

Supporting Information for “Analyzing Nonexponential Kinetics with Multiple Population-Period Transient Spectroscopy (MUPPETS)”

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Derivation of the Effect of Molecular Rotation on Parallel-Polarized MUPPETS

As with the classic derivations of the effect of molecular rotation on one-dimensional experiments,^{1,2} we adopt polar angles θ and ϕ to describe the orientation of the molecular dipole. The probability of finding a given molecular orientation is described in terms of the real spherical harmonics as defined by Morse and Feshbach,³

$$Y_{l,m}^e(\theta, \phi) = \sqrt{\varepsilon_m \frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos\theta) \cos m\phi \quad (S1)$$

$$\varepsilon_m = \begin{cases} 1; & m = 0 \\ 2; & m \neq 0 \end{cases} \quad (S2)$$

where P_l^m are the Legendre polynomials. The odd spherical harmonics do not occur in this derivation, in which all polarizations are parallel.

Unlike the treatments of one-dimensional experiments, we take the z -axis to be along the mean direction of the incoming beams. The angles of the beams relative to this axis are assumed to be small, such that the polarization vectors can be approximated as lying perfectly along the x -axis. In this approximation, the orientational transition operator for a pair of parallel polarized pulses is

$$\begin{aligned} T_j^o &= (\hat{E}_{j'} \cdot \hat{\mu}) (\hat{E}_{j''} \cdot \hat{\mu})^* \approx |\hat{x} \cdot \hat{\mu}|^2 \\ &= 4\pi (Y_{1,1}^e)^2 \end{aligned} \quad (S3)$$

where various constant factors have been ignored. The magnitudes of the electric field \hat{E} and transition dipole $\hat{\mu}$ are set to unity, because these magnitudes have already been included in the calculation of the orientationally averaged signal. Throughout, the normalizations are set so that the rotational averaged signal has a value of unity at time zero. The orientational contribution to the signal R in a transmission or heterodyne-detected-transient-grating experiment is the transmission of the probe pulse averaged over all angles Ω ,

$$R = \int d\Omega T_{pr}^o P. \quad (S4)$$

The advantage of using spherical harmonics is that the orientational time-evolution operator is diagonal in this basis in an isotropic sample. If the molecule undergoes rotational diffusion, this operator does not depend on the history of the sample. Thus the time evolution operator is

$$G_{ll',mm'}^o(t_2, t_1) = G_l^o(t_2 - t_1) \delta_{ll'} \delta_{mm'}. \quad (S5)$$

The only elements of this operator that we need are

$$G_2^o(t) = \frac{5}{2} r(t) \quad (S6)$$

and

$$G_0^o = 1. \quad (S7)$$

Putting together the steps in a MUPPETS experiment with all pulses polarized in the same direction gives

$$R(\tau_1, \tau_2) = \int d\Omega T_3^o G_l^o(\tau_2) T_2^o G_l^o(\tau_1) T_1^o P_{\text{eq}}. \quad (S8)$$

Taking the equilibrium population as $P_{\text{eq}} = Y_{0,0} / \sqrt{4\pi}$ and summing over all possible intermediate values of l and m yields 27 terms. Only seven terms survive the rotational average, and these terms combine to give the final result

$$R(\tau_2, \tau_1) = 1 + 2r(\tau_1) + 2r(\tau_2) + \frac{55}{7} r(\tau_1) r(\tau_2), \quad (S9)$$

which appears as eq 35 in the main text. The first term corresponds to propagation in $l = 0$ for both time periods; the second term corresponds to propagation in $l = 2$ in the first period and $l = 0$ in the second; the third term corresponds to propagation in $l = 0$ in the first period and $l = 2$ in the second; the last term corresponds to propagation in $l = 2$ for both periods. Population is created in $l = 4$ during the second period, but these terms do not survive rotational averaging in the detection step.

References and Notes

- (1) Tao, T. *Biopolymers* **1969**, *8*, 609.
- (2) Chuang, T. J.; Eisenthal, K. B. *J. Chem. Phys.* **1972**, *57*, 5094.
- (3) Morse, P. M.; Feshbach, H. *Methods of Theoretical Physics*; McGraw-Hill: New York, 1953.