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Solvation dynamics of room-temperature ionic liquids: evidence for collective solvent motion on sub-picosecond timescales

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Abstract

Little is known about the microscopic mechanism of solvation dynamics in room-temperature ionic liquids, but experimental studies have found that the solvent response has both sub-picosecond and nanosecond timescale components. We present the results of molecular dynamics calculations of the time-resolved fluorescence response of a chromophore in an ionic liquid, and analyze the solute–solvent interactions responsible for the observed signal. We find evidence for collective cation–anion motion on sub-picosecond timescales, contradicting earlier work suggesting the sub-picosecond response is purely anionic. We present an alternative hypothesis to explain our results and the widely disparate timescales for solvation response.

1. Introduction

Recent years have seen a growing experimental focus on a novel class of materials known as room-temperature ionic liquids (ILs). These materials represent salts that are molten at or near room-temperature, and they have been found capable of solvating a wide range of organic compounds. However, the nature of the solute–solvent interactions responsible for their solvation properties remains unknown. One approach to studying such interactions is examination of the time-resolved fluorescence behavior of a chromophore solvated in the medium of interest, and such photophysical studies of ILs have found the timescale for solvation response to be strongly dependent on the solvent cation [1–8]. Studies of ILs based on imidazolium cation [1,4–8] indicate significant picosecond or sub-picosecond response, followed by a response on nanosecond timescales. Shim and co-workers [9] have recently used molecular dynamics simulation to study the solvent response of ionic liquids based on the 1-ethyl-3-methylimidazolium cation to the photoexcitation of a model chromophore. The authors decompose the solvation response of the system into cation and anion components, and their results indicate that the sub-picosecond response is due entirely to anionic motion. This idea had been proposed for other classes of ILs [2], though no simulations of these systems have been reported.

In this work, we present the results of molecular dynamics simulations on the solvation response of an IL to photoexcitation of a chromophore. Our study makes use of the betaine-30 chromophore in BMIM[PF_6] (see Fig. 1), which we have previously studied in simulation [10]. While the betaine-30 system does not have emission properties conducive to experimental time-resolved fluorescence studies, its aromatic structure is similar to many dyes used in such a context and so may be viewed as a physically-motivated model system.

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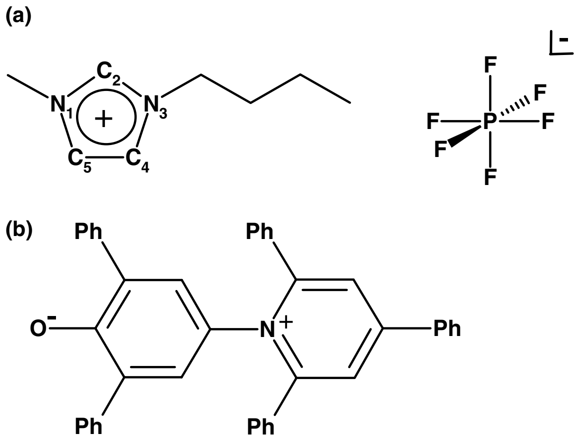

Fig. 1. (a) 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIM[PF_6]). (b) Betaine-30. Ph denotes a phenyl group.

Our results indicate the existence of collective cation–anion motions on sub-picosecond timescales, and that both species contribute to the initial solvation response to photoexcitation of the chromophore.

2. Methodology

2.1. Simulations

The model is identical to that used in previous work [10], and consists of a single betaine-30 chromophore interacting with 200 solvent ion pairs. The PF_6^- ion is represented by a single atomic site, and the BMIM ion is treated as a rigid ring bound to a flexible butyl-group. The betaine-30 chromophore is treated as a rigid body, and held fixed to eliminate all rotational and translational motion. Our analysis consists of a set of eight trajectories, each initially equilibrated in an NPT ensemble at 300 K and 1 atm for at least 1 ns. Data were collected by integration of each of these trajectories over 600 ps in an NVE ensemble.

In classical simulations of the type reported here, the energy of radiative emission or absorption associated with a given solvent configuration is taken to be the difference in energy between the ground and excited electronic states of the chromophore. For our rigid model chromophore, the time-dependence of this energy gap arises solely from the change in solute–solvent energies due to solvent motion. The process of electronic excitation is treated as the redistribution of electric charge among chromophore atomic sites without any corresponding change in their dispersive interactions, and the energy gap $\Delta E(t)$ is simply the difference in solute–solvent Coulomb interactions between ground and excited states (see Eq. (4) of [10]). Note that this definition sets the excitation energy of the isolated chromophore to be 0, eliminating intramolecular contributions to $\Delta E(t)$. For the present study we decompose the the energy gap into cation and anion components, such that,

$$\Delta E(t) = \Delta E_{\mathrm{cat}}(t) + \Delta E_{\mathrm{an}}(t), \tag{1}$$

where $\Delta E_{\mathrm{cat}}(t)$ is the difference in chromophore–cation interaction energies on excitation, and $\Delta E_{\mathrm{an}}(t)$ is defined analogously for anions.

2.2. Linear response theory treatment of solvation dynamics

We use linear response theory to calculate the time-dependent Stokes shift from equilibrium data. A normalized form for the time-resolved Stokes shift following excitation at $t = 0$ may be written as [11]

$$S(t) = \frac{\overline{\Delta E}(t) - \overline{\Delta E}(\infty)}{\overline{\Delta E}(0) - \overline{\Delta E}(\infty)}, \tag{2}$$

where the overbar indicates an average over non-equilibrium trajectories. This can be approximated by linear response theory as [11]

$$C(t) = \frac{\langle \delta\Delta E(0)\delta\Delta E(t)\rangle}{\langle (\delta\Delta E)^2\rangle}, \tag{3}$$

where angular brackets denote the equilibrium average and $\delta\Delta E = \Delta E - \langle\Delta E\rangle$. In our simulations, the equilibrium average is taken in the chromophore ground electronic state, an acceptable practice [11].

A key question in understanding solvation dynamics in IL systems is the role of the cation and anion in determining the time and energy profiles for the process. Consider the time correlation functions (TCFs) for cation and anion contributions to the Stokes shift, the former of which is written as

$$C_{\mathrm{cat}}(t) = \frac{\langle \delta\Delta E_{\mathrm{cat}}(0)\delta\Delta E_{\mathrm{cat}}(t)\rangle}{\langle (\delta\Delta E_{\mathrm{cat}})^2\rangle}, \tag{4}$$

with $C_{\mathrm{an}}(t)$ defined analogously; we also report their cross-correlation function [11]. It is important to recognize that $C_{\mathrm{cat}}(t)$ gives the time correlation function for the *gross* contribution of the cation to the spectral shift, but does not indicate the *net* contribution. If cation and anion motions are correlated, components of the time-dependence of $\Delta E_{\mathrm{cat}}(t)$ and $\Delta E_{\mathrm{an}}(t)$ may cancel, leading to elimination of those components from the time-dependence of $\Delta E(t)$. We therefore construct a more direct measurement of cation and anion contributions below.

Eqs. (1) and (3) may be combined to yield

$$\begin{aligned} C(t) &= \frac{\langle \delta\Delta E(0)(\Delta E_{\mathrm{cat}}(t) + \Delta E_{\mathrm{an}}(t) - \langle\Delta E\rangle)\rangle}{\langle (\delta\Delta E)^2\rangle} \\ &= \frac{\langle \delta\Delta E(0)(\delta\Delta E_{\mathrm{cat}}(t) + \delta\Delta E_{\mathrm{an}}(t))\rangle}{\langle (\delta\Delta E)^2\rangle}, \end{aligned} \tag{5}$$

where we have used $\langle\Delta E\rangle = \langle\Delta E_{\mathrm{cat}}\rangle + \langle\Delta E_{\mathrm{an}}\rangle$. This can be rewritten as

$$C(t) = g_{\mathrm{cat}}(t) + g_{\mathrm{an}}(t), \tag{6}$$

where

$$g_{\mathrm{cat}}(t) = \frac{\langle \delta\Delta E(0)\delta\Delta E_{\mathrm{cat}}(t)\rangle}{\langle (\delta\Delta E)^2\rangle}, \tag{7}$$

and $g_{\mathrm{an}}(t)$ is defined analogously. These terms represent time correlation functions between $\Delta E(t)$ and its respective cation and anion components, normalized to yield the total signal on their addition. We will refer to $g_{\mathrm{cat}}(t)$ and $g_{\mathrm{an}}(t)$ as component time component correlation functions (CTCFs). Shim and co-workers [9] further decompose Eq. (5) into pure cation, anion and cross-terms, but we believe the present formulation is better suited to our discussion of collective motion.

The CTCFs are distinct from the correlation functions for $\Delta E_{\mathrm{cat}}(t)$ and $\Delta E_{\mathrm{an}}(t)$, defined in Eq. (4). $C_{\mathrm{cat}}(t)$ gives the time correlation function for the cation contribution to the Stokes shift. In the limit where cation and anion motions are uncorrelated, this is equivalent to $g_{\mathrm{cat}}(t)$. However, if the solvent contains collective motion involving cations and anions, $\Delta E_{\mathrm{cat}}(t)$ and $\Delta E_{\mathrm{an}}(t)$ may be correlated. This permits cancellation of their respective contributions to $\Delta E(t)$, leading to significant differences in CTCFs compared to pure time correlation functions.

3. Results and discussion

It is worth examining the raw data in $\Delta E(t)$ and its components before calculating the time correlation functions. The large difference in magnitude between the average of $\Delta E_{\mathrm{cat}}(t)$ and $\Delta E_{\mathrm{an}}(t)$ shown in Fig. 2 indicates that on average cation interactions increase the difference in energy between ground and excited state energies (i.e., stabilize the ground state), while anion interactions contribute less to the total stabilization. This may arise due to the details of local solute–solvent interactions, some of which are discussed in our previous work [10]. From the standpoint of time-dependent behavior, however, both $\Delta E_{\mathrm{cat}}(t)$ and $\Delta E_{\mathrm{an}}(t)$ show similar fluctuations, so their relative importance to dynamical behavior is unclear from the raw data. The statistical data presented in Table 1 indicate that the fluctuations in $\Delta E(t)$ are smaller than those associated with $\Delta E_{\mathrm{cat}}(t)$ and $\Delta E_{\mathrm{an}}(t)$, which is possible only if $\Delta E_{\mathrm{cat}}(t)$ and $\Delta E_{\mathrm{an}}(t)$ are correlated. This implies the existence of collective motion, a point we discuss further below.

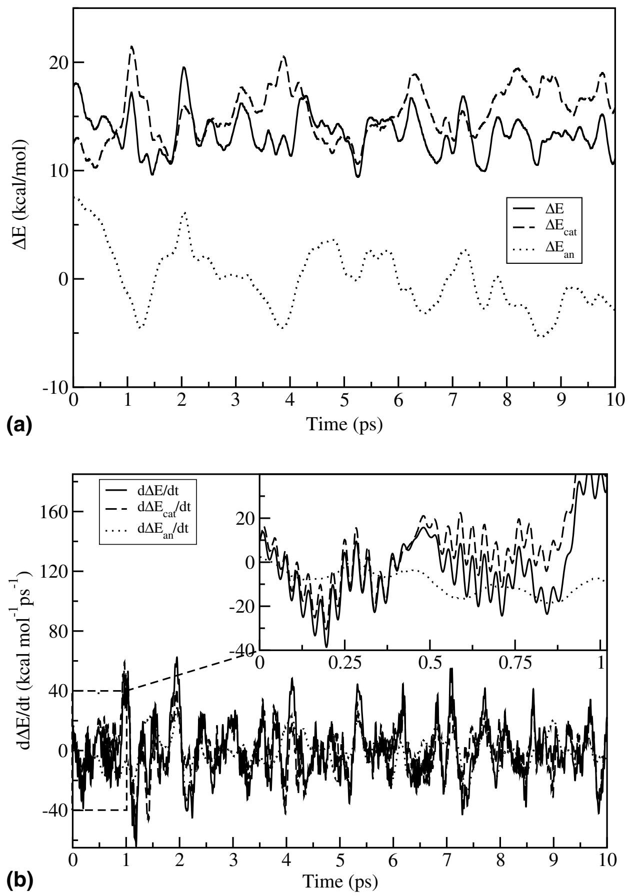

Fig. 2. (a) The value of ΔE and its cation and anion components for a sample trajectory. (b) The time-derivative of ΔE and its cation and anion components, same trajectory.

Table 1
Mean and standard deviation for the time-dependence of fluctuations in the excitation energy

	Mean (kcal/mol)	σ (kcal/mol)
$\Delta E(t)$	14.0	3.9
$\Delta E_{\mathrm{cat}}(t)$	8.4	6.6
$\Delta E_{\mathrm{an}}(t)$	5.5	7.5

Timescales for cation and anion motion are most obvious when considering the time derivatives in $\Delta E_{\mathrm{cat}}(t)$ and $\Delta E_{\mathrm{an}}(t)$ shown in Fig. 2b. Both signals oscillate on timescales of ~200 fs or longer, but the cation also displays a much shorter timescale motion on the order of 30 fs. This is likely associated with rotational (librational) motion, which is known to be faster than diffusion in most solvent systems [12]. The single-site treatment of the anion precludes rotational motion for this species.

Time correlation functions in these variables are presented in Fig. 3. The overall structure of $C(t)$ is consistent with existing data on solvation dynamics in ILs. The sub-picosecond solvent response accounts for ~30% of the Stokes shift for betaine-30, comparable to the ~50% inferred from experimental studies of coumarin-153 [1]. A more direct comparison to experimental data is not possible, as we are not aware of any published photophysical studies in imidazolium-based ILs with sub-picosecond time resolution. Comparing the TCFs, we observe that $C(t)$ decays much more rapidly than $C_{\mathrm{cat}}(t)$ and $C_{\mathrm{an}}(t)$, and that $C_{\mathrm{crs}}(t)$ decays more slowly

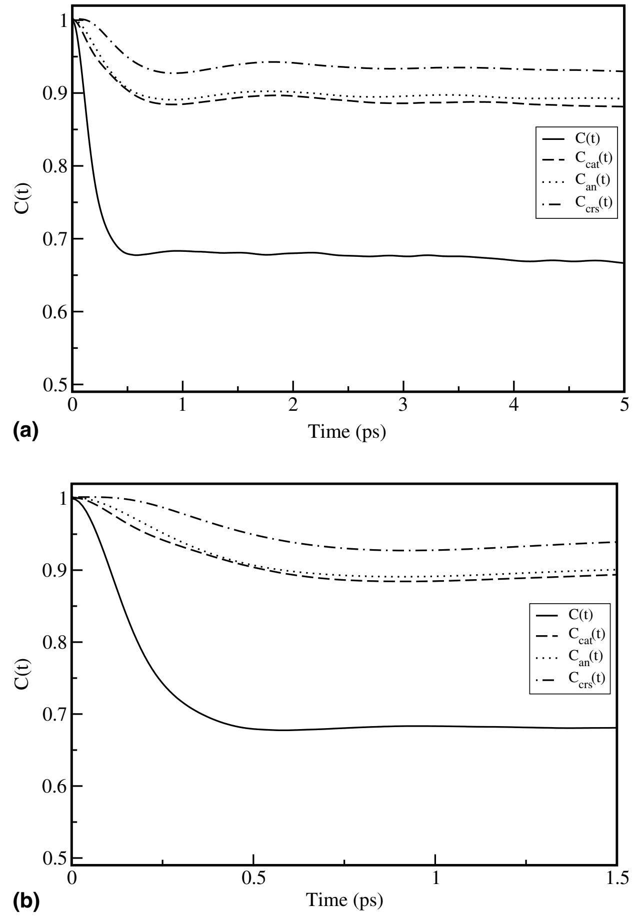

Fig. 3. (a) Time correlation functions vs. time, as described in the text. (b) As above, with axes rescaled.

still. These observations are quantified by fitting the first 2.5 ps of each TCF to a Gaussian function

$$F(t) = A \exp\left[-\frac{t^2}{\tau^2}\right] + B, \tag{8}$$

and the results of this fit are reported in Table 2. Using τ as the characteristic timescale, we observe that the initial response for the time-dependent Stokes shift is ~200 fs, consistent with experimental results on other chromophores [1]. The decay times for $\Delta E_{\mathrm{cat}}(t)$ and $\Delta E_{\mathrm{an}}(t)$, however, are both ~320 fs, and the decay time for their cross-correlation function is on the order of 400 fs.

Table 2
Characterization of time correlation functions and time component correlation functions, as described in the text

	τ (ps)	A	B	R^2
$C(t)$	0.192	0.309	0.681	0.994
$C_{\mathrm{cat}}(t)$	0.320	0.101	0.891	0.983
$C_{\mathrm{an}}(t)$	0.318	0.102	0.898	0.988
$C_{\mathrm{crs}}(t)$	0.390	0.0713	0.936	0.968
$g_{\mathrm{cat}}(t)$	0.157	0.137	−0.229	0.953
$g_{\mathrm{an}}(t)$	0.220	0.185	0.894	0.994

R^2 indicates the ‘goodness-of-fit’ correlation coefficient.

These time-dependent behaviors are possible only if the solvent exhibits long-lived collective modes incorporating both cation and anion motion, as suggested by examination of the standard deviation in $\Delta E(t)$ and its components. For at least some of these collective motions, cation and anion contributions to the time-resolved Stokes shift must cancel in displacement along the coordinate describing the mode. If they did not cancel, these longer-lived modes would increase the initial decay time for $C(t)$.

The fact that the lifetime of $C_{\mathrm{crs}}(t)$ is longer than that of $C_{\mathrm{cat}}(t)$ or $C_{\mathrm{an}}(t)$ is an indicator of more complex behavior. It suggests that the character of the collective motion may change on 320 fs timescales (leading to decay in $C_{\mathrm{cat}}(t)$ and $C_{\mathrm{an}}(t)$), but cation and anion motions remain correlated even after the destruction of the mode. An equally valid interpretation might be that the collective motion can survive small perturbations, and so the mode remains stable even after motion along it has been partially randomized by interaction with the bath. This would represent Brownian motion in a metastable mode. The existence of long-lived cation–anion correlations is further supported by examination of the region beyond the initial (sub-picosecond) decay in Fig. 3, where it is clear that $C_{\mathrm{cat}}(t)$, $C_{\mathrm{an}}(t)$ and $C_{\mathrm{crs}}(t)$ show oscillations on the order of 2 ps, and these oscillations are absent in $C(t)$.

The CTCFs are shown in Fig. 4, with the total $C(t)$ shown for reference. The negative value of $g_{\mathrm{cat}}(t)$ indicates that, based on the form of Eq. (3), the values of $\delta\Delta E(t)$ and $\delta\Delta E_{\mathrm{cat}}(t)$ are anticorrelated, such that $\Delta E(t) < \langle \Delta E \rangle$ when $\Delta E_{\mathrm{cat}}(t) > \langle \Delta E_{\mathrm{cat}} \rangle$, and vice versa. The reverse is true for $\Delta E_{\mathrm{an}}(t)$. The persistence of this phenomenon on 5 ps timescales indicates this cancellation is associated with a low frequency mode that is not one of the modes responsible for the short-time behavior of the TCFs plotted in Fig. 3.

As for the TCFs, the CTCFs were fitted to a Gaussian of the form of Eq. (8), and are reported in Table 2. The first point of interest is that the initial decay functions for $g_{\mathrm{cat}}(t)$ and $g_{\mathrm{an}}(t)$ are 157 and 220 fs respectively, indicating that they move on comparable timescales during the initial decay. The slightly more rapid response for the cation may arise from the inclusion of rotational motions. Eq. (6) indicates that the magnitudes of the CTCFs represent their contribution to the time-dependent Stokes shift. The value of A in Eq. (8) may be viewed as a measure of the magnitude of the contribution of $g_{\mathrm{cat}}(t)$ and $g_{\mathrm{an}}(t)$ to $C(t)$, and their respective values of 0.137 and 0.185 suggest both cations and anions play a significant role in the sub-picosecond decay process. These observations contradict the idea that cations and anions move on disparate timescales.

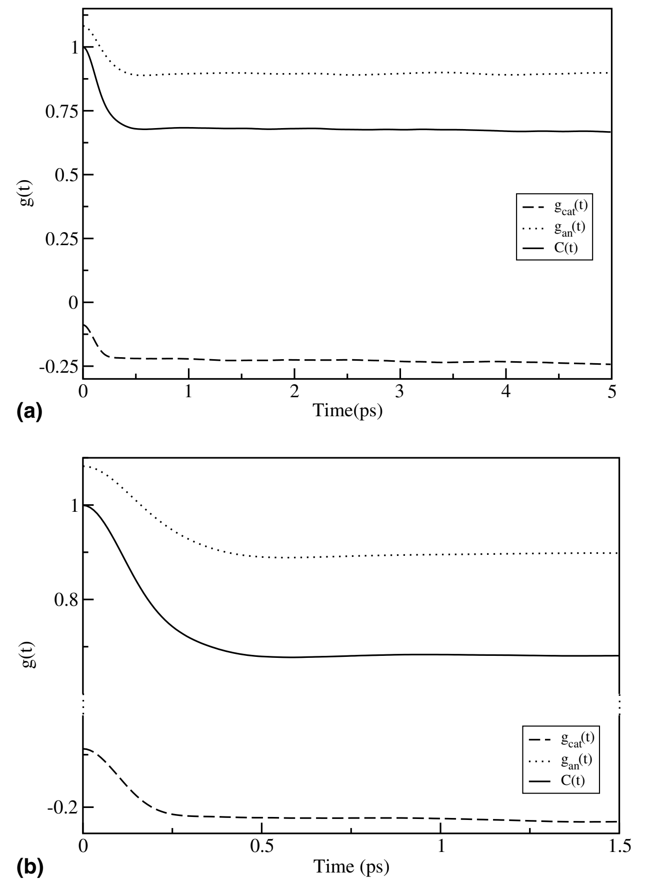

Fig. 4. (a) Cation and anion component time correlation functions vs. time, as described in the text. The time correlation function for the Stokes shift $C(t)$ is shown for reference. (b) As above, with axes rescaled. Note the break in the y-axis.

4. Conclusion

The results presented in this work are in disagreement with Shim and co-workers [9] earlier simulations of solvation dynamics in IL systems. The authors find that the magnitude of the cation contribution to the sub-picosecond response of $C(t)$ is much less than that for $C_{an}(t)$, and also observe a very weak sub-picosecond response in $C_{crs}(t)$. Based on this, the authors ascribe the initial sub-picosecond decay to purely anionic motion. While the authors use a slightly different force field and solvent system, both studies employ a rigid treatment of the imidazolium ring and a single-site treatment of the anion. The treatment of the solvent is therefore very similar in both studies and seems unlikely to be responsible for the observed discrepancies. The temperature difference between the two studies (400 vs. 300 K in the present study) might also be relevant, but the strength of inter-ion Coulomb interactions should still support collective motion at 400 K. We suspect that the discrepancy lies in the treatment of the chromophore, which in the Shim study is taken to be a diatomic species with a 3.5 Å bondlength. The relatively diffuse distribution charge in the cation ring may prevent close association with a solute on this lengthscale, leading to weak cation–chromophore interactions. This leads to a situation where $\langle(\delta\Delta E_{cat})^2\rangle \ll \langle(\delta\Delta E_{an})^2\rangle$, and the Stokes shift is dominated by anion interactions. In this scenario collective motions would still be necessary to facilitate anion motion, but the weakness of the cation signal would make them invisible to analysis of $C(t)$ or its components.

While the Shim model may be relevant to small-molecule dynamics, the betaine-30 chromophore employed in the present study represents a more physically realistic model for the aromatic chromophores typically used in photophysical studies. That being the case, we believe our analysis of $g_{cat}(t)$ and $g_{an}(t)$ demonstrates that both cation and anion species contribute to the experimentally observed sub-picosecond response of chromophores in IL systems. This contradicts the earlier suggestion that cation and anion motions occur on different timescales [2]. We speculate that the two timescales observed in imidazolium species may in fact be representative of different lengthscales for solvent response. Our previous work [10] demonstrates that solute–solvent interactions are screened within the first two solvation shells on thermodynamic timescales, but thermal fluctuations lead to long-ranged Coulomb interactions on timescales of hundreds of picoseconds. If the initial solvent response represents a reorganization of the nearest solvation shells, this reorganization may partially screen the electric field of the chromophore. Subsequent reorganization of more distant ions would then be contingent on the disruption of screening effects associated with thermal fluctuations of the solvent, retarding the process. Such a mechanism is consistent with the nanosecond timescale dynamics observed in experiment.

An equally intriguing result is the importance of collective cation and anion motion on sub-picosecond timescales. Strong Coulomb forces between ions make this a reasonable possibility, but the fact that the cross-correlation between cation and anion motion is longer-lived than the autocorrelation function in either ion is suggestive of complex dynamics. The fact that some of these modes have no net interaction with the chromophore makes them invisible to experimental studies of this type, but does not preclude their visibility to other experiments (e.g., Kerr effect spectroscopy). We note that in our previous study of solute–solvent interactions, we found that interactions with individual solvent ions were very strong, and only cancelled out on average. This creates the possibility that the collective motion may in fact be long-lived local modes associated with the intermolecular vibration of a single ion pair. Understanding these motions – and their susceptibility to various spectroscopies – will be the subject of future work.

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