Second Harmonic Scattering of Molecular Aggregates

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A Tensor Calculation.

In the main text, we have written :

$$\vec{\beta}_L(i) = \vec{T}_A \vec{\beta}_A(i) = \vec{T}_A \vec{T}(\hat{r}_i')\vec{\beta}_m(i) \quad \text{(S1)}$$

where $\vec{T}_A$ is the frame transformation tensor from the aggregate to the laboratory frame, $\vec{T}(\hat{r}_i')$ is the frame transformation tensor accounting for the transformation of the molecular first hyperpolarizability tensor from the molecular frame to the laboratory frame defined with the standard Euler angles according to Figure 1. Also, $\vec{\beta}_m(i)$ is the molecular first hyperpolarizability tensor of molecule *i*, $\vec{\beta}_A(i)$ the molecular first hyperpolarizability tensor of molecule *i* expressed in the aggregate reference frame and $\vec{\beta}_L(i)$ the molecular first hyperpolarizability tensor of molecule *i* expressed in the laboratory frame.

The transformation from one frame to the next with the transformation tensor is:

$$\beta_{L,IJK}(i) = \sum_{ijk} T_{Ii}(\hat{r}_i')T_{Jj}(\hat{r}_i')T_{Kk}(\hat{r}_i')\beta_{m,ijk}(i) \quad \text{(S2)}$$

where the summation runs over the three axes of the reference frames. In most cases, the molecular quadratic hyperpolarizability tensor possesses only a few independent non vanishing elements depending on the molecular symmetry of the probe molecule. For instance, for an efficient rod-like push-pull compound like DiA, only one element is independent and non vanishing, namely $\beta_{m,zzz}(i)$ where the molecular Oz axis is the charge transfer axis. With the introduction of the three Euler angles, the tensor $\vec{T}(\hat{r}_i')$ is simply given by [S1]:

$$\vec{\vec{T}}(\hat{r}_i') = \begin{vmatrix} \begin{matrix}-\sin\psi'\cos\theta'\sin\phi' \\ +\cos\psi'\cos\phi'\end{matrix} & \begin{matrix}\cos\psi'\cos\theta'\sin\phi' \\ +\sin\psi'\cos\phi\end{matrix} & \sin\theta'\sin\phi' \\ \begin{matrix}-\sin\psi'\cos\theta'\cos\phi' \\ -\cos\psi'\sin\phi'\end{matrix} & \begin{matrix}\cos\psi'\cos\theta'\cos\phi' \\ -\sin\psi'\sin\phi'\end{matrix} & \sin\theta'\cos\phi' \\ \sin\psi'\sin\theta' & -\cos\psi'\sin\theta' & \cos\theta' \end{vmatrix} \quad \text{(S3)}$$

Under this definition, the angles ψ' and ϕ' run from 0 to 2π whereas the angle θ' runs from 0 to π. The tensor $\vec{\vec{T}}_A$ is defined similarly to the tensor $\vec{\vec{T}}(\hat{r}_i')$ albeit with the subscript A for the three corresponding Euler angles.

[S1] P.F. Brevet in *Surface Second Harmonic Generation*, Presses Polytechniques Universitaires Romandes, Lausanne, 1997.