Distinguishing Steric and Electrostatic Molecular Probe Orientational Ordering Via Their Effects on Reorientation-Induced Spectral Diffusion

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Supplemental Material

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S1. Markov Chain Model

To examine the time dependence of the RISD correlation functions, a numerical Markov chain model similar to that developed by Garrett-Roe and coworkers was employed.[1] As was described in the main text, the Markov chain model describes the orientational relaxation of a probe molecule in a given angular potential, $V(\Omega)$, as a biased random walk on a discretized unit sphere. The Lebedev quadrature was used for the spherical discretization[2-4] as it provides a high degree of accuracy for angular integrals using a minimum number of points.

Using the Markov chain model, the probabilistic time evolution of the orientation of the probe molecule for a unit time can be encoded into a transition matrix **T**, where each element of the matrix $T_{ij} = \rho(\Omega_j|\Omega_i)$ is the probability of the probe molecule diffusing from angular orientation Ω_i to orientation Ω_j in the given time step. The transition matrix is the equivalent to a discretized Green's function, $G(\Omega(t)|\Omega(0),t)$, in the correlation function definition in Eq. 9 in the main text. This probability can be defined using an approximate spherical diffusion propagator[5, 6] and a bias term which satisfies detailed balance at equilibrium:[1]

$$T_{ij} = \left[\frac{1}{\tau}\left(1+\frac{\theta_{ij}^2}{12}\right)\exp\left(-\theta_{ij}^2/2\tau\right)\right]\left(\frac{\rho(\Omega_j)}{\rho(\Omega_i)}\right)^{1/2} \tag{S1}$$

where $\tau = 2D_m t$ is a reduced unit time step, θ_{ij} is the angular difference between state Ω_i and state Ω_j, and $\rho(\Omega_i)$ is the equilibrium probability of the probe molecule having orientation Ω_i, given a certain orientation of the electric field vector and steric restriction vector.

To conserve probability, the diagonal terms, T_{ii}, were set as one minus the sum of all other elements in the matrix column. The eigenvectors of **T** can be shown to be the equilibrium distribution $\rho(\Omega)$, and exponentiation of the full transition matrix allows the system to evolve through time, where $\mathbf{T}^N$ corresponds to N unit time steps having occurred.

Using the transition matrix, the time dependent RISD expressions can be evaluated:

$$R_p(N) = \frac{\sum_{\hat{H}} w(\hat{H}) \sum_{\hat{F}} w(\hat{F}) \rho(\hat{F} \mid \hat{H}) \left[\vec{m}_\alpha \circ \vec{f} \right]^{\mathrm{T}} \mathbf{T}^N \left[\vec{\rho}(\Omega) \circ \vec{m}_\beta \circ \vec{f} \right]}{\left\langle \cos^2 \theta_F \right\rangle I_p(N)} \tag{S2}$$

Where ∘ indicates element-wise multiplication. m and f are the polarization weight and local field

projection vectors that have elements defined as:

$$m_{\alpha,i} = w(\Omega_i) \left(\hat{\varepsilon}_\alpha \cdot \vec{d}(\Omega_i) \right)^2$$
$$f_i = \left(\hat{F} \cdot \vec{d}(\Omega_i) \right) \tag{S3}$$

$\vec{d}(\Omega_i)$ is the unit vector corresponding for orientational microstate Ω_i. $\hat{H}$ and $\hat{F}$ are the

orientations of the steric alignment potential and the electric field, respectively, and $\rho(\hat{F} \mid \hat{H})$ is

the probability of the electric field having orientation $\hat{F}$ given the steric alignment is in

orientation $\hat{H}$. The w terms are the weights for the given microstate in the Lebedev quadrature.[2-4] As these integrals are evaluated in the lab frame, the polarization weight terms can be evaluated

as follows:

$$\left(\hat{\varepsilon}_X \cdot \vec{d}(\Omega_i) \right)^2 = \cos^2 \theta_i$$
$$\left(\hat{\varepsilon}_Y \cdot \vec{d}(\Omega_i) \right)^2 = \frac{1}{2} \sin^2 \theta_i \tag{S4}$$

The intensity normalization factor $I(N)$ is calculated in an analogous way:

$$I_p(N) = \sum_{\hat{H}} w(\hat{H}) \sum_{\hat{F}} w(\hat{F}) \rho(\hat{F} \mid \hat{H}) \left[\vec{m}_\alpha \right]^{\mathrm{T}} \mathbf{T}^N \left[\vec{\rho}(\Omega) \circ \vec{m}_\beta \right]. \tag{S5}$$

The above equation can also be used to calculate the various Legendre polynomial orientational

correlation functions, $C_l(N)$, by replacing the polarization weights with the appropriate Legendre

polynomial, $P_l(\Omega)$. Eq. S3 can then be used with Eq. 5 to get the fully baselined $\tilde{R}_p(t)$.

For the frequency-dependent orientational dynamics calculations presented in Fig. 5, the results for each combined steric/electrostatic potential were placed in a separate bin based on the calculated value of $\langle \cos\theta_F \rangle$ for that particular potential. A dense grid spacing was used for the Lebedev quadrature (590 points[4]) and the bins of $\langle \cos\theta_F \rangle$ were spaced by 0.1 from -0.9 to 0.9.

S2. Analytic Calculations with Arbitrary Dipole Moment Orientations

As was detailed in the main text, expectation values for an azimuthally symmetric potential can be written compactly as:[7]

$$\int d\Omega(t) A(\Omega(t)) \rho(\Omega(t)) = \sum_l \frac{(2l+1)}{8\pi^2} S_l \int d\Omega(t) A(\Omega(t)) D_{00}^l(\Omega(t)) \tag{S6}$$

for $D_{mn}^l(\Omega)$ is a Wigner rotation matrix and S_l is an order parameter for the lth Legendre polynomial $P_l(\cos\theta)$ in the angular potential $V(\Omega)$ as summarized in Table 1. Similarly, in the long-time limit the correlation function takes the value:[7]

$$\begin{aligned}
\langle A(\Omega(t \to \infty)) B(\Omega(0)) \rangle &= \langle A(\Omega) \rangle \langle B(\Omega) \rangle \\
&= \int d\Omega(t) A(\Omega(t)) \rho(\Omega(t)) \\
&\times \int d\Omega(0) B(\Omega(0)) \rho(\Omega(0))
\end{aligned} \tag{S7}$$

where the initial and final measurements are independent and both at equilibrium.

The observables present in the correlation function (Eq. 10) can also be expressed in terms of rotation matrices. In particular, the polarization weights can be written most compactly as:[8]

$$\begin{aligned}
(\hat{\varepsilon}_X \cdot \hat{\mu}_T)^2 &= \frac{1}{3} + \frac{2}{3} D_{00}^2(\Omega_{LT}) \\
(\hat{\varepsilon}_Y \cdot \hat{\mu}_T)^2 &= \frac{1}{3} - \frac{1}{3} D_{00}^2(\Omega_{LT})
\end{aligned} \tag{S8}$$

Where Ω_{LT} is the orientation of the molecular transition dipole (subscript T) with respect to the lab frame (subscript L). Similarly, the Stark effect interaction can be written using:

$$\cos\theta_{FD}(t) = D_{00}^1\left(\Omega_{FD}(t)\right) \tag{S9}$$

Where Ω_{FD} is the orientation of the molecular difference dipole moment (subscript D) with respect to the frame of the electric field (subscript F).

In order to evaluate integrals such as in Eq. S6, it is necessary to change the coordinate systems in Eqs. S8 and S9 such that they are in the frame of the potential, V. This change of basis between either different reference frames or different molecular axes can be done straightforwardly using rotation matrices:[8-10]

$$D_{m0}^l\left(\Omega_{AC}\right) = \sum_{n=-l}^{l} D_{mn}^l\left(\Omega_{AB}\right)D_{n0}^l\left(\Omega_{BC}\right). \tag{S10}$$

The integrals over each basis set can then be calculated in a tedious but straightforward manner using:[8-10]

$$\int d\Omega D_{m_1 n_1}^{l_1}\left(\Omega\right) D_{m_2 n_2}^{l_2}\left(\Omega\right) D_{m_3 n_3}^{l_3}\left(\Omega\right) = 8\pi^2 \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}\begin{pmatrix} l_1 & l_2 & l_3 \\ n_1 & n_2 & n_3 \end{pmatrix} \tag{S11}$$

Where the terms in brackets are Wigner's 3-J symbols and have tabulated values. Importantly, the 3-J symbols are zero unless $\left|l_1 - l_2\right| \le l_3 \le \left|l_1 + l_2\right|$, $m_1 + m_2 + m_3 = 0$, and $n_1 + n_2 + n_3 = 0$, which reduces the total number of terms to be considered to a small set.

First we will work out the Stark expectation values for the generic case for the combined potential K (Comparable to Eq. 29):

$$\langle \cos \theta_{FD} \rangle = \sum_l \frac{(2l+1)}{8\pi^2} S_l \int d\Omega_{FP} D^1_{00}(\Omega_{FD}) D^l_{00}(\Omega_{KP})$$

$$= \sum_{m=-1}^{+1} \sum_{n=-1}^{+1} D^1_{0n}(\Omega_{KF}) D^1_{m0}(\Omega_{PD}) \sum_l \frac{(2l+1)}{8\pi^2} S_l \int d\Omega_{FP} D^1_{nm}(\Omega_{KP}) D^l_{00}(\Omega_{KP}) \quad \text{(S12)}$$

$$= D^1_{00}(\Omega_{KF}) D^1_{00}(\Omega_{PD}) S_1(V_K)$$

$$= \cos \zeta \cos \eta \, S_1(V_K)$$

The second line uses the change of basis in Eq. S10 twice to go from the frame of the observable, Ω_{FD}, to the frame of the potential, Ω_{KP}. The term $\Omega_{PD} = (\phi_{PD}, \zeta, \chi_{PD})$ represents the orientation of the molecular permanent dipole relative to the dipole difference vector and the term $\Omega_{KF} = (\phi_{KF}, \eta, \chi_{KF})$ represents the orientation of the combined potential relative to the orientation of the electric field. The third line uses the integration identity in Eq. S11, where the symmetry of the potential removes all m and $n \neq 0$ and the order of the observable removes $l \neq 1$. The fourth line uses the definitions of the rotation matrix to put the result in terms of simple trigonometric functions. Setting $\zeta = 0$ recovers Eq. 29 in the main text, which can be used to derive the pure electrostatic and steric cases as discussed in Section IV.B.

The analogous calculation can be done for the second Stark expectation value:

$$\langle \cos^2 \theta_{FD} \rangle = \sum_l \frac{(2l+1)}{8\pi^2} S_l \int d\Omega_{FP} \left(\frac{1}{3} + \frac{2}{3} D^2_{00}(\Omega_{FD}) \right) D^l_{00}(\Omega_{KP})$$

$$= \frac{1}{3} + \frac{2}{3} \sum_{m=-2}^{+2} \sum_{n=-2}^{+2} D^2_{0n}(\Omega_{KF}) D^2_{m0}(\Omega_{DP}) \sum_l \frac{(2l+1)}{8\pi^2} S_l \int d\Omega_{FP} D^2_{nm}(\Omega_{KP}) D^l_{00}(\Omega_{KP}) \quad \text{(S13)}$$

$$= \frac{1}{3} + \frac{2}{3} D^2_{00}(\Omega_{KF}) D^2_{00}(\Omega_{DP}) S_2(V_K)$$

$$= \frac{1}{3} + \frac{2}{3} P_2(\cos \zeta) P_2(\cos \eta) S_2(V_K)$$

Where setting $\zeta = 0$ recovers what corresponds to Eq. 33 in the main text.

The polarization-weighted correlation functions are most easily evaluated by first considering a generic case:

$$\langle A(0)A(\infty)\rangle_{XXXX} = \left\langle A(\Omega_{KP})\left(\frac{1}{3}+\frac{2}{3}D_{00}^2(\Omega_{LT})\right)\right\rangle\left\langle A(\Omega_{KP})\left(\frac{1}{3}+\frac{2}{3}D_{00}^2(\Omega_{LT})\right)\right\rangle$$

$$= \frac{1}{9}\left(\begin{array}{l} \langle A(\Omega_{KP})\rangle^2 + 4\langle A(\Omega_{KP})\rangle\int d\Omega_{LK}\sum_n D_{0n}^2(\Omega_{LK})\langle A(\Omega_{KP})D_{n0}^2(\Omega_{KT})\rangle \\[2mm] +4\int d\Omega_{LK}\sum_{n'}\sum_n D_{0n'}^2(\Omega_{LK})D_{0n}^2(\Omega_{LK})\langle A(\Omega_{KP})D_{n'0}^2(\Omega_{KT})\rangle\langle A(\Omega_{KP})D_{n0}^2(\Omega_{KT})\rangle \end{array} \right)$$

$$= \frac{1}{9}\left(\langle A(\Omega_{KP})\rangle^2 + \frac{4}{5}\sum_n\langle A(\Omega_{KP})D_{n0}^2(\Omega_{KT})\rangle^2\right)$$

(S14)

Where Ω_{LK} is the orientation of the angular potential K in the lab frame. By construction we presumed that these potentials are isotropically distributed in the lab frame, so upon integration over all orientations we drop the cross terms in line 2 and drop all terms where $n \neq n'$. Performing the same calculation in the perpendicular polarization weighting gives:

$$\langle A(0)A(\infty)\rangle_{XXYY} = \left\langle A(\Omega_{KP})\left(\frac{1}{3}+\frac{2}{3}D_{00}^2(\Omega_{LT})\right)\right\rangle\left\langle A(\Omega_{KP})\left(\frac{1}{3}-\frac{1}{3}D_{00}^2(\Omega_{LT})\right)\right\rangle$$

$$= \frac{1}{9}\left(\langle A(\Omega_{KP})\rangle^2 - \frac{2}{5}\sum_n\langle A(\Omega_{KP})D_{n0}^2(\Omega_{KT})\rangle^2\right)$$

(S15)

Which allows the polarization weighted observables to be written as a sum of an isotropic part and an anisotropic part as follows:

$$\langle A(0)A(\infty)\rangle_p = \frac{1}{9}\left(\langle A(\Omega_{KP})\rangle^2 + p\sum_n\langle A(\Omega_{KP})D_{n0}^2(\Omega_{KT})\rangle^2\right)$$

(S16)

Where $p = +4/5$ for parallel and $-2/5$ for perpendicular as in the main text.

The pump-probe correlation function is then easily calculable ($A = 1$ in Eq. S16). Starting with the anisotropic order parameter:

$$\left\langle D_{n0}^2\left(\Omega_{KT}\right)\right\rangle = \sum_l \frac{(2l+1)}{8\pi^2} S_l \int d\Omega_{FP} D_{n0}^2\left(\Omega_{KT}\right) D_{00}^l\left(\Omega_{KP}\right)$$

$$= \sum_{m=-2}^{+2} D_{m0}^2\left(\Omega_{PT}\right) \sum_l \frac{(2l+1)}{8\pi^2} S_l \int d\Omega_{FP} D_{nm}^2\left(\Omega_{KP}\right) D_{00}^l\left(\Omega_{KP}\right) \qquad \text{(S17)}$$

$$= D_{00}^2\left(\Omega_{PT}\right) S_2(V_K)\delta(n)$$

$$= P_2\left(\cos\psi\right) S_2(V_K)\delta(n)$$

Where $\Omega_{PT} = (\phi_{PT}, \psi, \chi_{PT})$ is the orientation of the molecular permanent dipole relative to the transition dipole moment and δ is the Kronecker delta function. Plugging back into Eq. S16 gives:

$$\left\langle I(t \to \infty)\right\rangle_p = \frac{1}{9}\left(1 + p\left(P_2\left(\cos\psi\right)S_2(V_K)\right)^2\right) \qquad \text{(S18)}$$

Which for $\psi = 0$ yields Eq. 17. The angular dependence in Eq. S18 arises from the fact the angular potential is centered on the permanent dipole, μ_P, instead of the transition dipole, μ_T.

For the numerator of the RISD function $R_p(t)$, $A = \cos\theta_{FD}$. The isotropic part $\left\langle\cos\theta_{FD}\right\rangle^2$ is then given by Eq. S12. The anisotropic part is then (cont. on next page):

$$P = \sum_{n=-2}^{+2} \left\langle D_{n0}^2 \left(\Omega_{KT} \right) \cos \theta_{FD} \right\rangle^2$$

$$= \sum_{n=-2}^{+2} \left(\sum_l \frac{(2l+1)}{8\pi^2} S_l \int d\Omega_{KP} D_{00}^1 \left(\Omega_{FD} \right) D_{n0}^2 \left(\Omega_{KT} \right) D_{00}^l \left(\Omega_{KP} \right) \right)^2$$

$$= \sum_{n=-2}^{+2} \left(\begin{array}{c} \sum_{m=-2}^{+2} \sum_{k=-1}^{+1} \sum_{j=-1}^{+1} D_{0k}^1 \left(\Omega_{FK} \right) D_{j0}^1 \left(\Omega_{PD} \right) D_{m0}^2 \left(\Omega_{PT} \right) \\ \times \sum_l \frac{(2l+1)}{8\pi^2} S_l \int d\Omega_{KP} D_{nm}^2 \left(\Omega_{KP} \right) D_{kj}^1 \left(\Omega_{KP} \right) D_{00}^l \left(\Omega_{KP} \right) \end{array} \right)^2$$

$$= \sum_{k=-1}^{+1} \left| D_{0k}^1 \left(\Omega_{FK} \right) \right|^2 \left(\begin{array}{c} \sum_{j=-1}^{+1} D_{j0}^1 \left(\Omega_{PD} \right) D_{-j0}^2 \left(\Omega_{PT} \right) \\ \times \sum_l \frac{(2l+1)}{8\pi^2} S_l \int d\Omega_{FP} D_{-k,-j}^2 \left(\Omega_{KP} \right) D_{kj}^1 \left(\Omega_{KP} \right) D_{00}^l \left(\Omega_{KP} \right) \end{array} \right)^2$$

$$= \frac{1}{25} \cos^2 \eta \left[\begin{array}{c} \cos \zeta \, P_2 \left(\cos \psi \right) \left(2S_1 + 3S_3 \right) \\ -\frac{3}{2} \sin \zeta \sin 2\psi \cos \left(\phi_{PD} - \phi_{PT} \right) \left(S_1 - S_3 \right) \end{array} \right]^2$$

$$+ \frac{3}{25} \sin^2 \eta \left[\begin{array}{c} \cos \zeta \, P_2 \left(\cos \psi \right) \left(S_1 - S_3 \right) \\ -\frac{1}{4} \sin \zeta \sin 2\psi \cos \left(\phi_{PD} - \phi_{PT} \right) \left(3S_1 - 5S_2 + 2S_3 \right) \end{array} \right]^2 \qquad (S19)$$

Line 3 follows from the change in frame per Eq. S10. Line 4 has two simplifications. The triangle equality in Eq. S11 is employed to drop all terms other than $k = -n$ and $j = -m$. The azimuthal angles are also arbitrary for Ω_{FK}, so all terms that depend on them can be dropped. The final line comes from evaluating the integral and rewriting the D matrices in terms of trigonometric functions. The pure electrostatic case has $\eta = 0$, while the pure steric case is the integral over all η such that $\left\langle \cos^2 \eta \right\rangle = \frac{1}{2} \left\langle \sin^2 \eta \right\rangle = \frac{1}{3}$. The simpler cases examined in the main text can then be recovered with $\zeta = \psi = 0$.

The final, fully general RISD offset is then:

$$R_p(\infty) = \frac{\langle \cos\theta_{FD} \rangle^2 + pP}{\langle \cos^2\theta_{FD} \rangle I_p(\infty)}$$

$$= \frac{3\cos^2\zeta \cos^2\eta S_1^2 + 3pP}{\left(1 + 2P_2(\cos\zeta)P_2(\cos\eta)S_2\right)\left(1 + p\left(P_2(\cos\psi)S_2\right)^2\right)} \tag{S20}$$

Additionally, the same weak-field limit can be examined. Setting S_2 and $S_3 = 0$ in Eq. S19 gives:

$$3P \approx S_1^2 \frac{3\left(4\cos^2\eta + 3\sin^2\eta\right)}{25} \left[\begin{array}{c} \cos\zeta P_2(\cos\psi) \\ -\frac{3}{4}\sin\zeta \sin 2\psi \cos(\phi_{PD} - \phi_{PT}) \end{array} \right]^2 \tag{S21}$$

Which gives the same result as the main text, where the pure electrostatic case, $\eta = 0$, is exactly

1.2x the pure steric case, $\langle \cos^2\eta \rangle = \frac{1}{2} \langle \sin^2\eta \rangle = \frac{1}{3}$. With knowledge of the angles between the

various dipoles of the given probe molecule, one can then in principle reconstruct the full RISD

from the appropriate steric case alone. As is discussed in the next section, this is unfortunately

not trivially done. The polarization differences are then once again driven by the baselining

procedure, although the Stark effect parameters (Eqs. S12 and S13) have additional dependence

on the angle ζ between the permanent dipole and difference dipole moments.

S3. Note on RISD Time Dependence with Arbitrary Dipole Moment Orientations

A key fact needed for the development of the time-dependent RISD approximation in the

main text (Eq. 26) arises from the similarity between the RISD correlation functions in the case

of free diffusion and the long-time offset of the RISD correlation function in the case of steric

hindrance. In particular, the free diffusion time dependence for $\zeta = \psi = 0$ is:

$$R_p(t) = \frac{C_1(t) + \frac{p}{5}\left(2C_1(t) + 3C_3(t)\right)}{1 + pC_2(t)} \tag{S22}$$

and the long-time offset is:

$$R_{p,H}(t \to \infty) = \frac{S_1^2 + \frac{p}{5}\left(2S_1^2 + 3S_3^2\right)}{1 + pS_2^2}. \tag{S23}$$

Significantly, Eq. S23 is the same as Eq. S22 with the identity $C_l(t \to \infty) = S_l^2$. As was

mentioned in the main text, this is not the case for $\mu_T \neq \mu_D$. We will consider the case where $\mu_P =$

$\mu_T \neq \mu_D$ in particular, such that $\psi = 0$ and $\zeta \neq 0$ in the notation of the previous section. In this

case, the identity for C_l examined above still holds, as the angular potentials are oriented with

respect to the transition dipole.

Using the notation of this paper, the RISD correlation function in the case of free

diffusion for this general case has been previously found to be:[8]

$$R_p(t) = \frac{C_1(t) + \frac{p}{15}\begin{pmatrix} 3\left(P_2 \cos\zeta + 1\right)C_1(t) \\ -5\left(P_2 \cos\zeta - 1\right)C_2(t) \\ +\left(2P_2 \cos\zeta + 7\right)C_3(t) \end{pmatrix}}{1 + pC_2(t)} \tag{S24}$$

While the offset as calculated from Eq. S20 for a pure steric case is then:

$$R_{p,H}(t \to \infty) = \cos^2\zeta\, \frac{S_1^2 + \frac{p}{5}\left(2S_1^2 + 3S_3^2\right)}{1 + pS_2^2}. \tag{S25}$$

where it is apparent that the correspondence that existed between S22 and S23 is broken. This

result can be understood in part from the RISD correlation functions describing the orientational

motion of the dipole difference moment, while the pump-probe experiment describes the motion

of the transition dipole moment. If these dipole moments are not coincident, the one-to-one

correspondence between the C_l's in the RISD correlation function expressions and the pump-

probe experiment is broken.

In general, one cannot indiscriminately use the analytic results of RISD functions derived assuming free diffusion with arbitrary $C_l(t)$ that assume some form of steric hindrance. However, Eq. S24 shows one cannot neglect the impact on the time dependence if μ_T and μ_D have substantially different orientations. While the previous section suggests that similar equivalencies can be drawn for $\zeta = \psi \neq 0$ for RISD between the electrostatic or combined potential cases and the pure steric case, it is clear that there is not presently a full description for the steric RISD correlation function in this more general case.

S4. Approximating the Effective Potential V_X

The effective potential V_X used in Section IV.B is defined as an integral of the combined potential in Eq. 27 over all relative angles of the orientations of the component potentials, γ:

$$\exp\left(\beta V_X \cos\theta_{KP}\right) \sim \int d\gamma \sin\gamma \exp\left(\beta V_K\left(\gamma\right)\cos\theta_{KP} + \kappa\cos\gamma\right) \tag{S26}$$

where κ is a parameter that describes the relative alignment between the steric and electrostatic potentials. The right hand side was evaluated using Mathematica, and the natural logarithm of the expression was expanded in terms of $\cos\theta_{KP}$, κ, and f, for $f = V_F/V_H$. Taking the term linear in $\cos\theta_{KP}$ and to second order in κ and f gives the following approximation for V_X:

$$V_X = V_H\left(1 + \frac{f^2 + f\kappa}{3} - \frac{f^2\kappa^2}{45}\right). \tag{S27}$$

This approximation works best for $f < 1$ and moderate κ, as the term quadratic in $\cos\theta_{KP}$ goes as $5f^2 - f^2\kappa^2$.

Once V_X is calculated, the various order parameters can be estimated using the following approximation:

$$A\left(\beta V_X\right) \approx \int d\gamma \sin\gamma A\left(\beta V_K\left(\gamma\right)\right)\exp\left(\beta V_K\left(\gamma\right)\cos\theta_{KP} + \kappa\cos\gamma\right). \tag{S28}$$

The different moments of $\cos(\eta)$ (describing the angle between each combined potential and its electric field component) can also be examined, with:

$$\langle \cos\eta \rangle \approx \frac{V_F + V_H \langle \cos\gamma \rangle}{V_X}$$
$$\approx \frac{V_F + V_H S_1(\kappa)}{V_X} \quad . \tag{S29}$$

and

$$\langle P_2(\cos\eta) \rangle \approx \frac{3}{2} \frac{V_F^2 + V_H^2 \langle \cos^2\gamma \rangle + 2V_F V_H \langle \cos\gamma \rangle}{V_X^2} - \frac{1}{2}$$
$$\approx \frac{3V_F^2 + V_H^2 - V_X^2 + 6V_F V_H S_1(\kappa) - 2V_H^2 S_2(\kappa)}{2V_X^2} \quad . \tag{S30}$$

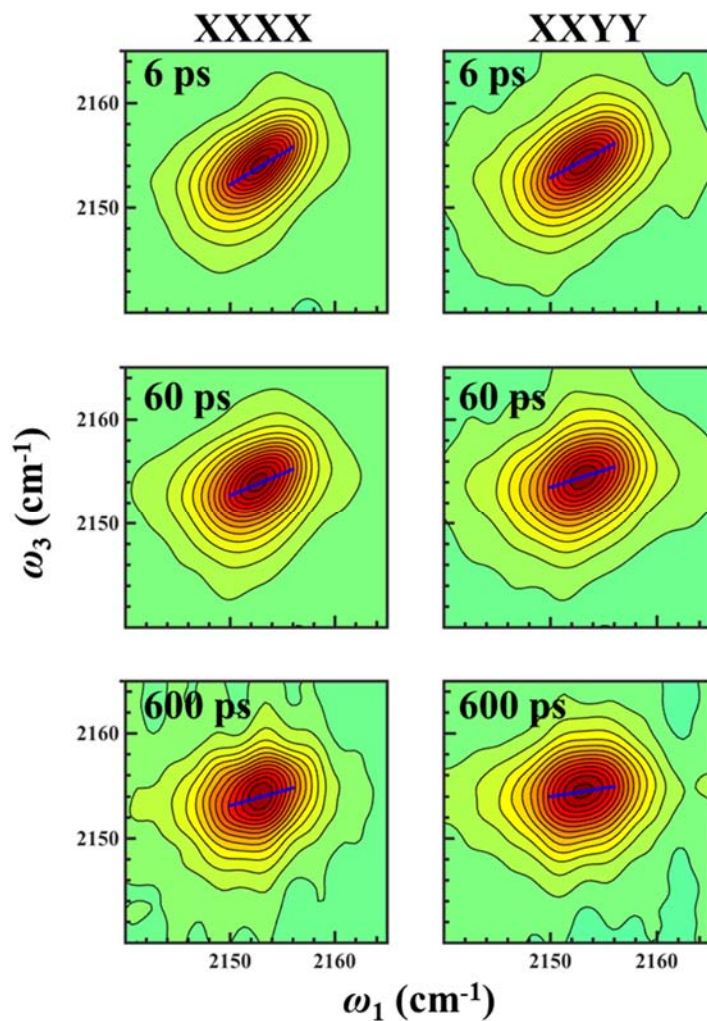## S5. Representative 2D Spectra and RISD Fit Residuals

Fig. S1: Representative polarization-selective 2D spectra of PhSeCN in the polystyrene oligomer over three decades of time. The blue lines are the center lines used in the CLS analysis.
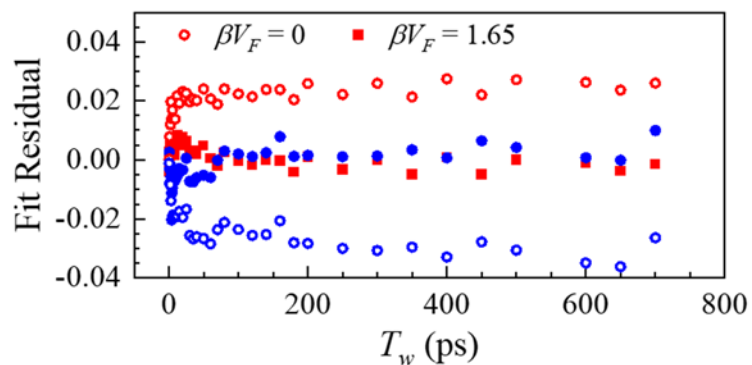

Fig. S2: Fit residuals for the two RISD fits demonstrated in Fig. 7 of the main text. Red symbols: XXXX, Blue symbols: XXYY. The open symbols are the standard RISD theory which systematically misses the experimental data. The filled symbols is the new theory that incorporates electrostatic ordering and steric hindrance.

SI References

1.   Z. Ren and S. Garrett-Roe, "Reorientation-induced spectral diffusion of non-isotropic orientation distributions," J. Chem. Phys. **147**, 144504 (2017).

2.   V. I. Lebedev, "Values of nodes and weights for spherical, quadrature formulas of Gauss-Markov type exact to order 9-17 and invariant under the octahedra[group with inversion," Zh. Vychisl. Mat. Mat. Fiz. **15** (1), 48-54 (1975).

3.   V. I. Lebedev, "Quadratures on the sphere," Zh. Vychisl. Mat. Mat. Fiz. **16** (2), 293-306 (1976).

4.   V. I. Lebedev and A. L. Skorokhodov, "Quadrature formulas of orders 41, 47, and 53 for the sphere," Dokl. Math. **45**, 587-592 (1992).

5.   J. Faraudo, "Diffusion equation on curved surfaces. I. Theory and application to biological membranes," J. Chem. Phys. **116**, 5831 (2002).

6.   A. Ghosh, J. Samuel and S. Sinha, "A "Gaussian" for diffusion on the sphere," EPL **98**, 30003 (2012).

7.   S. Stallinga, "Effect of rotational diffusion in an orientational potential well on the point spread function of electric dipole emitters," J. Opt. Soc. Am. A **32**, 213 (2015).

8.   J. E. Thomaz, P. L. Kramer, S. M. Fica-Contreras, D. J. Hoffman and M. D. Fayer, "Reorientation-induced Stokes shifts caused by directional interactions in electronic spectroscopy: Fast dynamics of poly(methyl methacrylate)," J. Chem. Phys. **150** (2019).

9.   D. M. Brink and G. R. Satchler, *Angular Momentum*, 2nd ed. ed. (Oxford University Press, Oxford, 1968).

10.   R. N. Zare, *Angular Momentum*. (Wiley-Interscience, 1988).