	0.0000	-5.4470	5.4470

Table 4. SOS results (in 10^4 a.u. order) involving different number of intermediate states - Test of convergence behaviour

No. of intermediate	TPA transition probability (in a.u.)			
	o-betain		p-betain	
	1st excited state	2nd excited state	1st excited state	2nd excited state
1	17.05	2.96	9.70	0.11
2	17.93	1.26	9.60	0.87
3	17.95	1.34	9.89	0.87
4	18.72	1.52	9.88	0.87
5	18.72	1.52	9.90	0.84
6	17.66	1.59	10.09	0.81
7	13.54	1.84	10.06	0.81
8	13.22	1.84	9.99	0.82
Response theory results	13.10	0.90	11.40	0.93

Table 5.Theoretical and experimental excitation energy (in eV) of o- and p-betain in water medium

systems	Excited states	Ground to excited state excitation energy (in eV) calculated using aug-cc-pVDZ basis set and following functionals		Experimental excitation energy (in eV)
		CAMB3LYP	LC-PBE	
o-betain	1	2.934	3.551	3.280
		4.072	4.612	
p-betain	2	3.048	3.651	3.397
		4.030	4.432	