Nonequilibrium versus equilibrium molecular dynamics studies of solvation dynamics after photoexcitation of OCIO

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The results of our earlier work [C. Brooksby, O. V. Prezhdo, and P. J. Reid, J. Chem. Phys. 119, 9111 (2003)] rationalizing the surprisingly weak solvent dependence of the dynamics following photoexcitation of chlorine dioxide in water, chloroform, and cyclohexane are thoroughly tested. Comparisons are made between equilibrium and nonequilibrium solvent response, equilibrium response in the ground and excited electronic states, as well as the cumulant and direct evaluation of the optical response function. In general, the linear response and cumulant approximations are found to hold, although minor deviations are found with all solvents. The ground state, linear response, and cumulant data show best agreement with experiment, most likely due to the better tested ground-state force field and the robust behavior of the linear response and cumulant approximations. The main conclusion of our earlier work explaining the weak solvent dependence by the domination of the van der Waals interaction component remains intact within the more advanced treatments. However, the molecular origin of this surprising experimental observation is different in water and chloroform compared to cyclohexane. © 2007 American Institute of Physics. [DOI: 10.1063/1.2790422]

I. INTRODUCTION

Halooxides are an important class of compounds in atmospheric chemistry since the environmental impact of these compounds arises from their ability to produce atomic halogens (e.g., Cl).1–6 The fascinating aspect of this chemistry is that the extent of halogen production depends on the environment in which the chemistry occurs. For example, the halooxide chlorine dioxide (OCI0) has received considerable interest due to its potential as a reservoir species for Cl in the stratosphere. The following reaction channels are available to OCI0 following photoexcitation resonant with the \( ^2B_1 \rightarrow ^2A_2 \) electronic transition centered at \( \sim 360 \) nm:  

\[
\begin{align*}
\text{OCI0} + h\nu &\rightarrow \text{ClO}^2(2\Pi) + O(3P_g), \\
\text{OCI0} + h\nu &\rightarrow \text{Cl}(2P_u) + O_2(1\Delta_g, 3\Sigma_g^-), \\
\text{OCI0} + h\nu &\rightarrow \text{ClOO} + \text{Cl}(2P_u) + O_2(3\Sigma_g^-, 1\Delta_g) .
\end{align*}
\]

Of relevance to halogen-mediated ozone depletion is the ability of OCI0 to photochemically produce Cl via reactions (ii) and (iii). The quantum yield for Cl production \( (\Phi_{\text{Cl}}) \) is dependent on phase, with \( \Phi_{\text{Cl}} \leq 0.04 \) in the gas phase, but increasing in condensed environments.\(^2\)\(^7\)\(^\ldots\)\(^14\) The dependence of \( \Phi_{\text{Cl}} \) makes this compound an excellent case in which to investigate solvent-dependent photochemical reactivity in an environmental context. In order to understand the origin of the phase-dependent reactivity of OCI0, it is critical to understand not only the solvent-dependent properties of OCI0 itself, but also the response of the surrounding solvent molecules to OCI0 photoexcitation. This solvent response is clearly complex since the experimental data indicate that, while branching between the OCI0 dissociation pathways is dependent on presence of a solvent,\(^15\) the initial structural evolution out of the Franck-Condon region of the optically-prepared \( ^2A_2 \) state is not extremely dependent on the details of the surrounding solvent.\(^16\) Specifically, the initial OCI0 structural-relaxation dynamics and optical dephasing times are the same in water (polar and protic), chloroform (polar and aprotic), and cyclohexane (nonpolar).

We previously reported classical molecular dynamics studies of the solvent response to OCI0 photoexcitation.\(^17\)\(^,18\) The specific goal of these studies was to ascertain the origin of the solvent-invariant homogeneous linewidth as determined by resonance Raman intensity analysis, and to determine whether the invariance of this linewidth to solvent reflected a common component of the solvent response.\(^15\),16,19 We found that the solvation dynamics following OCI0 photoexcitation were dominated by short-ranged mechanical solute-solvent interactions regardless of the identity and electrostatic properties of the solvent. Low-frequency translational motions dominated the coupling spectrum, and virtually no contribution to the relaxation was achieved through intramolecular solvent motions. The calculated timescales of solvent-induced optical dephasing were in good agreement with experiment for all solvents, supporting the conclusion that mechanical or nonpolar solvation is responsible for the optical dephasing.

Our earlier MD studies invoked two major assumptions. First, we assumed that linear response (LR) was operative, allowing use of the fluctuation-dissipation theorem to relate the nonequilibrium solvent response to the fluctuations of the...
excitation energy gap due to fluctuations of the solvent at equilibrium. Second, the cumulant expansion truncated at the second order was used to compute the optical response function for comparison to the experimentally determined homogeneous linewidth. Here, we present additional MD studies in which these assumptions are tested. Specifically, we report here a comparison of the solvent response to OClO photoexcitation determined by nonequilibrium and equilibrium MD studies. The central result of this comparison is that linear-response is indeed valid, and that the solvent invariance of the homogeneous linewidth reflects the dominance of short-ranged mechanical forces in the solvent response to OClO photoexcitation. The dominance of mechanical solvation is surprising considering that OClO undergoes a 25% change in charge distribution while only experiencing a 10% change in size. If photoexcitation were to result in a change in the charge distribution of the solute only, then the solvent motions that facilitate the relaxation should be well represented in an equilibrium simulation. In part, this is due to the fact that the electrostatic interaction is long-ranged and involves many solvent molecules that have not been displaced far from the equilibrium by the perturbed solute. In contrast, translational motion by the nearby solvent is expected to be the main source of relaxation upon a change in the size of the solute. These motions often differ between the equilibrium and nonequilibrium cases, leading to a breakdown of the linear-response approximation. To complicate the matter further, in a system that experiences both a change in size and a change in charge simultaneously, the two types of relaxation play off one another, making accurate predictions of whether the response is linear or not more challenging. The above arguments, plus the fact that OClO is one of the relatively few small but real molecules whose solvation dynamics has been extensively studied experimentally, motivates us to continue our investigations of this system by a nonequilibrium simulation.

The paper is organized as follows. The relevant results from the solvent response and optical line shape theories as well as the simulation details are first presented. This presentation is followed by a discussion of solvation of the ground and excited solute in water, chloroform, and cyclohexane. The equilibrium and nonequilibrium solvation dynamics are analyzed and compared in order to identify the solvent motions that are operative in the solvation process, and to test the validity of the LR assumption. Finally, we investigate solvent-induced dephasing and optical line shape, and test the cumulant approximation with comparison to experiment. The key results are summarized in Sec. V.

II. THEORY

The nonequilibrium solvent response function $S(t)$ is defined through the evolution of the electronic energy gap $U(t)$ by

$$S(t) = \frac{U(t) - U(\infty)}{U(0) - U(\infty)},$$

where $U(t)=E_{\text{exc}}(t)-E_{\text{gnd}}(t)$. Apart from the very early times following the photoexcitation, when the geometry of the solute evolves from the ground to the excited state equilibrium, the dynamics of the electronic energy gap is determined by the response of the solvent to the change in the solute’s geometric and electronic structure.

The fluctuation-dissipation theorem relates the nonequilibrium dissipation of the excess energy to the fluctuation of the energy gap at equilibrium. The result should be independent of whether one considers the ground or excited state equilibrium. The fluctuation-dissipation theorem leads to the LR approximation for the solvent response function, $C(t)$,

$$C(t) = \frac{\langle \delta U(t) \delta U(0) \rangle}{\langle \delta U^2 \rangle},$$

where $\delta U(t) = U(t) - \langle U \rangle$. Both $S(t)$ and $C(t)$ defined above are normalized to 1 at $t=0$. The overbar in the definition of $S(t)$ refers to a nonequilibrium average, performed over an ensemble of nonequilibrium trajectories corresponding to different solvent configurations at the instant when the solute molecule is photoexcited. The angular brackets in the definition of $C(t)$ denote an average over an equilibrium ground or excited state trajectory.

An equality of these two response functions would validate the application of the LR theory to a particular system. With notable exceptions, molecular dynamics simulations have found that LR is obeyed in a wide variety of solute/solvent combinations. Generally, LR can be expected to hold if changes in the solute properties induce a small perturbation in the solvation structure.

The solvation structure is typically characterized by solute-solvent distribution functions, the simplest of which is the radial distribution function defined by

$$g(r) = \frac{\rho(r)}{\rho},$$

where $\rho(r)$ is the density of solvent molecules at distance $r$ from the solute, and $\rho$ is the average density in the solvent. The location of the solute and solvent molecules is determined by their centers of mass. The oscillatory structure of RDF indicates the location of the solvent shells surrounding the solute molecule. The decay of the oscillation identifies the scale on which the solvent feels the presence of the solute. At large $r$ the RDF defined by Eq. (3) becomes unity. A comparison of the ground and excited state equilibrium RDFs shows how much the solvent shells are changed in response to the excitation.

The solute energy gap $U(t)$ that is used to define the solvent response function, Eqs. (1) and (2), can also be used to elucidate information about the underlying molecular motions involved in the solvate’s relaxation in response to the solute excitation. The Fourier transform (FT) of the energy gap produces a spectral density,

$$F(\omega) = \left| \frac{1}{\sqrt{2 \pi}} \int_{-\infty}^{\infty} dt e^{-i \omega t} [U(t) - \langle U \rangle] \right|^2,$$

that can be compared to the known spectral densities of the pure solvents. Comparison of the spectral densities determined by the energy gap of the solute with the spectral densities of the pure solvents leads to identification of the mo-
molecular motions that do and do not participate in the relaxation mechanism. The spectral densities of pure water, chloroform, and cyclohexane were reported in our earlier work.\textsuperscript{17,18}

Solvent response can be related to a number of optical properties.\textsuperscript{33–36} The nonequilibrium solvent response function is in direct correspondence with the time-dependent Stokes shift. The equilibrium response is most easily compared with the linewidth of the electronic transition. In the absence of inhomogeneous broadening, associated with an ensemble of solute molecules interacting with different solvent environments, the homogeneous linewidth $\Gamma$ equals the inverse of the dephasing time $T_2$,

$$\Gamma = \frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2}.$$  \hspace{1cm} (5)

The two contributions to the homogeneous linewidth are the excited state lifetime $T_1$ and pure dephasing $T_2$. The excited state lifetime of OCIO is many times greater than the pure dephasing time. Therefore, the $T_1$ contribution to the linewidth is small, and $\Gamma$ is dominated by the $T_2$ term.\textsuperscript{16}

The results of equilibrium MD can be used to evaluate the pure dephasing time. Pure dephasing was calculated in our previous work\textsuperscript{17,18} via a cumulant expansion method\textsuperscript{15} using the energy gap autocorrelation function, i.e., the unnormalized solvent response function,

$$\langle \delta U(t) \delta U(0) \rangle = C(t) \ast \langle \delta U^2 \rangle.$$  \hspace{1cm} (6)

The pure dephasing function $D(t)$ is computed from the unnormalized solvent response function by double integration and subsequent exponentiation,

$$g(t) = \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \langle \delta U(\tau_2) \delta U(0) \rangle,$$

$$D(t) = \exp[-g(t)].$$  \hspace{1cm} (7)

In the present, we test application of the cumulant expansion approach to the solvation dynamics of OCIO in water, chloroform, and cyclohexane by computing the dephasing function directly.\textsuperscript{34–36}

$$D(t) = \exp[i\omega t] \langle \exp[-i\hbar U(\tau)] \rangle_T,$$

$$\omega = \langle U(\tau) \rangle_{\tau \neq \hbar}.$$  \hspace{1cm} (8)

Equation (7) is the second-order cumulant approximation to Eq. (8).

In order to assign solvent relaxation timescales and determine the pure dephasing time, the solvent response and dephasing functions are fitted to the following functional forms. The solvent response functions, Eqs. (1) and (2), are represented by a sum of the Gaussian and exponential components,

$$y = A \ast \exp[-(\omega t)^2/2] + (1-A) \ast \exp[-it/\tau].$$  \hspace{1cm} (9)

The Gaussian part of the relaxation represents the faster inertial solvent response, while the exponential component describes the slower diffusive regime. The constant $A$ represents the weight of the Gaussian component. The homogeneous dephasing functions, Eqs. (7) and (8), are fitted to a Gaussian form,

$$D(t) = \exp[-(\Gamma t/\hbar)^2].$$  \hspace{1cm} (10)

The $\Gamma$ from the fit is compared directly to the experimental linewidth.

### III. MODELS AND SIMULATION DETAILS

The classical models for the water, chloroform, and cyclohexane solvents and the OCIO molecule in its ground and excited electronic states are the same as in our previous simulations.\textsuperscript{17,18} Given the choice between the standard OCIO model and that fine-tuned by Benjamin and co-workers,\textsuperscript{37–40} we focus on the Benjamin model, which gave better agreement with the experimental data. The properties of the OCIO molecule in its equilibrium ground and excited state geometries are derived based on the contracted multipreference configuration interaction (CMRCI) calculations of Peterson.\textsuperscript{41} Upon photoexcitation, the OCIO bond length increases and the bond angle decreases by 10%. At the same time, the atomic charges change by 25%. The use of fixed solute geometry and charges was justified because the solvent response was nearly complete before the expected lifetime of the $^2A_2$ excited state, $\sim$200 fs in water and cyclohexane and $\sim$400 fs in chloroform. Water was described by the SPC/F model.\textsuperscript{42} Chloroform is represented by the all-atom model developed by Kollman et al.\textsuperscript{43,44} The cyclohexane model was taken from the CHARMM parameter set.\textsuperscript{45,46} All three solvent models are completely explicit and fully flexible.

The MD simulations were performed using TINKER programs.\textsuperscript{47} Initial equilibrium was established for each of the neat solvents in a cubic box; 500 water, 400 chloroform, or 200 cyclohexane molecules were used to provide appropriate densities for the solvents at 298 K and 1 atm. A single OCIO molecule held rigid by the RATTLE algorithm, but allowed to translate and rotate freely, was added to each solvent. The systems were re-equilibrated in the presence of the solute.

The ground-state equilibrium results are reproduced from Refs. 17 and 18. The excited state MD data reported here are based on the 100 ps microcanonical trajectory obtained with the velocity Verlet algorithm and a 1.0 fs time step. The nonequilibrium MD simulations were carried out to mimic the experimental conditions. A ground-state 400 ps trajectory was used as the source for the initial conditions. This trajectory was divided into 1 ps intervals. The interval size ensured that the chosen starting points would be uncorrelated with initial points in subsequent intervals. A random initial condition for the nonequilibrium simulation was chosen within each interval. The nonequilibrium system was also analyzed using a microcanonical trajectory with the velocity Verlet algorithm. In all of the calculations, periodic boundary conditions were used with a smooth spherical cutoff that terminated all potential energy interactions at a dis-
Fig. 1. Radial distribution functions, Eq. (3), for the solvation of OCIO in water, chloroform, and cyclohexane. The ground and excited electronic states of the OCIO molecule are represented by the solid and dashed lines, respectively.

IV. RESULTS AND DISCUSSION

A. Solvation structure of the ground and excited states

First, consider the difference in the solvation structure of the ground and excited state OCIO molecules in the three solvents. The structural difference between the equilibrated solutions can provide clues to the nonequilibrium dynamics that lead from the ground to the excited state equilibrium. The solvation structure is represented by the RDFs shown in Fig. 1.

The RDFs exhibit a well-pronounced peak corresponding to the first solvation shell and a less well-defined and broader peak corresponding to the second solvation shell. The distance between the solute molecule and the first solvation shell is largest in cyclohexane and smallest in water. This correlates with the size of the solvent molecules. Cyclohexane is a larger molecule than water or chloroform; thus, it is sterically more difficult for the cyclohexane to get close to the OCIO molecule. Similarly, chloroform is larger than water and, therefore, it remains farther away from OCIO.

Particularly interesting are the changes in the first solvation shell induced by the photoexcitation. In water, the first RDF peak shifts to shorter distances, indicating that water molecules are able to approach OCIO more closely. Even though the OCIO bonds become weaker and longer upon photoexcitation, the bond angle decreases, making the molecule more compact and allowing water into a closer proximity. The first solvation peak of chloroform becomes substantially broader, with the front shoulder also extending to shorter distances. In contrast, the solvation structure of cyclohexane changes much less. This result, in combination with the bulky size of the cyclohexane molecules and the longest first solvation shell distance, indicates that cyclohexane creates a relatively large cavity. The OCIO molecule fits in quite freely, and the 10% change in the molecule size is easily accommodated inside the cavity.

The comparison of the ground and excited state RDFs leads to an interesting conclusion that the domination of the van der Waals solvent response over the electrostatic component has different origins in water and chloroform on the one hand and cyclohexane on the other hand. Water and chloroform are polar solvents and, therefore, should exhibit electrostatic response. The mechanical response dominates, however, because the solvent nearest to the solute changes its structure, perturbing the short-ranged van der Waals interaction. Cyclohexane is nonpolar and, therefore, cannot respond by electrostatic interaction. Even though the cyclohexane solvation structure changes far less, only mechanical response is possible.

B. Equilibrium and nonequilibrium solvent response

Our previous studies were based on the ground-state equilibrium solvent response simulation. Currently, we test the earlier conclusions with the excited state equilibrium simulation as well as nonequilibrium MD, the latter directly mimicking the experimental situation.

Figure 2 presents the normalized solvent response functions for the ground and excited state equilibria, Eq. (2), together with the nonequilibrium solvent response, Eq. (1), for the solute/solvent systems studied. Table I shows the corresponding unnormalized initial values. It is worth noting that the electrostatic component is extremely small and approaches zero in the nonaqueous solvents. The cross correlation between the van der Waals and electrostatic components of the response is even smaller. The solvent response functions have been fitted using Eq. (9) with the fitting parameters presented in Table II. In addition to the total response function, Fig. 2 shows the response due to the electrostatic and van der Waals interaction components separately. Although there are slight differences in the response functions obtained by the excited equilibrium, ground equilibrium, and nonequilibrium calculations, overall the relaxation times are very similar. Also, the relative contributions by the electrostatic and mechanical relaxation are the same in each case. This indicates that the application of LR and fluctuation-dissipation theorem is appropriate for the OCIO systems.

The results of the nonequilibrium analysis confirm earlier results from the equilibrium data showing that the response of the solvent to the photoexcitation of OCIO is predominately due to short-ranged mechanical forces. Even though the electrostatic response is markedly different between the three solvents in both amplitude and timescale, it is significantly weaker than the mechanical response. As expected, the amplitude of the electrostatic component in the cyclohexane environment is close to zero, Table I. However, even in the extremely polar water the electrostatic contribu-
The inertial and diffusive components of the solvent response, described by the Gaussian and exponential parts of the fitting function, Eq. (9), exhibit markedly different magnitudes. The inertial response occurs purely by solute-solvent interactions and can be well described ignoring energy redistribution within the solvent. On the contrary, the diffusive response relies on longer-ranged solute-solute interactions and involves energy exchange between different solute molecules and solvation shells. The inertial response seen in the OCIO systems results in extremely fast relaxation that, in conjunction with the lack of dependency on solvent type, supports agreement with the mechanical nature of the solvent response. In addition, the relaxation is essentially over 200 fs following the OCIO photoexcitation. The differences among the three solvents arising due to the long-range electrostatic forces cannot manifest themselves on this timescale.

An unusual behavior is seen with the nonequilibrium solvent response functions for water and chloroform: The functions exhibit an initial rise. By definition of the nonequilibrium solvent response, Eq. (1), the initial rise implies that, for a brief period of time after initiating the photoexcitation, the OCIO energy gap continues to increase before decreasing. Normally, solvation dynamics following the photoexcitation lowers the excited state energy, at the same time destabilizing the ground state. Upon closer examination of the energy gap data, we noticed that the excited state was indeed lowered; however, the ground-state energy was briefly lowered as well. This occurred with the van der Waals response component, but not with the electrostatic component. The origin of this unusual behavior should lie with the peculiarities of the initial restructuring of the first solvation shell: As evidenced by the RDFs shown in Fig. 1, the excited OCIO is more closely solvated by water and chloroform than the ground-state OCIO.

C. Molecular motions participating in the solvent response

The FT of the OCIO energy gaps along the ground and excited state equilibrium trajectories defines the influence...
spectrum, Eq. (4), which characterizes the solvent motions actuating the solvent response. The influence spectra are shown in Fig. 3. The influence spectra for the systems in the ground state versus the excited state are similar in general. The motions responsible for relaxation have low frequencies, less than 200 cm\(^{-1}\), indicating that the relaxation of the solvents occurs by translational motions. Even water, with many pronounced high-frequency modes, responds to the OClO photoexcitation only with its slow modes. The participation of the low-frequency motions in the solvation dynamics justifies the use of classical MD and obviates the need for more sophisticated treatments.\(^{48-50}\) Comparing the influence spectra of van der Waals and electrostatic components on the OClO energy gaps we observe for the electrostatic components of the spectral density are presented. The response of the solvent to the photoexcitation of OClO is dominated by low-frequency translational motions.

**D. Pure-dephasing function and homogeneous linewidth**

The cumulant, Eq. (7), and direct, Eq. (8), pure-dephasing functions obtained from the excited state equilibrium trajectories are plotted in Fig. 4. The ground-state data were reported previously.\(^{17,18}\) The functions were fit to the Gaussian form, Eq. (10). The linewidth fitting parameter \(\Gamma\) is presented in Table III together with the experimentally measured linewidths.\(^{19}\)

The direct and cumulant approaches agree very closely for the water and chloroform systems; see the top two panels of Fig. 4. Generally, the cumulant ensemble average, Eq. (7), converges much faster than the direct function, Eq. (8). The latter involves a significant amount of phase cancellation. The direct function for chloroform shown in the middle panel of Fig. 4 does approach zero, but remains off the figure scale. The direct and cumulant approaches disagree somewhat for cyclohexane (bottom panel of Fig. 4), most likely due to the more complicated structure of the solvent. MD of cyclohexane involves a number of large-scale anharmonic intramolecular motions, for instance those transforming the molecule between the bath and armchair conformation. These kinds of motions can lead to nontrivial time correlations that are not captured by the second-order correlation function, Eq. (2).

Comparison between the simulation results with the experimental data, Table III, indicated that simulation is in good agreement with experiment. Remarkably, the best

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
& Ground state & Excited state & Experimenta \\
& cumulant\(^b\) (cm\(^{-1}\)) & cumulant (cm\(^{-1}\)) & direct (cm\(^{-1}\))  \\
\hline
Water & 89 & 109 & 107 & 85  \\
Chloroform & 82 & 66 & 70 & 95  \\
Cyclohexane & 76 & 76 & 52 & 80  \\
\hline
\end{tabular}
\caption{The pure-dephasing contribution to the homogeneous linewidth \(\Gamma\) of the OClO photoexcitation determined experimentally (Ref. 16) and calculated by fitting the homogeneous dephasing functions shown in Fig. 4 to a Gaussian form, Eq. (10). The ground-state cumulant results are reproduced from Refs. 17 and 18.}
\end{table}

\(^{a}\)References 17 and 18.
\(^{b}\)Reference 16.
V. CONCLUSIONS

The unexpectedly weak solvent dependence of the timescale and mechanism of the relaxation dynamics following the OCIO photoexcitation in water, chloroform, and cyclohexane has been studied by direct nonequilibrium simulation, equilibrium simulation in the ground and excited electronic states, as well as the cumulant and direct evaluation of the optical response function. This comprehensive analysis has generally supported our earlier conclusion that the solvents respond predominantly by short-ranged mechanical forces. The uniform behavior of all three solvents, in spite of the dramatic differences in their polarities, is due to the very small contribution of the electrostatic interaction to the solvent relaxation. Support for this conclusion is found in the similarity of the response functions for all the solute/solvent systems between the equilibrium and nonequilibrium results: The response functions decay very rapidly and on the same timescale, dominated by the inertial Gaussian decay component. The conclusion is also further supported by the similarity of the influence spectra, which reveal only low-frequency translational solvent motions, irrespective of the solvent and solute’s electronic state.

The mechanisms of the solvent response do differ between water and chloroform on the one hand, and cyclohexane on the other. The change in the OCIO geometry induced by the photoexcitation affects the structure of the first solvation shells of water and chloroform with little impact on molecules further removed from the solute. Due to the involvement of only a few molecules, the differences in solvent physical properties and their impact on the response are minimized. RDFs of these solvents indicate that the solute molecules are able to approach the solute more closely when the latter is in the excited electronic state. Even though water and chloroform are polar solvents and should exhibit electrostatic response, the mechanical response dominates because the solute nearest to the solute changes its structure and perturbs the short-ranged van der Waals interaction. The solvation structure of cyclohexane does not change upon OCIO photoexcitation. However, only mechanical response is possible, since cyclohexane is a nonpolar solvent.

The similarity in the timescales of the mechanical response in the three solvents is surprising, since the molecular masses of water, chloroform, and cyclohexane are substantially different. The molecular mass difference is offset by the difference in the solvent-solvent and solute-solvent interactions. Water is a special solvent. Strong hydrogen bonding between water molecules produces an increased effective mass for aqueous translational modes. Cyclohexane and chloroform are significantly heavier than water; but the intermolecular interactions in these solvents are much weaker, and therefore, the effective masses are similar to the molecular masses. Cyclohexane is lighter than chloroform, and one may expect that cyclohexane will respond faster to a mechanical perturbation. However, the perturbation is notably weaker in cyclohexane, since it creates a larger cavity and its solvation structure remains practically unchanged upon the OCIO photoexcitation, Fig. 1.

The extensive simulations reported here validate both the LR assumption and the cumulant evaluation of the optical pure-dephasing function. These two approximations used in our earlier work are found to hold, although minor deviations can be seen with all solvents. The approximations hold because the changes in the OCIO properties induced by the photoexcitation are relatively small. The best agreement with the experimental data is achieved by the ground-state equilibrium simulation using the second-order cumulant approximation. This can be explained by the better-tested ground-state force field and the robust nature of the LR and cumulant approximations.

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