Time-Domain Calculations of the Infrared and Polarized Raman Spectra of Tetraalanine in Aqueous Solution

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Supporting Information

Derivation of the limiting value of $M(t)$ upon complete mode mixing of a three-mode system

The limiting value of $M(t)$ (defined by eq 10 in section 3B) upon complete mode mixing of a three-mode system, denoted as $M^{(3)}_{\text{cmm}}$, is calculated as the average of $\cos^2 \theta$ in the region where $\cos^2 \theta$ is larger than $\sin^2 \theta \cos^2 \psi$ and $\sin^2 \theta \sin^2 \psi$, where $\theta$ and $\psi$ (as well as $\phi$) are the Euler angles of three-dimensional coordinate transformation. This region is denoted as $\Gamma$ hereafter. Therefore, $M^{(3)}_{\text{cmm}}$ is expressed as

$$M^{(3)}_{\text{cmm}} = \int_{\Gamma_1} d\Omega \cos^2 \theta \frac{1}{\int_{\Gamma_1} d\Omega}$$

(S1)

Without losing generality and preciseness, we restrict our calculation to the upper hemisphere of $\theta (0 \leq \theta \leq \pi/2)$, and omit the integration over $\phi$.

$\Gamma$ is divided into two sub-regions: $\Gamma_1$, where $\cos^2 \theta$ is larger than $\sin^2 \theta (0 \leq \theta \leq \pi/4)$, and $\Gamma_2$, where $\cos^2 \theta$ is smaller than $\sin^2 \theta$ but larger than $(1/2)\sin^2 \theta \left[ \pi/4 \leq \theta \leq \cos^{-1}(1/\sqrt{3}) \right]$ with a condition also for $\psi$. The integration in $\Gamma_1$ is rather straightforward. At any value of $\theta$ in the range of $\pi/4 \leq \theta \leq \cos^{-1}(1/\sqrt{3})$, the width of the range of $\psi$...
satisfying the condition that \( \cos^2 \theta \) is larger than \( \sin^2 \theta \cos^2 \psi \) and \( \sin^2 \theta \sin^2 \psi \) is \( 2\pi - 8\cos^{-1}(\cot \theta) \). Therefore, the denominator of eq S1 is expressed as

\[
\int_{\Omega} d\Omega = 2\pi \left( 1 - \frac{1}{\sqrt{3}} \right) - 8F[\pi/4, \cos^{-1}(1/\sqrt{3}), 0]
\]

where \( F[a,b,n] \) is defined as

\[
F[a,b,n] = \int_{a}^{b} d\theta \ \sin \theta \ \cos^n \theta \ \cos^{-1}(\cot \theta)
\]

Changing the integration variable to \( \xi = \cos^{-1}(\cot \theta) \), we have

\[
F[\pi/4, \cos^{-1}(1/\sqrt{3}), n] = \int_{0}^{\pi/4} d\xi \ \frac{\sin \xi}{(1 + \cos^2 \xi)^{3/2}} \left( \frac{\cos^2 \xi}{1 + \cos^2 \xi} \right)^{n/2} \xi
\]

In fact, as easily recognized, \( \Gamma \) occupies one third of the hemisphere, so that eq S2 is equal to \( 2\pi/3 \). We therefore obtain

\[
F[\pi/4, \cos^{-1}(1/\sqrt{3}), 0] = \frac{\pi}{12} (2 - \sqrt{3})
\]

The numerator of eq S1 is expressed as

\[
\int_{\Omega} d\Omega \ \cos^2 \theta = \frac{2\pi}{3} \left( 1 - \frac{1}{3\sqrt{3}} \right) - 8F[\pi/4, \cos^{-1}(1/\sqrt{3}), 2]
\]

Integrating eq S4 for \( n = 2 \) by parts, we have

\[
F[\pi/4, \cos^{-1}(1/\sqrt{3}), 2] = \left[ \frac{\cos \zeta}{3(1 + \cos^2 \zeta)^{3/2}} \right]_{0}^{\pi/4} + \frac{1}{3} \left[ \frac{\sin \zeta}{(1 + \cos^2 \zeta)^{3/2}} \right]_{0}^{\pi/4} - \frac{1}{3} \left[ \frac{\cos \zeta}{(1 + \cos^2 \zeta)^{3/2}} \right]_{0}^{\pi/4}
\]

The first and second terms on the right-hand side are equal to \( \sqrt{3} \pi/54 \) and \( (1/3) F[\pi/4, \cos^{-1}(1/\sqrt{3}), 0] = \pi(2 - \sqrt{3})/36 \) according to eq S5, respectively. The integral in the third term is evaluated by changing the integration variable to \( u = \sin \zeta \) as
\[
\int_0^{\pi/4} d\xi \frac{\cos \xi}{(1 + \cos^2 \xi)^{3/2}} = \int_0^{1/\sqrt{2}} du \frac{1}{(2 - u^2)^{3/2}} = \frac{1}{2\sqrt{3}} \quad (S8)
\]

As a result, \( M_{\text{cmm}}^{(3)} \) is calculated as

\[
M_{\text{cmm}}^{(3)} = \frac{1}{3} \left( 1 + \frac{2\sqrt{3}}{\pi} \right) \approx 0.701 \quad (S9)
\]