

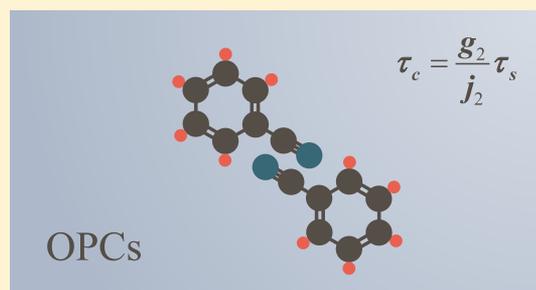
## Orientational Pair Correlations in a Dipolar Molecular Liquid: Time-Resolved Resonant and Nonresonant Pump–Probe Spectroscopies

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## Supporting Information

**ABSTRACT:** Orientational pair correlations (OPCs), when they are sufficiently strong in a liquid, contain information on the interplay between structure and dynamics that arise from intermolecular interactions. Consequently, the quantification of OPCs remains a subject of substantial interest in current experimental and theoretical works. In the case of benzonitrile, the importance of OPCs remains ambiguous, owing to the use of model-dependent analyses or reliance on a single spectroscopic technique. Here, IR polarization-selective pump–probe (PSPP) and optical heterodyne-detected optical Kerr effect (OHD-OKE) experiments were used to quantify OPCs in benzonitrile. These methods measure single molecule and collective orientational relaxation dynamics, respectively. A comparison of the orientational correlation function (PSPP) of the naturally abundant <sup>13</sup>CN stretching mode and the polarizability anisotropy relaxation (OHD-OKE) of the liquid revealed that the collective reorientation time was a factor of  $1.56 \pm 0.08$  slower than the single molecule reorientation time. The two types of measurements on dilute benzonitrile in carbon tetrachloride were the same within experimental error. These results support the proposition that OPCs exist and arise from the formation of parallel-aligned intermolecular structures in the neat liquid.



## 1. INTRODUCTION

The question of whether or not orientational pair correlations (OPCs) exist in benzonitrile (Figure 1) has remained

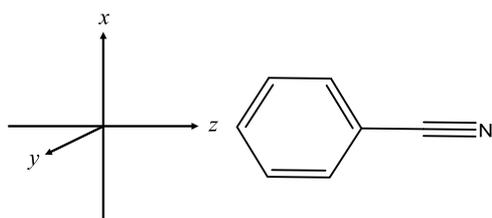


Figure 1. Principal axis system for benzonitrile.

unsettled<sup>1–7</sup> despite the greater consensus on the ability of neighboring molecules in the liquid to align their permanent dipoles into antiparallel structures.<sup>8,9</sup> A liquid exhibits OPCs if collective orientational relaxation occurs on a timescale different from the single molecule randomization time. This can be summarized by the relation<sup>10,11</sup>

$$\tau_c = (g_2/j_2)\tau_s \quad (1)$$

where  $\tau_s$  and  $\tau_c$  are the single molecule and collective orientational correlation times, and  $g_2$  and  $j_2$  are the static and dynamic OPC parameters, respectively. Equation 1 implies that a measure of the ratio  $g_2/j_2$  requires robust methods that probe the time evolution of single and collective orientational dynamics in a liquid. The reported values of  $g_2/j_2$  for benzonitrile range widely from 1<sup>1,5</sup> (no OPCs) to 1.58.<sup>3</sup>

One difficulty has been the limited availability of methods that probe collective dynamics, namely dielectric relaxation,<sup>8</sup> depolarized Rayleigh scattering,<sup>1,3</sup> and optical heterodyne-detected optical Kerr effect (OHD-OKE) spectroscopy.<sup>5</sup> In the context of benzonitrile, perhaps the greater issue has been difficulty incorporating a second technique that probes single molecule dynamics in a straightforward manner, so that the reliance on model calculations of  $\tau_s$  can be avoided.<sup>3</sup> The quantification of OPCs reveals key information on the interplay between structure and dynamics in molecular liquids, and the accurate description of the nature and magnitude of OPCs is an endeavor of substantial interest in simulations.<sup>12–18</sup> The focus of the present study is the elucidation of OPCs in benzonitrile by combining two ultrafast time-resolved methods, IR polarization selective pump–probe (PSPP) and OHD-OKE spectroscopies. PSPP and OHD-OKE spectroscopies were used to measure the single molecule and collective orientational correlation times, respectively.

## 2. EXPERIMENTAL METHODS

## 2.1. Sample Preparation and Linear IR Spectroscopy.

Benzonitrile and anhydrous carbon tetrachloride (CCl<sub>4</sub>) were purchased from Sigma-Aldrich and used without further purification. The samples were prepared in a glovebox (N<sub>2</sub> (g) atmosphere) to avoid water contamination. The two

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samples prepared were pure benzonitrile and 1:100 benzonitrile/ $\text{CCl}_4$ . The sample cells used in the PSPP experiments consisted of two 3 mm thick, 1 in. diameter  $\text{CaF}_2$  windows separated by a 250  $\mu\text{m}$  thick Teflon spacer. The liquid samples were introduced into the 250  $\mu\text{m}$  gap. The Fourier transform infrared (FT IR) spectra were measured with a Thermo Scientific Nicolet 6700 FT IR spectrometer as previously described.<sup>19</sup> The OHD-OKE samples were filtered (0.02  $\mu\text{m}$ , Whatman Anotop) into 1 cm path length fused silica cuvettes (Starna Cells). Wax was melted over the top to prevent water contamination. All PSPP and OHD-OKE experiments were performed at 295 K.

**2.2. Polarization-Selective Pump–Probe Spectroscopy.** The PSPP experiment, as performed on the present optical setup, has been described in detail previously.<sup>19</sup> Briefly, a Ti:sapphire regenerative amplifier pumps an optical parametric amplifier/difference frequency generation system, producing 150 fs ( $\sim 110\text{ cm}^{-1}$  full width at half-maximum bandwidth) mid-IR pulses (6–8  $\mu\text{J}$  energy per pulse) tuned to the center frequency of the CN stretch mode of benzonitrile. The mid-IR pulses are split into a strong pump and a weaker probe pulse with a beam splitter. In the experiment, the CN stretch mode of benzonitrile is excited upon the arrival of the resonant pump pulse.<sup>20</sup> Following a time delay,  $t$ , a probe pulse interacts with the sample. The PP signal can be understood as the transient difference in the transmitted probe intensity with the pump pulse on versus off.<sup>20</sup> To acquire the signal, the pump is chopped at 500 Hz (half the laser repetition rate) with an acousto-optic modulator.<sup>21</sup> The signal,  $S(t)$ , is measured in two polarization configurations referred to as parallel and perpendicular. The probe is linearly polarized at  $0^\circ$  (in the plane of the optical table), and the pump is linearly polarized at  $45^\circ$  relative to the probe. After the sample, a polarizer in a computer-controlled rotation mount resolves the signal at  $+45^\circ$  or  $-45^\circ$ , which correspond to parallel,  $S_{\parallel}(t)$ , and perpendicular,  $S_{\perp}(t)$ , configurations, respectively. The time delay,  $t$ , is varied by introducing optical path length into the probe beam using a mechanical delay line.

**2.3. OHD-OKE Spectroscopy.** The OHD-OKE technique is a pump–probe experiment that measures the collective orientational dynamics of molecules in a liquid by tracking the time-dependent birefringence induced in the sample by a nonresonant pump pulse. This provides information on the equilibrium orientational dynamics, as described by linear response theory.<sup>22</sup> The implementation of the OHD-OKE method has been described in detail previously.<sup>23</sup> The key components are given below. The pulses are generated by an 86 MHz Ti:sapphire oscillator. A 5 kHz Ti:sapphire regenerative amplifier increases the pulse power. These amplified pulses are then split into pump and probe beams using a beam splitter. The pump beam arrives at the sample linearly polarized. The probe beam is polarized at  $45^\circ$  relative to the pump. Before the sample, the probe passes down a mechanical delay line that introduces optical path length into the probe beam. This allows data to be collected at multiple time delays. Finally, heterodyne detection is introduced via the creation of a local oscillator collinear with the probe. This local oscillator amplifies the signal and enables a four-shot phase cycling sequence.<sup>22,24,25</sup>

OHD-OKE measures the time derivative of the collective polarizability anisotropy time correlation function (TCF). This is the collective orientational correlation function after subpicosecond collisions result in brief, multiparticle contri-

butions to the signal. This correlation function can be extracted through the use of schematic mode coupling theory (MCT)<sup>26</sup> which uses a set of differential equations to couple the orientational correlation function from the OHD-OKE data to the density correlation function. The results of the MCT analysis fit the data exceptionally well; however, in addition to being excessively computationally expensive, they fail to provide numerical comparisons for the various randomization processes that contribute to the correlation functions. The MCT results indicate that the OHD-OKE data present as a series of power laws preceding a single exponential, which is the final complete randomization of the system.<sup>27</sup> Thus, a phenomenological fitting function with these qualities can be used to extract quantitative information about the power laws and the exponential. The current work focuses solely on the exponential region, which can be fit with a single exponential decay.

### 3. THEORY

Infrared PSPP and OHD-OKE spectroscopies are nonlinear (third-order) techniques that use linearly polarized, femto-second pulses to probe molecular orientational dynamics through resonant vibrational<sup>20</sup> and nonresonant Raman<sup>28</sup> excitations, respectively. In PSPP spectroscopy, molecules interact with the incident pulses through their transition dipole moment,  $\mu_{01}$ .<sup>29</sup> The direction of  $\mu_{01}$  is denoted by the unit vector  $\vec{e}$ . For the CN stretching vibrational mode of benzonitrile,  $\vec{e}$  is along the CN bond vector, which coincides with the symmetry ( $z$ ) axis of the molecule (Figure 1). In a PSPP experiment, the sample is vibrationally excited with a linearly polarized pump pulse, and the transient absorption of a time-delayed probe pulse polarized parallel,  $S_{\parallel}(t)$ , and perpendicular,  $S_{\perp}(t)$ , to the pump is measured.<sup>20</sup> Single molecule orientational dynamics are determined by calculating the anisotropy<sup>20,30</sup>

$$r(t) = \frac{S_{\parallel}(t) - S_{\perp}(t)}{S_{\parallel}(t) + 2S_{\perp}(t)} = 0.4C_2(t) = 0.4\langle P_2(\vec{e}(0) \cdot \vec{e}(t)) \rangle \quad (2)$$

where  $C_2(t)$  is the (single molecule) second-order Legendre polynomial orientational correlation function,  $P_2(x) = 1/2(3x^2 - 1)$ , with  $x = \cos \theta$ , and  $\langle \rangle$  denotes an isotropic ensemble average.

The property relevant to OHD-OKE spectroscopy is the polarizability (second rank) tensor,  $\alpha$ , of the benzonitrile molecule. In an OHD-OKE experiment, a strong, linearly polarized pump pulse,  $E$ , generates an induced molecular dipole moment,  $\mu_{\text{in}}$ , with the components  $\mu_i = \alpha_{ij}E_j$  (where repeated indices are summed).<sup>11,31</sup> An ultrafast torque,  $\mu_{\text{in}} \times E$ , is exerted on the molecules, causing them to rotate into a *slight* alignment with the applied field.<sup>31</sup> This induces a difference in the liquid refractive index parallel and perpendicular to the pump pulse (birefringence).<sup>31,32</sup> The transient birefringence of the liquid is monitored by a time-delayed, linearly polarized probe pulse that acquires elliptical polarization on passing through the sample.<sup>32</sup> Several processes contribute to the decay of the elliptical polarization and recovery of the equilibrium state. Molecular reorientation is the largest contributor to the decay on long timescales.<sup>13–15,17,28</sup>

In contrast to spherical molecules, in general, the polarizability tensor,  $\alpha$ , of an optically anisotropic molecule such as benzonitrile has off-diagonal elements. Principal axes of the

polarizability tensor can be found (Figure 1), such that, with these axes as basis vectors,  $\alpha$  is diagonal. In the principal axis system, the components of the induced dipole moment,  $\mu_{\text{in}}$ , are parallel to the components of the incident electric field,  $E$ . Here, we treat benzonitrile as a rigid molecule. Thus, the polarizability components will be time-invariant in the molecule-fixed frame (principal axis system), whereas in the laboratory frame they will be time-dependent because of molecular reorientation.<sup>11</sup> The OHD-OKE experiment measures the time derivative of the anisotropic (traceless) parts of the collective polarizability TCF<sup>13–15,17,28</sup>

$$R(t) \propto -\frac{\partial}{\partial t} \psi_{xy}(t) = -\frac{\partial}{\partial t} \frac{15}{N\gamma^2} \langle \Pi_{xy}(0) \Pi_{xy}(t) \rangle \quad (3)$$

where  $N$  is the number of molecules in the system,  $\Pi_{xy}$  is an off-diagonal element of the collective polarizability, and  $\gamma$  is the anisotropic part of the polarizability tensor,<sup>13,14,17</sup> which is related to the principal components of the molecule-fixed  $\alpha$  by

$$\gamma = \{0.5[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2]\}^{1/2} \quad (4)$$

The collective polarizability of the liquid can be partitioned into molecular (M) and interaction-induced (I) terms<sup>13–17,28</sup>

$$\Pi = \Pi^{\text{M}} + \Pi^{\text{I}} \quad (5)$$

$$\Pi^{\text{M}} = \sum_{i=1}^N \alpha_i \quad (6)$$

where  $\Pi^{\text{M}}$  is the sum of  $\alpha_i$ , and  $\Pi^{\text{I}}$  arises from intermolecular interactions in the liquid. In general,  $\Pi^{\text{I}}$  has a complex form depending on the translational and rotational degrees of freedom.<sup>13–17,28,33</sup> The collective polarizability anisotropy TCF in eq 3 can be separated into four terms based on eq 5

$$\psi_{xy}(t) = \psi_{xy}^{\text{MM}}(t) + \psi_{xy}^{\text{II}}(t) + \psi_{xy}^{\text{MI}}(t) + \psi_{xy}^{\text{IM}}(t) \quad (7)$$

where  $\psi_{xy}^{\text{XY}}(t) = 15 \langle \Pi_{xy}^{\text{X}}(0) \Pi_{xy}^{\text{Y}}(t) \rangle / N\gamma^2$ .<sup>11,13–17</sup> However, it is often more informative to separate  $\psi_{xy}(t)$  in terms of the different dynamic fluctuations involved. The rapidly decaying relaxation processes resulting from the existence of  $\Pi^{\text{I}}$  and the more slowly varying reorientation timescales can be separated by projecting the portion of  $\Pi^{\text{I}}$  that has the same time dependence as  $\Pi^{\text{M}}$ , which relaxes through collective reorientation.<sup>13–17,33</sup> The collective polarizability can alternatively be written as

$$\Pi = \Pi^{\text{R}} + \Pi^{\Delta} \quad (8)$$

where  $\Pi^{\text{R}}$  and  $\Pi^{\Delta}$  are, respectively, the rotational and collision-induced (interaction-induced) contributions. Here, the projected quantity of interest is<sup>13–17,33</sup>

$$\Pi_{xy}^{\text{R}} = (1 + G_{xy}) \Pi_{xy}^{\text{M}} \quad (9)$$

where the constant  $G_{xy} = \psi_{xy}^{\text{MI}}(0) / \psi_{xy}^{\text{MM}}(0)$ . Then

$$\psi_{xy}(t) = \psi_{xy}^{\text{RR}}(t) + \psi_{xy}^{\Delta\Delta}(t) + \psi_{xy}^{\text{RA}}(t) + \psi_{xy}^{\Delta\text{R}}(t) \quad (10)$$

where the various correlation functions are defined in a similar way as in eq 7. This work focuses on the long-time OHD-OKE signal, for which it has been concluded in many systems that  $\psi_{xy}^{\text{RR}}(t)$  is the largest term.<sup>13–17,28</sup> The substitution of eq 6 into 9, 9 into 10, and 10 into 3 yields, at long time,

$$\begin{aligned} R(t) &\propto -\frac{\partial}{\partial t} \psi_{xy}^{\text{RR}}(t) \\ &= -(1 + G_{xy})^2 \frac{\partial}{\partial t} \psi_{xy}^{\text{MM}}(t) \\ &= -(1 + G_{xy})^2 \frac{\partial}{\partial t} \left\{ \frac{15}{N\gamma^2} \sum_{i=1}^N \langle \alpha_{i,xy}(0) \alpha_{i,xy}(t) \rangle \right. \\ &\quad \left. + \frac{15}{N\gamma^2} \sum_{i=1}^N \sum_{j \neq i}^N \langle \alpha_{i,xy}(0) \alpha_{j,xy}(t) \rangle \right\} \end{aligned} \quad (11)$$

where the first and second summations in brackets are respectively the single molecule and pair contributions to the polarizability anisotropy TCF. The local field factor  $(1 + G_{xy})^2$  modifies the portion of the polarizability anisotropy that decays via collective reorientation. We note that the separation of the TCF into two contributions does not necessarily imply a multiexponential decay. Using Mori's theory of collective motion in many-particle systems,<sup>34</sup> it has been shown that the TCF (eq 11) for a symmetric top decays on a single timescale, even when the single and pair correlation functions differ in their time dependence (eq 1).<sup>11,35–38</sup> With this in mind, the remainder of this work focuses on a quantitative comparison of dynamics described by eqs 2 and 11.

#### 4. RESULTS AND DISCUSSION

The OHD-OKE signal from neat benzonitrile is displayed in Figure 2 (black curve). The long time decay is described by a

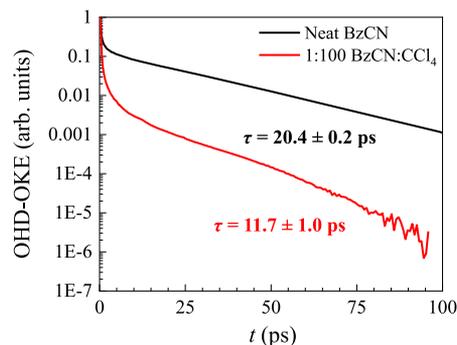
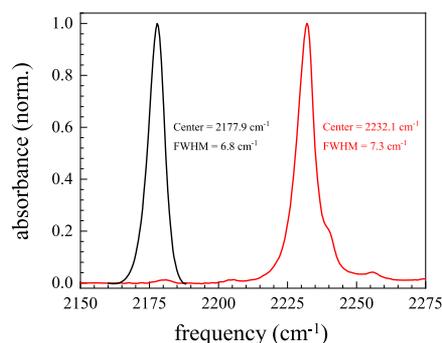
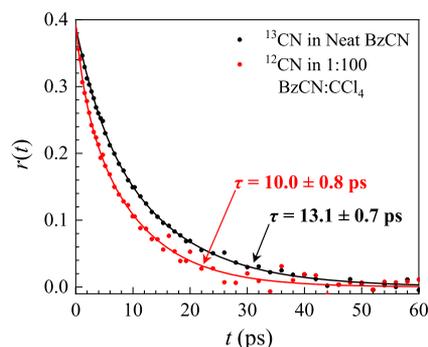


Figure 2. OHD-OKE signal decays in neat benzonitrile (black curve) and 1:100 benzonitrile/ $\text{CCl}_4$  solution (red curve).

single exponential with a time constant  $\tau = 20.4 \pm 0.2$  ps. PSPP spectroscopy, which measures the single molecule reorientation time (eq 2), was performed on the CN stretch in neat benzonitrile at an identical temperature of 295 K for comparison with the OHD-OKE data. In the neat liquid, however, the  $^{12}\text{CN}$  stretch has a massive absorption because of the high concentration of molecules with  $^{12}\text{CN}$ . This transition cannot be studied for several reasons,<sup>39</sup> including significant depletion of the probe pulse intensity, heating artifacts, and excitation transfer between neighboring molecules. These issues were avoided by instead studying the naturally abundant ( $\sim 1.1\%$ )  $^{13}\text{CN}$  stretching mode.<sup>39</sup> The  $^{13}\text{CN}$  linear IR absorption spectrum (black curve) is shown in Figure 3. The  $r(t)$  of  $^{13}\text{CN}$  in neat benzonitrile (black points) is shown in Figure 4. The decay is biexponential. Owing to the  $C_{2v}$  symmetry of benzonitrile, the molecule-fixed axis system (Figure 1) is simultaneously a principal axis system for the



**Figure 3.** FT IR spectra of the  $^{13}\text{CN}$  stretch in neat benzonitrile (solid black curve) and the  $^{12}\text{CN}$  stretch in 1:100 benzonitrile/ $\text{CCl}_4$  solution (solid red curve).



**Figure 4.** Anisotropy decays of the  $^{13}\text{CN}$  stretch in neat benzonitrile (black points) and the  $^{12}\text{CN}$  stretch in 1:100 benzonitrile/ $\text{CCl}_4$  solution (red points). The solid curves of the same color are fits of the wobbling-in-a cone expression (eq 13) to the data.

moment of inertia tensor, the rotational diffusion tensor, and the polarizability tensor.<sup>11,40</sup> Taking into consideration that  $\mu_{01}$  only has a component along  $z$  (the symmetry axis) in the molecular frame, the theory of rotational diffusion of an asymmetric rotor<sup>30,41–45</sup> (see the Supporting Information, Sections SA and SB) dictates that the maximum number of exponentials observed can be two

$$r(t) = 0.4C_2(t) = \frac{2}{5N^2} \{a^2 \exp[-(6D + 2\Delta)t] + b^2 \exp[-(6D - 2\Delta)t]\} \quad (12)$$

where the constants  $N$ ,  $a$ ,  $b$ ,  $\Delta$ , and  $D$ , defined in Table S1, are functions of the principal components of the diffusion tensor. Therefore, the theory stipulates that the amplitudes and timescales of  $r(t)$  must be determined by one set of diffusion coefficients  $D_{xx}$ ,  $D_{yy}$ , and  $D_{zz}$ . However, no physically meaningful set of diffusion coefficients could be determined that fits the biexponential  $r(t)$  of  $^{13}\text{CN}$  in neat benzonitrile (Section SB). 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. A qualitatively

different physical picture of the reorientation process is necessary to rationalize the data.

Many nitriles have been observed to undergo restricted orientational sampling in bulk liquids on shorter timescales than the complete orientational randomization by rotational diffusion.<sup>19</sup> The restricted orientational motions manifest as additional exponential components in the anisotropy and can be interpreted within the framework of the wobbling-in-a-cone model.<sup>46,47</sup> In this model, the rotational diffusion equation is solved for a transition dipole moment confined in a cone of half-angle  $\theta_c$ . For a single cone, the anisotropy decays to an offset equivalent to the square of an order parameter,  $Q^2 = [\{\cos\theta_c(1 + \cos\theta_c)\}/2]^2$ . These considerations led to the assignment of the fast exponential component in  $r(t)$  to wobbling-in-a-cone, whereas the final exponential reflects free diffusion of the dipole moment. The wobbling-in-a-cone analysis implies that the free diffusion regime of benzonitrile is single exponential. This can be understood if benzonitrile reorientation is very close to that of a symmetric top (Figure 1), for which  $D_{xx} \cong D_{yy} = D_{\perp}$ . In this limit, eq 12 reduces to  $r(t) \propto \exp[-6D_{\perp}t]$ , where  $\tau_{\perp} = 1/6D_{\perp}$  represents the free rotational diffusion timescale. The measured  $r(t)$  was therefore analyzed with the following expression incorporating an inertial cone, a diffusive cone, and free diffusion, as has been previously described<sup>19</sup>

$$r(t) = 0.4T^2(S^2 + (1 - S^2)\exp[-t/\tau_c])\exp[-t/\tau_{\perp}] \quad (13)$$

where  $T$ ,  $S$ ,  $\tau_c$ , and  $\tau_{\perp} = 1/6D_{\perp}$  are respectively the inertial cone order parameter, diffusive cone order parameter, diffusive cone correlation time, and free diffusion correlation time. The analysis is identical to a previous analysis on  $\text{SeCN}^-$  reorientation in bulk  $\text{D}_2\text{O}$ .<sup>19</sup> The cone angles for the inertial and diffusive cones,  $\theta_{\text{in}}$ ,  $\theta_c$ , and  $\theta_{\text{total}}$  are obtained directly from the order parameters  $T$ ,  $S$ , and  $Q_{\text{total}} = TS$ . The diffusion coefficient for the diffusive cone,  $D_c$  is dependent on  $\tau_c$  and  $\theta_c$ .<sup>19,47</sup> For  $\theta_c \leq 30^\circ$ ,  $D_c \cong 7\theta_c^2/24\tau_c$  is a good approximation.<sup>47</sup> The results of the analysis are given in Table 1. A large relative error is observed for  $\theta_{\text{in}}$ , as this value depends on the extrapolated value of the anisotropy at time zero. Nonetheless, the inertial cone is essentially negligible. Within the error, all cone angles are identical between the neat and dilute samples. However, in the neat liquid, rotational diffusion always proceeds more slowly, as indicated by the consistently smaller diffusion coefficients. The single molecule orientational correlation time is  $\tau_{\perp} = 13.1 \pm 0.7$  ps.

In the absence of OPCs, and provided  $\alpha_{xx} \cong \alpha_{yy} = \alpha_{\perp}$ ,  $\alpha_{zz} = \alpha_{\parallel}$ , and  $D_{xx} \cong D_{yy} = D_{\perp}$  (near symmetric-top limit), the polarizability anisotropy TCF can also be shown (Section SC) to decay as<sup>11</sup>

$$R(t) \propto 2D_{\perp}[\alpha_{\parallel} - \alpha_{\perp}]^2 \exp[-6D_{\perp}t] \quad (14)$$

The similarity of the principal components of  $\alpha$  perpendicular to the symmetry axis is reasonable, given the shape of benzonitrile, which approaches that of a symmetric rotor, and it has been treated in this way previously.<sup>48</sup> These considerations strongly indicate that the difference in

**Table 1.** Benzonitrile Wobbling-in-a Cone Parameters

sample	$\theta_{\text{in}}$ (deg)	$\theta_c$ (deg)	$\theta_{\text{tot}}$ (deg)	$\tau_c$ (ps)	$\tau_{\perp}$ (ps)	$D_c$ ( $\text{ps}^{-1}$ )	$D_{\perp}$ ( $\text{ps}^{-1}$ )
$^{13}\text{CN}$ in neat BzCN	$5 \pm 6$	$23 \pm 4$	$24 \pm 3$	$6 \pm 2$	$13.1 \pm 0.7$	$0.007 \pm 0.002$	$0.0127 \pm 0.0007$
$^{12}\text{CN}$ in 1:100 BzCN/ $\text{CCl}_4$	$6 \pm 3$	$25 \pm 3$	$25 \pm 3$	$2.2 \pm 0.8$	$10.0 \pm 0.8$	$0.025 \pm 0.004$	$0.017 \pm 0.001$

correlation times measured with OHD-OKE ( $20.4 \pm 0.2$ ) and PSPP ( $13.1 \pm 0.7$  ps) is due to the OPCs in the neat liquid, represented by a non-negligible second term in the final line of eq 11.

To support the proposition that the difference in the decay constants is a result of OPCs, OHD-OKE and PSPP experiments were performed on dilute benzonitrile dissolved in  $\text{CCl}_4$  (1:100 mole fraction) at 295 K. If correlations in  $\alpha$  of nonidentical molecules are mediated through intermolecular interactions, they should vanish in the limit of infinite dilution in a solvent with zero optical anisotropy ( $\gamma = 0$ ). In this dilute sample, the  $^{12}\text{CN}$  stretch, with the linear absorption spectrum (red curve) shown in Figure 3, was studied as the  $^{13}\text{CN}$  signal was too small. The OHD-OKE signal (red curve) and  $r(t)$  data (red points) are shown in Figures 2 and 4, respectively. In the dilute sample, the long-time OHD-OKE signal is a single exponential with a correlation time of  $\tau_{\perp} = 11.7 \pm 1.0$  ps.  $r(t)$  is again biexponential, giving a single molecule orientational correlation time of  $\tau_{\perp} = 10.0 \pm 0.8$  ps, following wobbling-in-a-cone analysis (Table 1).  $\tau_{\perp}$  are essentially the same in the dilute limit (within the experimental error). This result supports the prediction that both observables measure identical single molecule orientational dynamics, that is, they decay as  $\exp[-6D_{\perp}t]$ , given the effective symmetry of the rotational diffusion and polarizability tensors perpendicular to the symmetry axis of benzonitrile and that  $\mu_{01}$  is parallel to that axis. Moreover, the equivalent  $\tau_{\perp}$  in the dilute sample shows that the difference between the two observed decay times in the neat liquid is caused by OPCs which are mediated through short-range intermolecular interactions between adjacent molecules. We note that the single molecule  $\tau_{\perp}$  is directly proportional to the viscosity,  $\eta$ , according to the Stokes–Einstein–Debye relation for rotational diffusion.<sup>49</sup> The modest decrease in  $\tau_{\perp}$  (Figure 4) going from neat ( $13.1 \pm 0.7$  ps) to dilute ( $10.0 \pm 0.8$  ps) solution is consistent with the viscosity decrease going from benzonitrile (1.38 mPa·s at 293 K)<sup>50</sup> to  $\text{CCl}_4$  (0.97 mPa·s at 293 K),<sup>51</sup> in agreement with the hydrodynamic prediction.

The magnitude of OPCs in neat benzonitrile can now be assessed in accordance with eq 1 by taking the ratio  $\tau_c/\tau_s$  using the results from the OHD-OKE and PSPP experiments. The result is  $g_2/j_2 = 1.56 \pm 0.08$ . In the case of a symmetric rotor, Gierke has theoretically shown that the depolarized Rayleigh scattering spectrum depends solely on the static OPC parameter,  $g_2$ , and consequently  $j_2$  is rigorously unity.<sup>10</sup> It has often been assumed that  $j_2 = 1$ ,<sup>5,11</sup> and experimental evidence exists in favor of this conclusion.<sup>2,3,11</sup> Depolarized Rayleigh scattering and the OHD-OKE signal are frequency-time analogues and are related through a FT.<sup>22,49,52</sup> The present OHD-OKE and PSPP data show that benzonitrile behaves indistinguishably from a symmetric rotor. Thus, the current results give  $g_2 = 1.56 \pm 0.08$ . For a symmetric rotor, it can be shown that<sup>10,11,35</sup>

$$g_2 = 1 + \left\langle \sum_{i \neq j} \frac{P_2(\vec{e}_i \cdot \vec{e}_j)}{N - 1} \right\rangle \quad (15)$$

where the second term can be positive or negative. If the molecules surrounding a given molecule are, on average, oriented parallel to it,  $g_2 > 1$ . For spectroscopic techniques of order  $l = 2$ , a distinction cannot be made between parallel and antiparallel;<sup>53</sup> so, we refer to the arrangement as parallel for simplicity. Thus, on the free diffusion timescale, the collective

polarizability anisotropy TCF relaxes more slowly than the single molecule orientational correlation function because benzonitrile molecules tend to arrange themselves with their symmetry axes parallel to each other in the liquid. To a certain extent, this structuring is related to the large permanent dipole moment of the molecule ( $\sim 4.5$  D),<sup>2,48,54</sup> which also lies along the symmetry axis. Several studies have concluded that an antiparallel arrangement,<sup>2,8,9</sup> which tends to balance the asymmetric charge distribution of the molecule, is energetically preferred. However, a reference interaction site model calculation of the liquid structure of acetonitrile reproduced the neutron and X-ray diffraction structure factor of the liquid and revealed strong OPCs between neighboring molecules.<sup>12</sup> Thus, molecular shape and packing are also important factors determining the magnitude of OPCs. Nonetheless, for similarly shaped monosubstituted derivatives of benzene, a strong correlation between the strength of the OPCs and the square of the molecular dipole moment was observed.<sup>2</sup>

The result  $g_2/j_2 = 1.56 \pm 0.08$  is in agreement with the result of Alms and Patterson,<sup>3</sup> who found  $g_2/j_2 = 1.58$  from the analysis of the depolarized Rayleigh scattering spectrum. In contrast to their study, which relied on model hydrodynamic calculations of the single molecule reorientation time, in this work,  $\tau_c$  and  $\tau_s$  were independently measured directly in the time domain. Other studies concluding  $g_2/j_2 = 1$ ,<sup>1,4,5</sup> which also performed concentration studies, either observed no concentration dependence in  $\tau_c$ <sup>1</sup> or omitted dilution data using  $\text{CCl}_4$ , which has the desirable property that  $\gamma = 0$ , on the basis that the results were “anomalous”.<sup>5</sup> We observe that although the OHD-OKE signal exhibits a significant concentration dependence (Figure 2), the anisotropy exhibits very little change (Figure 4), which is explained by the modest decrease in viscosity going from neat benzonitrile to  $\text{CCl}_4$  solution. Here, the union of two methods sensitive to collective (OHD-OKE) and single molecule-only (PSPP) dynamics makes the identification of OPCs particularly clear.

## 5. CONCLUDING REMARKS

This work has identified and quantified OPCs in liquid benzonitrile using two ultrafast spectroscopic methods, OHD-OKE and PSPP spectroscopies, which respectively measure collective and single molecule orientational dynamics. In the process, the relationship between the dynamic observables, the collective polarizability anisotropy TCF and the orientational anisotropy, based on two distinct molecular properties,  $\alpha$  and  $\mu_{01}$ , was elucidated. Given what is known about the local liquid structure from other methods,<sup>8,9</sup> the results  $g_2/j_2 = 1.56 \pm 0.08$  and  $g_2 > 1$  suggest that the formation of intermolecular structures, which favor a parallel (antiparallel) orientation of the molecular symmetry axes of benzonitrile pairs, is responsible for the significantly slower relaxation of the OHD-OKE signal compared to  $r(t)$ . Given the strength of these correlations in benzonitrile, this ordering may extend out to several solvent layers.<sup>53</sup> The future quantification of OPCs in other liquids will inform the development of accurate liquid models and simulations, as well as aid in the identification of molecular characteristics that lead to their formation.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpccb.8b10711.

Rotational diffusion of an asymmetric rotor: theory, connection to the single molecule orientational correlation function, and connection to the OHD-OKE signal (PDF)

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### Notes

The authors declare no competing financial interest.

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