Supporting Information for

Orientational Pair Correlations in a Dipolar Molecular Liquid: Time-Resolved Resonant and Nonresonant Pump-Probe Spectroscopies

Steven A. Yamada[†], Heather E. Bailey[†], and Michael D. Fayer*

Department of Chemistry
Stanford University, Stanford, CA 94305, USA
*Phone: 650 723-4446, Email: fayer@stanford.edu

[†]Steven A. Yamada and Heather E. Bailey contributed equally to this work.

SI. Theory and Data Analysis.

This section relates the solution to the problem of rotational Brownian motion of a completely asymmetric rigid body, as originally treated by Favro,[1] to the measurements presented in this work.

A. Rotational Diffusion of an Asymmetric Rotor: Theory.

As shown by Favro,[1] if the molecules in an ensemble rotate in a random fashion through infinitesimally small angular steps, the probability of finding a randomly chosen member of the ensemble with orientation $\boldsymbol{\Omega}$ at time t, $P(\boldsymbol{\Omega},t)$, obeys the diffusion equation

$$(\partial/\partial t)P(\boldsymbol{\Omega},t) = -(\mathbf{L}\cdot\mathbf{D}\cdot\mathbf{L})P(\boldsymbol{\Omega},t), \tag{S1}$$

where $\boldsymbol{L}$ is the quantum mechanical angular momentum operator and $\boldsymbol{D}$ is the rotational diffusion tensor. Here, $\boldsymbol{\Omega}$ is the orientation of some molecule fixed coordinate system with respect to the laboratory fixed system. For example, the orientation, $\boldsymbol{\Omega}$, can be identified in terms of the three Euler angles (α,β,γ) which rotate the laboratory fixed system into the molecule fixed system.[2]

It is convenient to choose the molecule fixed coordinate system that diagonalizes $\boldsymbol{D}$. With this choice, Eq. (S1) reduces to

$$(\partial/\partial t)P(\boldsymbol{\Omega},t) = -\mathcal{H}P(\boldsymbol{\Omega},t), \tag{S2}$$

where $\mathcal{H} = \sum_i D_i L_i^2$ and the summation runs over the *i* principal axes. With the simple substitution $D_i \rightarrow \hbar^2/2I_i$, the operator $\mathcal{H}$ can be identified with the quantum mechanical

Hamiltonian operator for an asymmetric rigid rotor, where I_i are the principal moments of inertia. As will be seen shortly, the solution to Eq. (S2) can be expressed in terms of the eigenfunctions and eigenvalues of a rigid rotor. This solution can be written in the form[1]

$$P(\boldsymbol{\Omega},t) = \int P(\boldsymbol{\Omega}_0) G(\boldsymbol{\Omega}_0 \left| \boldsymbol{\Omega}, t \right.) d\boldsymbol{\Omega}_0, \tag{S3}$$

where $P(\boldsymbol{\Omega}_0)$ is the probability that a molecule has orientation $\boldsymbol{\Omega}_0$ at $t = 0$, and the Green's function, $G(\boldsymbol{\Omega}_0 \left| \boldsymbol{\Omega}, t \right.)$, is the conditional probability that the molecule will be found with orientation $\boldsymbol{\Omega}$ at time t, provided that it was initially oriented at $\boldsymbol{\Omega}_0$. The Green's function can be expanded in the complete set of eigenfunctions $\psi_n(\boldsymbol{\Omega})$ of $\mathcal{H}$[1]

$$G(\boldsymbol{\Omega}_0 \left| \boldsymbol{\Omega}, t \right.) = \sum_n \psi_n^*(\boldsymbol{\Omega}_0) \psi_n(\boldsymbol{\Omega}) e^{-E_n t}, \tag{S4}$$

where E_n is the eigenvalue corresponding to the state $\psi_n(\boldsymbol{\Omega})$ and the initial condition is $G(\boldsymbol{\Omega}_0 \left| \boldsymbol{\Omega}, 0 \right.) = \delta(\boldsymbol{\Omega}_0, \boldsymbol{\Omega})$. Therefore, in Favro's formalism, the solution to Eq. (S2) is reduced to the problem of finding the eigenvalues and eigenfunctions of a rigid rotor.

The eigenfunctions of $\mathcal{H}$ are linear combinations of symmetric top eigenfunctions, $\phi_{K,M}^{(l)}(\boldsymbol{\Omega})$,[1-2]

$$\psi_n(\boldsymbol{\Omega}) \equiv \psi_{\tau,M}^{(l)}(\boldsymbol{\Omega}) = \sum_{K=-l}^{l} a_{\tau,K}^{(l)} \phi_{K,M}^{(l)}(\boldsymbol{\Omega}), \tag{S5}$$

where $a_{\tau,K}^{(l)}$ are the expansion coefficients. The expansion coefficients and eigenvalues, $E_\tau^{(2)}$,[1, 3-5] are tabulated in Table S1 for $l = 2$.

B. Rotational Diffusion of an Asymmetric Rotor: Connection to the Single Molecule Orientational Correlation Function.

Several authors have incorporated Favro's results into the theoretical framework of time-dependent fluorescence depolarization experiments.[4, 6-7] The mathematical development is identical for IR depolarization experiments, *i.e.* PSPP spectroscopy. However, the derivations and results have been cast into different forms, and some have been subject to algebraic errors.[4] For clarity, we outline the derivation originally presented by Tao,[4] which leads to a general expression for the anisotropy of a completely asymmetric rotor in the form used here. However,

we note that in that same work, the spherical harmonics of order $l = 2$ were improperly expressed in terms of the Cartesian components of the transition dipole moment unit vector, $\vec{\mathbf{e}}$, affecting the final result. Explicit expressions are provided below for clarity in Table S2.

Tao noted that if $\vec{\mathbf{e}}$ is an arbitrary unit vector fixed in the molecule, then for every orientation (θ,ϕ) of $\vec{\mathbf{e}}$ in the laboratory, there is a corresponding orientation, $\mathbf{\Omega}$, of the molecule fixed axes in the laboratory. Then if $P(\theta_0,\phi_0)$ and $f(\theta,\phi)$ are, respectively, the initial distribution of the orientation of $\vec{\mathbf{e}}$ in the laboratory frame and some arbitrary function of the orientation of $\vec{\mathbf{e}}$, a corresponding initial distribution, $P(\mathbf{\Omega}_0)$, and function, $f(\mathbf{\Omega})$, exist for the orientation of the molecule fixed axes. The ensemble averages of the function f can be written

$$\langle f\rangle_{\theta,\phi} = \int d^2\mathbf{\Gamma} f(\theta,\phi)\int d^2\mathbf{\Gamma}_0 P(\theta_0,\phi_0)G(\theta_0,\phi_0|\theta,\phi,t), \tag{S6}$$

and

$$\langle f\rangle_{\mathbf{\Omega}} = \int d^3\mathbf{\Omega} f(\mathbf{\Omega})\int d^3\mathbf{\Omega}_0 P(\mathbf{\Omega}_0)G(\mathbf{\Omega}_0|\mathbf{\Omega},t), \tag{S7}$$

where $d^2\mathbf{\Gamma} = \sin\theta d\theta d\phi$ and $d^3\mathbf{\Omega} = d\alpha\sin\beta d\beta d\gamma$. The same result must be obtained whether one averages f over (θ,ϕ) or over $\mathbf{\Omega}$:

$$\langle f\rangle_{\theta,\phi} = \langle f\rangle_{\mathbf{\Omega}}. \tag{S8}$$

With the choices

$$P(\theta_0,\phi_0) = \frac{3}{4\pi}\cos^2\theta_0 = \frac{1}{4\pi}[1+4\sqrt{\frac{\pi}{5}}Y_{2,0}(\theta_0,\phi_0)], \tag{S9}$$

and

$$f(\theta,\phi) = Y^*_{2,0}(\theta,\phi), \tag{S10}$$

and recalling that the Green's function, expanded in terms of the spherical harmonics, is given by[4, 8]

$$G(\theta_0,\phi_0|\theta,\phi,t) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} C_l(t)Y^*_{l,m}(\theta_0,\phi_0)Y_{l,m}(\theta,\phi), \tag{S11}$$

Eq. (S6) becomes

$$\langle f\rangle_{\theta,\phi} = \frac{1}{\sqrt{5\pi}}C_2(t) \tag{S12}$$

Eq. (S9) is the normalized, initial excited state distribution obtained from an isotropic ensemble when the incident pump pulse polarization is defined to lie along the z axis in the laboratory

frame, as the probability that a given molecule is excited is proportional to $\left|\vec{\mathbf{e}}\cdot\vec{k}\right|^2$. We note that, in Eq. (S9), Tao omitted the factor of $4\sqrt{\pi/5}$ in front of $Y_{2,0}(\theta_0,\phi_0)$, but it has no effect on the final result for $C_2(t)$. The next step is to calculate $\langle f\rangle_{\mathbf{\Omega}}$ by writing $P(\mathbf{\Omega}_0)$, $f(\mathbf{\Omega})$, and $G(\mathbf{\Omega}_0|\mathbf{\Omega},t)$ in terms of the $\phi^{(l)}_{K,M}(\mathbf{\Omega})$. This is accomplished with the following relationships from the theory of angular momentum:[2, 4]

$$Y_{l,m}(\theta,\phi)=\sum_{m'=-l}^{l} D^{(l)*}_{m'm}(\mathbf{\Omega})Y_{l,m'}(\theta',\phi'), \tag{S13}$$

and

$$D^{(l)*}_{m',m}(\mathbf{\Omega})=[8\pi^2/(2l+1)]^{1/2}\phi^{(l)}_{m,m'}(\mathbf{\Omega}), \tag{S14}$$

where (θ',ϕ') refer to the orientation of $\vec{\mathbf{e}}$ in the body-fixed axes, and $D^{(l)}_{m',m}(\mathbf{\Omega})$ are the elements of the Wigner rotation matrix that rotate the laboratory-fixed axes by the angles $\mathbf{\Omega}$ into the body-fixed axes. Using Eqs. (S13) and (S14) to rewrite Eq. (S9) and (S10), one obtains:

$$P(\mathbf{\Omega}_0)=(1/8\pi^2)\left[1+\frac{4}{5}\sqrt{8\pi^3}\sum_{m'=-2}^{2}\phi^{(2)}_{0,m'}(\mathbf{\Omega}_0)Y_{2,m'}(\theta',\phi')\right], \tag{S15}$$

and

$$f(\mathbf{\Omega})=\sqrt{8\pi^2/5}\sum_{m''=-2}^{2}\phi^{(2)*}_{0,m''}(\mathbf{\Omega})Y^{*}_{2,m''}(\theta',\phi'). \tag{S16}$$

Substituting Eqs. (S15), (S16), (S4), and (S5) into Eq. (S7), and using the orthonormality of the $\phi^{(l)}_{K,M}(\mathbf{\Omega})$ to simplify the expression, one obtains:

$$\langle f\rangle_{\mathbf{\Omega}}=\frac{4}{5}\sqrt{\frac{\pi}{5}}\sum_{\tau=-2}^{2}e^{-E^{(2)}_{\tau}t}\left|\sum_{m=-2}^{2}a^{(2)}_{\tau,m}Y_{2,m}(\theta',\phi')\right|^2. \tag{S17}$$

Finally, using the identity Eq. (S8), an expression for the orientational correlation function, $C_2(t)$, is obtained:

$$C_2(t)=(4\pi/5)\sum_{\tau=-2}^{2}e^{-E^{(2)}_{\tau}t}\left|\sum_{m=-2}^{2}a^{(2)}_{\tau,m}Y_{2,m}(\theta',\phi')\right|^2. \tag{S18}$$

The $a^{(2)}_{\tau,m}$ and $E^{(2)}_{\tau}$ are found in Table S1. The $Y_{2,m}(\theta',\phi')$, expressed in terms of the Cartesian components of $\vec{\mathbf{e}}$,

$$\begin{aligned} \mathrm{e}_x &= \sin\theta'\cos\phi' \\ \mathrm{e}_y &= \sin\theta'\sin\phi' \\ \mathrm{e}_z &= \cos\theta', \end{aligned} \tag{S19}$$

are provided in Table S2. Substituting these various quantities into Eq. (S18), the expression for $C_2(t)$ is:

$$C_2(t) = \sum_{\tau=-2}^{\tau=2} c_\tau^{(2)} \exp[-E_\tau^{(2)}(t)] \tag{S20}$$

$$c_{-2}^{(2)} = 3\mathrm{e}_x^2\mathrm{e}_y^2$$

$$c_{-1}^{(2)} = 3\mathrm{e}_x^2\mathrm{e}_z^2$$

$$c_0^{(2)} = \frac{3}{12N^2}\left\{b^2\left(3\mathrm{e}_z^2-1\right)^2 - 2\sqrt{3}ab\left(3\mathrm{e}_z^2-1\right)\left(\mathrm{e}_x^2-\mathrm{e}_y^2\right) + 3a^2\left(\mathrm{e}_x^2-\mathrm{e}_y^2\right)^2\right\}$$

$$c_1^{(2)} = 3\mathrm{e}_y^2\mathrm{e}_z^2$$

$$c_2^{(2)} = \frac{3}{12N^2}\left\{a^2\left(3\mathrm{e}_z^2-1\right)^2 + 2\sqrt{3}ab\left(3\mathrm{e}_z^2-1\right)\left(\mathrm{e}_x^2-\mathrm{e}_y^2\right) + 3b^2\left(\mathrm{e}_x^2-\mathrm{e}_y^2\right)^2\right\}.$$

We note that Eq. (S20) is identical to Eq. (3.23) of Ehrenberg and Rigler[6] if the angle between the absorption and emission transition dipole unit vectors is taken to be zero, which was the assumption made here. For benzonitrile, we have $\mathrm{e}_x = 0$, $\mathrm{e}_y = 0$, and $\mathrm{e}_z = 1$. The general expression for $r(t)$ is then substantially reduced to the following biexponential form,

$$\begin{aligned} r(t) &= 0.4C_2(t) \\ &= \frac{2}{5N^2}\left\{a^2\exp[-(6D+2\Delta)t] + b^2\exp[-(6D-2\Delta)t]\right\}, \end{aligned} \tag{S21}$$

where the various quantities are defined in Table S1. Thus, the theory predicts that, in the most general situation, the maximum number of exponential decays that can be observed is two. If the data present as a biexponential decay, the average diffusion constant, D, and Δ can be determined straightforwardly from the exponential time constants. The parameters a and b can be obtained from the amplitudes. The three components of the diffusion tensor can then be determined:

$$D_{xx} = D + \frac{1}{3}\left(\Delta + \frac{\sqrt{3}a}{2} - \frac{b}{2}\right) \tag{S22}$$

$$D_{yy} = D + \frac{1}{3}\left(\Delta - \frac{\sqrt{3}a}{2} - \frac{b}{2}\right)$$

$$D_{zz} = D + \frac{1}{3}(b - 2\Delta).$$

This procedure was used to analyze the data in Fig. 4. However, no physically meaningful set of diffusion coefficients could be determined that fit the biexponential $r(t)$. One diffusion coefficient was consistently found to be unreasonably small or negative in some cases, implying an exceedingly large time constant for rotation about the corresponding principal axis of benzonitrile. This problem motivated a different analysis of the data. In the near symmetric-top limit, i.e. $D_{xx} \cong D_{yy} = D_{\perp}$, Eq. (S21) further simplifies to

$$r(t) = 0.4\exp[-6D_{\perp}t]. \qquad \text{(S23)}$$

In this limit, the $r(t)$ is single-exponential, with the time constant related to the diffusion coefficient for rotation perpendicular to the symmetry axis of the symmetric-top. This analysis requires a distinct physical interpretation of the additional time constant observed in the experimentally measured $r(t)$ (Fig. 4). This is discussed in greater detail in the main text.

C. Rotational Diffusion of an Asymmetric Rotor: Connection to the OHD-OKE Signal.

Berne and Pecora have incorporated Favro's solution to the asymmetric diffusor problem into the formalism of depolarized Rayleigh scattering experiments.[9] They treat the problem in the limit of no orientational pair correlations. Depolarized Rayleigh scattering and the OHD-OKE signal are frequency-time analogues and are related through a Fourier Transform.[10-12] Both experiments measure the polarizability anisotropy TCF. The mathematical treatment is similar to that in the case of fluorescence/IR depolarization. As mentioned in the main text, benzonitrile has sufficient symmetry that the body-fixed axis system is a principal axis system for both the polarizability tensor, $\boldsymbol{\alpha}$, and rotational diffusion tensor, $\boldsymbol{D}$. In this case, the following result[9] is obtained for the long-time OHD-OKE signal:

$$
\begin{aligned}
R(t) &\propto -\frac{\partial}{\partial t}\psi_{xy}^{RR}(t) \propto -\frac{\partial}{\partial t}\psi_{xy}^{MM}(t) \\
&\propto -\frac{\partial}{\partial t}\frac{15}{N\gamma^2}\sum_{i=1}^{N}\langle\alpha_{i,xy}(t)\alpha_{i,xy}(0)\rangle \qquad \text{(S24)} \\
&\propto (A_1/\tau_1)\exp[-t/\tau_1]+(A_2/\tau_2)\exp[-t/\tau_2],
\end{aligned}
$$

with

$$
\begin{aligned}
A_1 &= \frac{1}{3}\left(\frac{a^2}{N^2}\right)[\alpha_{zz}-\frac{1}{2}(\alpha_{xx}+\alpha_{yy})]^2 \\
&\quad +\frac{ab}{N^2\sqrt{3}}[\alpha_{zz}-\frac{1}{2}(\alpha_{xx}+\alpha_{yy})](\alpha_{xx}-\alpha_{yy}) \\
&\quad +\frac{b^2}{2N^2}[\alpha_{xx}-\alpha_{yy}]^2 \\
\tau_1 &= 1/(6D+2\Delta) \\
\tau_2 &= 1/(6D-2\Delta),
\end{aligned}
$$

and where A_2 is identical to A_1 except that a and b are interchanged and the ab term has a negative sign. Therefore, in the general case, one expects to observe a maximum of two exponential components in the OHD-OKE signal. The time constants of Eq. (S24) are identical to those in Eq. (S21). In the near symmetric-top limit, i.e. $\alpha_{xx} \cong \alpha_{yy} = \alpha_\perp$, $\alpha_{zz} = \alpha_\parallel$, and $D_{xx} \cong D_{yy} = D_\perp$, Eq. (S24) further simplifies to

$$
R(t) \propto 2D_\perp[\alpha_\parallel - \alpha_\perp]^2 \exp[-6D_\perp t], \qquad \text{(S25)}
$$

which shows that, in this limit, the anisotropy (Eq. (S23)) and long-time OHD-OKE signal (Eq. (S25), derived in the absence of orientational pair correlations) of benzonitrile decay as a single exponential with time constant $\tau_\perp = 1/6D_\perp$.

Table S1. Expansion Coefficients and Eigenvalues for the Asymmetric Rigid Rotator Eigenfunctions ($l = 2$).

$a^{(2)}_{\tau,K}$						$E^{(2)}_{\tau}$
τ	K = 2	K = 1	K = 0	K = -1	K = -2	
2	$b/\sqrt{2}N$	0	a/N	0	$b/\sqrt{2}N$	$6D+2\Delta$
1	0	$1/\sqrt{2}$	0	$1/\sqrt{2}$	0	$3(D_{xx}+D)$
0	$-a/\sqrt{2}N$	0	b/N	0	$-a/\sqrt{2}N$	$6D-2\Delta$
-1	0	$1/\sqrt{2}$	0	$-1/\sqrt{2}$	0	$3(D_{yy}+D)$
-2	$1/\sqrt{2}$	0	0	0	$-1/\sqrt{2}$	$3(D_{zz}+D)$

$a = \sqrt{3}(D_{xx} - D_{yy})$;

$b = 2D_{zz} - D_{xx} - D_{yy} + 2\Delta$; $N = 2(\Delta b)^{1/2}$;

$\Delta = [(D_{xx} - D_{yy})^2 + (D_{zz} - D_{xx})(D_{zz} - D_{yy})]^{1/2}$;

$D = (D_{xx} + D_{yy} + D_{zz})/3$

Table S2. Representation of Spherical Harmonics ($l = 2$) in Terms of the Cartesian Components of $\vec{\mathbf{e}}$.

Spherical Harmonic	Representation in terms of components of $\vec{\mathbf{e}}$
$Y_{2,2}(\theta',\phi')$	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\left(\mathrm{e}_x^2 - \mathrm{e}_y^2 + 2i\mathrm{e}_x\mathrm{e}_y\right)$
$Y_{2,1}(\theta',\phi')$	$-\frac{1}{2}\sqrt{\frac{15}{2\pi}}\left(\mathrm{e}_x\mathrm{e}_z + i\mathrm{e}_y\mathrm{e}_z\right)$
$Y_{2,0}(\theta',\phi')$	$\frac{1}{4}\sqrt{\frac{5}{\pi}}\left(3\mathrm{e}_z^2 - 1\right)$
$Y_{2,-1}(\theta',\phi')$	$\frac{1}{2}\sqrt{\frac{15}{2\pi}}\left(\mathrm{e}_x\mathrm{e}_z - i\mathrm{e}_y\mathrm{e}_z\right)$
$Y_{2,-2}(\theta',\phi')$	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\left(\mathrm{e}_x^2 - \mathrm{e}_y^2 - 2i\mathrm{e}_x\mathrm{e}_y\right)$

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