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Resonance Raman intensity analysis of chlorine dioxide dissolved in chloroform: The role of nonpolar solvation

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Absolute resonance Raman cross sections for chlorine dioxide (OCIO) dissolved in chloroform are obtained at several excitation wavelengths spanning the photochemically relevant ${}^{2}B_{1} - {}^{2}A_{2}$ optical transition. The absolute scattering cross sections of OCIO are determined by reference to the 666 cm^{-1} transition of chloroform whose absolute scattering cross sections are reported here. The time-dependent theory for Raman and absorption are used to develop a mode-specific description of the ${}^{2}A_{2}$ excited state surface. This description demonstrates that photoexcitation of OCIO leads to significant structural evolution along the symmetric stretch and bend coordinates, with only limited evolution occurring along the asymmetric stretch. This description is similar to that determined for OCIO dissolved in cyclohexane and water demonstrating that the excited-state structural evolution of OCIO is similar in these solvents. Analysis of the OCIO absolute scattering cross sections establishes that the homogeneous linewidth is 95 ± 15 cm⁻¹ in chloroform, essentially identical to the linewidths in cyclohexane and water. To establish the origin of this linewidth, the fluorescence cross section for OCIO dissolved in cyclohexane is measured and found to be consistent with an excited-state lifetime of ~ 200 fs. Comparison of this lifetime to the homogeneous linewidth establishes that the homogeneous broadening is dominated by solvent-induced pure dephasing. It is proposed that the apparent solvent independence of the homogeneous linewidth reflects the mechanical response of the solvent to the photoinitiated change in solute geometry. In support of this hypothesis, the homogeneous linewidth is reproduced using the viscoelastic continuum model of nonpolar solvation. Finally, it is argued that the restricted evolution along the asymmetric-stretch coordinate is due to dielectric solvent-solute interactions consistent with the increase in inhomogeneous linewidth with an increase in solvent polarity. © 2001 American Institute of Physics. [DOI: 10.1063/1.1362297]

INTRODUCTION

The photochemistry of chlorine dioxide (OClO) has been the subject of recent interest due to its participation in the reactive chlorine reservoir and potential role in stratospheric ozone layer depletion.¹⁻⁴ Photoexcitation resonant with the ${}^{2}B_{1} - {}^{2}A_{2}$ electronic transition ($\lambda_{max} \sim 360 \text{ nm}$) results in population of the predissociative ${}^{2}A_{2}$ state.^{1,5} Internal conversion from this state to the ${}^{2}A_{1}$ state is followed by internal conversion to the ${}^{2}B_{2}$ surface from which photoproduct production is believed to occur.^{6,7} In the gas phase, OClO photoexcitation results predominately in the formation of ClO and O, with a modest amount of Cl and O2 also produced.^{1,6–22} The production of Cl and O_2 may be preceded by the formation of the peroxy isomer, ClOO, produced by OCIO photoisomerization.⁶ Although Cl production is modest in the gas phase, with the quantum yield for atomic chlorine formation (Φ_{Cl}) being ≤ 0.04 , the production of Cl becomes substantial in condensed media with Φ_{CI} =0.1-0.2 in water and methanol, and approaching unity in low-temperature matrixes.²³⁻³⁸ In addition, the mechanism of Cl formation is dependent on solvent polarity with the $Cl+O_2({}^1\Delta_g)$ and $Cl+O_2({}^3\Sigma_g^-)$ channels dominating in nonpolar and polar solvents, respectively.³⁹ Current interest in OClO photochemistry involves understanding the factors responsible for the environment-dependent reactivity of this compound.

Recent solution phase studies of OCIO have sought to identify the solvent-solute interactions which influence the photoproduct quantum yields.^{23,24,27-31,40-48} In particular, femtosecond transient absorption and time-resolved resonance Raman studies have been performed to monitor the processes occurring after excited-state internal conversion. Two main insights have emerged from this work. First, it has been established that geminate recombination of the CIO and O photofragments resulting in OCIO formation is extremely efficient in condensed environments.^{28-30,43-46} Second, these studies have shown that Cl is produced through two distinct pathways.^{47,48} The majority of Cl is formed within 5 ps of photoexcitation, with a modest amount of Cl produced on the hundreds-of-picosecond time scale through the thermal decomposition of ClOO. This work has provided insight into the reaction dynamics of OCIO following internal conversion to the ground state, and how these dynamics are modified by the presence of solvent.

In addition to the ground-state reaction dynamics, the presence of solvent also influences the excited-state reaction dynamics of OCIO. We have explored this issue through

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resonance Raman intensity analysis (RRIA), and have found that the extent of evolution along the asymmetric-stretch coordinate is environment dependent.^{40–42,49} Our first studies were performed in cyclohexane where we anticipated that modest solvent-solute coupling would result in excited-state dynamics similar to those in the gas-phase; however, we found that the dynamics are substantially perturbed in this solvent. In the gas-phase, substantial evolution occurs along the asymmetric-stretch coordinate, but the evolution along this coordinate is extremely modest in cyclohexane.^{40,41} Extension of this work to aqueous OClO demonstrated that evolution along the asymmetric stretch is essentially nonexistent in this solvent.⁴² These observations suggest that in contrast to the gas phase where substantial evolution along the asymmetric-stretch results in a reduction in symmetry from C_{2v} to C_s , the limited evolution along this coordinate in condensed environments results in the preservation of C_{2n} symmetry. Through comparison with *ab initio* calculations and symmetry-defined state-correlation diagrams, we have proposed that this preservation of symmetry is largely responsible for enhanced Cl production in condensed environments.

A second result to emerge from the RRIA studies was that vibronic dephasing time as reflected by the homogeneous linewidth is essentially identical in cyclohexane and water. Analysis of the absolute scattering intensities established that the homogeneous linewidths in cyclohexane and water were 80 ± 15 cm⁻¹ and 85 ± 15 cm⁻¹, respectively.^{40,42} The apparent absence of fluorescence intensity in cyclohexane implied that the homogeneous linewidth was dominated by excited-state internal conversion from the optically prepared ${}^{2}A_{2}$ state to a nearby state of ${}^{2}A_{1}$ symmetry. The energetic proximity of the ${}^{2}A_{1}$ state relative to the ${}^{2}A_{2}$ state was established by analysis of the resonance Raman depolarization ratios⁴¹ and verified by fluorescence studies of matrix-isolated OClO.50 However, recent femtosecond transient absorption studies have shown that decay of the ${}^{2}A_{2}$ state in water and cyclohexane occurs on the \sim 200 fs time scale suggesting that the homogeneous linewidth is not dominated by decay of the ${}^{2}A_{2}$ surface, but is instead due to solvent-induced pure dephasing.⁵¹ This observation raises the following question, "What solvent-solute interactions are operative following OCIO photoexcitation, and why would these interactions be relatively independent of solvent?" The experiments outlined here were performed to address this question.

In this paper, we present an absolute RRIA of OCIO dissolved in chloroform. This work is motivated by the following. The dominant solvent-solute interactions between OCIO and water are expected to be dielectric and intermolecular hydrogen bonding. In contrast, both of these interactions are modest and/or absent in cyclohexane. Polar, aprotic chloroform represents an intermediate case in which dielectric solvation should be operative, but intermolecular hydrogen bonding is not. The absolute resonance Raman cross sections of OCIO are measured at a variety of excitation wavelengths spanning the ${}^{2}B_{1}-{}^{2}A_{2}$ optical transition. The quantitative determination of these cross sections; therefore,

the intensity of the 666 cm⁻¹ transition of chloroform was standardized for use as an internal scattering standard. The absolute scattering cross sections of this transition were measured at the excitation wavelengths employed in this study, and analyzed using a standard A-term cross section expression. Following standardization of the solvent, the absorption and absolute resonance Raman cross sections for OClO were obtained and modeled using the time-dependent formalism. The central result of this analysis is that the excited-state dynamics of OClO in chloroform are similar to those previously observed in water and cyclohexane, with excited-state structural evolution dominated by motion along the symmetric stretch and bend coordinates. Limited evidence is found for evolution along the asymmetric-stretch coordinate in accord with previous work. The absolute scattering cross sections constrain the homogeneous linewidth in chloroform to 95 ± 15 cm⁻¹, essentially identical to the values determined in water or cyclohexane. To ascertain the contribution of excited-state internal conversion to this linewidth, the fluorescence cross section of OCIO dissolved in cyclohexane was measured and found to be modest (5.7 ± 2.8) $\times 10^{-9} \text{ Å}^2$). When combined with an estimate for the radiative decay rate, the fluorescence cross section constrains the excited-state decay time to \sim 200 fs. This result demonstrates that the homogeneous linewidth is indeed dominated by solvent-induced pure dephasing, and that the nature of this dephasing is similar in all solvents studied to date. We propose that mechanical or nonpolar solvation dynamics are responsible for this dephasing. $^{52-62}$ In support of this proposal, we demonstrate that the homogeneous linewidth as determined by RRIA can be reproduced using a viscoelastic continuum model for nonpolar solvation, consistent with mechanical solvation dynamics dominating the solvent response to OClO photoexcitation. Finally, comparison of the inhomogeneous broadening observed in chloroform to that in cyclohexane and water demonstrates that the extent of inhomogeneous broadening increases with solvent polarity. The contribution of dipolar solvent-solute interactions to slowertime broadening processes reflects the limited evolution in the molecular dipole moment of OCIO upon photoexcitation. It is proposed that the restricted evolution along the asymmetric-stretch coordinate is due to dielectric solventsolute interactions that remain roughly at equilibrium following photoexcitation.

MATERIALS AND METHODS

Materials

The preparation of chlorine dioxide (OClO) has been presented elsewhere; therefore, only a brief description is provided here.^{40,63} Potassium chlorate (Aldrich) was combined with oxalic acid (Baker) and 2.3 M sulfuric acid (Baker). The reagents were heated to ~60 °C with continuous stirring resulting in the formation of gaseous OClO. The gaseous product was passed through a drying tube containing phosphorous pentoxide (Baker), and then bubbled through neat chloroform (Fisher, spectrophotometric grade) to produce a OClO in chloroform solution that was refrigerated until use. Caution must be used in handling this solution in that OCIO undergoes a slow reaction with chloroform over the course of a few days resulting in the production of a noxious gas of unknown composition. To maintain sample integrity, sample preparation was performed at least every other day, and the absence of sample decomposition was verified through measurement of the absorption spectrum, with the presence of a transition at \sim 230 nm serving as an indicator of sample decay.

Resonance Raman spectra and depolarization ratios

Resonance Raman spectra of OCIO dissolved in chloroform were obtained at 282.4 nm, 319.9 nm, 354.7 nm, 368.9 nm, 435.7 nm, and 532.0 nm using the direct or hydrogenshifted second and third harmonic outputs from a 30 Hz Nd:YAG laser (Spectra Physics GCR 170). Solutions of OCIO were flowed through a glass capillary (532.0 nm, 435.7 nm, 368.9 nm, and 354.7 nm) or wire-guided jet (282.4 nm, 319.9 nm, 354.7 nm, and 368.9 nm) at a rate sufficient to replenish the illuminated sample volume between excitation pulses. The scattered light was collected using standard UV-quality refractive optics, and passed through a polarization scrambler located at the entrance of a 0.75 m focal length spectrograph (Acton). The scattered light was dispersed using either a 1200 groove/mm classically ruled or a 2400 groove/mm holographic grating. Scattered light was detected using an 1100×300 pixel, back-thinned, liquid-nitrogen-cooled CCD detector (Princeton Instruments). Sample concentrations (10-40 mM) were monitored before and after each experiment using a HP diode array spectrometer, with the concentration change limited to $\leq 10\%$ for a given experiment.

Quantitative determination of the OClO resonance Raman cross sections requires knowledge of the chloroform scattering cross sections at all of the excitation wavelengths employed; however, absolute scattering cross sections for this solvent have been reported for only two excitation wavelengths.⁶⁴ Therefore, a measurement of the solvent absolute scattering cross sections was performed. Several methods have been used to quantitatively measure the absolute Raman scattering cross sections of solvents. The integrating cavity method developed by Trulson and Mathies can be used to directly measure the total cross section of the solvent of interest.⁶⁵ Asher and co-workers have measured absolute cross sections by comparing the Raman scattering of a solvent to the scattering from a suspension of barium sulfate.⁶⁶ Experimentally less complex standardization methods have also been employed, with these techniques generally involving comparative methods in which scattering intensities for the solvent of interest are compared to those of a standardized solvent.⁶⁷ This can be done in an "internal" arrangement where a mixture of two solvents is studied, or in an "external" arrangement where the Raman spectrum of the unstandardized solvent is obtained, and then the spectrum of the standardized solvent is obtained employing the identical experimental apparatus. The external method has been shown to be comparable in accuracy to the integrating cavity method.⁶⁷ Given the comparability of measurement accuracy combined with the fact that the external standard method was much easier to implement with our current experimental setup, we employed the external method to standardize the 666 cm^{-1} transition of chloroform. This mode, corresponding to the C–Cl stretching, was chosen since it is the most intense transition in the frequency region of interest, and is well separated from the OCIO transitions. The absolute scattering cross section of this transition was determined through comparison to the 802 cm⁻¹ line of cyclohexane, a well-known scattering standard.^{65,67} Both 135° and 90° scattering geometries were employed, resulting in identical cross sections within the error of the measurements (see below).

Measurement of absolute scattering cross sections also requires knowledge of depolarization ratios, defined as the intensity of light scattered with polarization perpendicular to that of the excitation light divided by the intensity of light scattered with polarization parallel to that of the excitation light.⁶⁸ Raman and resonance Raman depolarization ratios were measured at each excitation wavelength employed in this study. The excitation beam was passed through a set of quartz microscope slides oriented at Brewster's angle to define the incident polarization resulting in a contrast ratio of 1000:1. A large aperture Glan-Taylor calcite polarizer was placed before the polarization scrambler serving to define the polarization of the scattered light passed to the spectrograph. Raman spectra were measured for both parallel and perpendicular polarization components, with spectra corresponding to a given component interleaved. The literature value for the depolarization ratio for the 666 cm⁻¹ transition of chloroform $(0.02)^{69}$ was verified in this study.

Intensity corrections

Scattered intensities were corrected for the wavelength sensitivity of the detection apparatus using a standardized quartz–tungsten–halogen lamp (Oriel) for 532.0, 435.7, 368.9, and 355.0 nm excitation, or a standardized deuterium lamp (Hellma) for 319.9 and 282.4 nm excitation. Correction for self-absorption of the sample was performed as described elsewhere,⁴² with this correction resulting in only a modest ($\leq 2\%$) modification of the intensities.

Determination of absolute Raman cross sections

Absolute Raman cross sections for OClO were determined through comparison to the 666 cm^{-1} mode of chloroform using the following expression:

$$\sigma_{\rm OCIO} = \frac{I_{\rm OCIO}C_{\rm CHCl_3} \left(\frac{1+2\rho}{1+\rho}\right)_{\rm OCIO}}{I_{\rm CHCl_3}C_{\rm OCIO} \left(\frac{1+2\rho}{1+\rho}\right)_{\rm CHCl_3}} \sigma_{\rm CHCl_3}, \tag{1}$$

where ρ is the Raman depolarization ratio for a given transition, σ is the scattering cross section, *C* is concentration, and I_{OCIO} and I_{CHCl_3} are the experimentally determined scattered intensities of OCIO and chloroform, respectively. Given the separation of the solvent and solute transitions, intensities were determined through measurement of the area under the transition of interest by trapezoidal integration.

Fluorescence spectra

In order to determine the excited-state lifetime of OCIO and the contribution of excited-state internal conversion to the homogeneous linewidth, the fluorescence quantum yield of OCIO in cyclohexane was determined. The experimental apparatus used for this study was essentially unchanged from that described above. The fluorescence generated by photoexcitation at 435.7 nm was delivered to the 0.75 m spectrograph using standard refractive optics, and dispersed using a 300 groove/mm classically ruled grating. The substantial Stokes-shift and breadth of the fluorescence spectrum required the acquisition of four spectral frames with approximately 10 nm of spectral overlap between adjacent frames. Total integration times of 30 minutes were used to acquire each spectral frame. To guard against differences in concentration affecting the observed intensity between adjacent spectral frames, four sample solutions of identical concentration were prepared, and a fresh solution employed for each frame. At a given spectrograph setting, a spectrum of OCIO in solution, a spectrum of the solvent only, and a spectrum with the incident beam blocked were obtained. The later spectrum was used to judge the contribution of background light to the data, but was found to be negligible for all spectral frames. The spectra corresponding to OCIO in cyclohexane and cyclohexane only were corrected for the wavelength sensitivity of the detection apparatus using a standardized quartz-tungsten-halogen lamp as described above. The spectra were not corrected for the chromatic aberration of the collection optics.

Computational analysis

The absorption spectrum and Raman cross sections were modeled using the time-dependent formalism for absorption and Raman scattering:^{70–72}

$$\sigma_{R}(E_{1}) = \frac{8\pi E_{s}^{3} E_{l} e^{4} M_{eg}^{4}}{9\hbar^{6} c^{4}} \int_{-\infty}^{\infty} \partial E_{00} H(E_{00}) \\ \times \left| \int_{0}^{\infty} \langle f | i(t) \rangle e^{i(E_{l} + E_{l})t/\hbar} D(t) dt \right|^{2}, \qquad (2)$$

$$\sigma_A(E_l) = \frac{4\pi e^2 E_l M_{eg}^2}{6\hbar^2 cn} \int_{-\infty}^{\infty} \partial E_{00} H(E_{00})$$
$$\times \int_{-\infty}^{\infty} \langle i|i(t)\rangle e^{i(E_l + E_i)t/\hbar} D(t) dt.$$
(3)

In the above expressions, M_{eg} is the transition length, E_l and E_s are the incident and scattered frequencies, respectively, n is the refractive index of the solvent, E_i is the initial vibrational energy, and E_{00} is the energy difference between the ground vibrational levels of the ground and excited electronic states. $H(E_{00})$ represents inhomogeneous broadening corresponding to the distribution of E_{00} energies created by different solvent environments that are static on the time scale of Raman scattering. The solvent site distribution was modeled as Gaussian with reported values for the inhomogeneous broadening (Θ) representing the standard deviation of this distribution. D(t) is the homogeneous damping function

corresponding to both excited-state population decay and pure dephasing. Consistent with previous work, a Gaussian functional form for D(t) was found to best reproduce the absorption spectrum, and was employed in this analysis.

The optically prepared, ${}^{2}A_{2}$ potential-energy surface was modeled in the ground-state dimensionless-coordinate basis as follows:

$$V_{e} = \frac{1}{2} \frac{\omega_{el}^{2}}{\omega_{gl}} (q_{1} - \Delta_{1})^{2} + \frac{1}{2} \frac{\omega_{e2}^{2}}{\omega_{g2}} (q_{2} - \Delta_{2})^{2} + \frac{1}{2} \frac{\omega_{e3}^{2}}{\omega_{g3}} (q_{3})^{2} + \frac{1}{6} \chi_{111} \left(\frac{\omega_{el}}{\omega_{gl}}\right)^{3/2} (q_{1} - \Delta_{1})^{3}.$$
(4)

In the above expression, ω_e and ω_g are the vibrational frequencies of the ground and excited states, and the subscripts 1, 2, and 3 refer to the symmetric-stretch, bend, and asymmetric-stretch coordinates, respectively. Also, q is a given normal coordinate, Δ is the displacement of the excited-state potential relative to the ground state along a given coordinate, and χ is the cubic anharmonicity term along the symmetric stretch. We have assumed that there is no anharmonic coupling between coordinates such that the absorption ($\langle i|i(t)\rangle$) and Raman ($\langle f|i(t)\rangle$) time correlators are separable into three independent overlaps along each coordinate:

$$\langle i|i(t)\rangle = \prod_{k=1}^{3} \langle i_{k}|i_{k}(t)\rangle, \qquad (5)$$

$$\langle f|i(t)\rangle = \langle f_1|i_1(t)\rangle \prod_{k=2}^3 \langle i_k|i_k(t)\rangle.$$
(6)

For harmonic modes, the analytic expressions of Mukamel were used to calculate the time-dependent overlaps along a



FIG. 1. Experimental (solid) and calculated (dotted) electronic absorption spectrum of OCIO dissolved in chloroform. The parameters used in calculating this spectrum are presented in Table III.

TABLE I. Absolute Raman cross section for the 666 $\rm cm^{-1}$ mode of chloroform.

Excitation wavelength (nm)	$\sigma_R (imes 10^{12} \mathrm{\AA}^2)^{\mathrm{a}}$
532.0	0.6 ± 0.1^{b}
435.7	1.6 ± 0.5
368.9	3.7 ± 0.3
355.0	4.3 ± 0.4
319.9	7.5 ± 0.3
282.4	13.0 ± 4.0

^aCross sections were determined by comparison to the 801 cm^{-1} mode of cyclohexane as described in the text.

^bErrors represent one standard deviation from the mean.

given coordinate.⁷³ For anharmonic modes, we used the approximate time-propagator method of Feit and Fleck.^{74,75}

$$|i(t)\rangle = e^{i(\Delta t)\nabla^2/4M}e^{-1(\Delta t)V}e^{i(\Delta t)\nabla^2/4M}|i(0)\rangle + \vartheta(\Delta t^3),$$
(7)

where ∇^2 is the Laplacian in position space, V is the potential of the excited state, and Δt is the size of the propagation time step in femtoseconds. Given that the error in the approximate time-propagator method scales as the their power of the time step, a minimum step size of 0.5 fs was employed. Overlaps were determined for times up to ~1 ps.

RESULTS

Absorption spectrum

The absorption spectrum of OCIO in chloroform is presented in Fig. 1. Similar to the absorption spectra of OCIO dissolved in cyclohexane and water,^{40,42} the spectrum in chloroform displays vibronic structure arising from progressions involving the symmetric stretch. The broadening evident in the spectrum is intermediate between the substantial



FIG. 2. Absolute Raman cross sections for the 666 cm^{-1} transition of chloroform measured in this study (circles), and the cross sections reported by Abe *et al.* (squares) (Ref. 64). Absolute cross sections are presented in Table I. The *A*-term fit to these cross sections as described in the text is given by the solid line. Errors represent one standard deviation from the mean.



FIG. 3. Resonance Raman spectrum of OCIO dissolved in chloroform (10 mM) obtained at 368.9 nm excitation. Transitions due to the solvent are marked with asterisks. Transitions corresponding to the symmetric-stretch (v_1) and bend (v_2) are indicated. The inset shows an enlargement of the region of the asymmetric-stretch overtone transitions, and demonstrates the absence of intensity for this transition.

broadening observed in water and the modest broadening observed in cyclohexane. We have assumed that the absorption cross section at the maximum is 0.042 $Å^2$, identical to the cross sections in water and cyclohexane.

Absolute Raman cross sections for chloroform

As illustrated by Eq. (1), measurement of the absolute scattering cross sections of OCIO requires knowledge of the absolute Raman scattering cross sections of the solvent. Therefore, absolute scattering cross sections for the 666 cm⁻¹ mode of chloroform were measured at the excitation wavelengths employed. The measured scattering cross sections for this transition are reported in Table I and presented in Fig. 2. Also presented in Fig. 2 is the best fit to these cross sections employing an "A-term" expression:^{65–67}

$$\sigma_{R}(v_{0}) = K v_{0}(v_{0} - v)^{3} \left(\frac{v_{e}^{2} + v_{0}^{2}}{(v_{e}^{2} - v_{0}^{2})^{2}} \right)^{2}.$$
(8)

In Eq. (8), v_e is the energy of the excited state from which the preresonant intensity is derived, v_0 is the incident frequency, v is the frequency of the mode of interest, and K is the coupling strength. Parameters derived from best fit to the *A*-term expression are $v_e = 123400 \text{ cm}^{-1}$ and $K = 1.313 \times 10^{-9} \text{ Å}^2$. The value for v_e is consistent with the prediction of several excited states around 110000 cm^{-1} , with intensity likely derived from more than one of these states.⁷⁶ Cross sections for this transition have also been measured by Abe *et al.* at two excitation wavelengths (514.5 and 337.1 nm), and these values are also presented in Fig. 2. Inspection of the figure demonstrates that the agreement between our results, previous measurements, and the *A*-term fit are all quite reasonable.

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TABLE II. Absolute Raman cross sections of chlorine dioxide in chloroform.

$^{2})^{b}$ (×10 ¹⁰ A ²	²) (×10 ¹⁰ Å ²)	$(\times 10^{10} \text{\AA}^2)$	$(\times 10^{10} \text{ Å}^2)$
)2			
5 1.8±0.3			
6.1 ± 0.7	1.9 ± 0.4	0.5 ± 0.2	≤0.18 ^d
9.9 ± 0.7			
4.3 ± 0.5			
3 0.7±0.5			
	$\begin{array}{c} 2)^{b} & (\times 10^{10} \text{ Å}^{2} \\ \hline \\ 02 \\ 5 \\ 1.8 \pm 0.3 \\ 0 \\ 6.1 \pm 0.7 \\ 0 \\ 9.9 \pm 0.7 \\ 0 \\ 4.3 \pm 0.5 \\ 8 \\ 0.7 \pm 0.5 \end{array}$	$\begin{array}{c} \overset{2)}{\overset{b}{}} & (\times 10^{10} \text{ \AA}^2) & (\times 10^{10} \text{ \AA}^2) \\ \hline \end{array} \\ \begin{array}{c} \overset{5}{}{} & 1.8 \pm 0.3 \\ 0 & 6.1 \pm 0.7 & 1.9 \pm 0.4 \\ 0 & 9.9 \pm 0.7 \\ 0 & 4.3 \pm 0.5 \\ 8 & 0.7 \pm 0.5 \end{array}$	$ \begin{array}{c} \overset{2}{} \overset{2}{} \overset{b}{} & (\times 10^{10} \text{ Å}^2) & (\times 10^{10} \text{ Å}^2) & (\times 10^{10} \text{ Å}^2) \\ \hline 02 \\ \hline 02 \\ \hline 5 \\ 5 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\$

^aRaman depolarization ratio for the symmetric-stretch fundamental transition. This ratio is defined as the scattered intensity with polarization perpendicular to that of the incident radiation divided by the scattered intensity with polarization parallel to the incident radiation.

^bAbsolute Raman scattering cross sections. These values were determined by comparison to the 666 $\rm cm^{-1}$ mode of chloroform as described in the text.

^cErrors represent one standard deviation from the mean.

^dThe value represents an upper limit for the cross section. This limiting value was determined by comparison to the intensity of the symmetric-stretch overtone transition and the signal-to-noise of the measurements.

Resonance Raman intensity analysis

The resonance Raman spectrum of OCIO in chloroform obtained with 368.9 nm excitation is shown in Fig. 3. The absolute cross sections for all transitions investigated in this study at the excitation wavelengths employed are reported in Table II. Fundamental transitions corresponding to the symmetric stretch (938 cm⁻¹) and the bend (450 cm⁻¹) coordinates are readily observed, as are overtones and combination bands involving these coordinates. This pattern of scattered intensity is similar to that observed for OCIO dissolved in water and cyclohexane demonstrating that the excited-state structural evolution in all three solvents is similar.^{40,42} In addition, the transition frequencies observed in chloroform are consistent with those observed in cyclohexane. For example, the frequencies of the symmetric-stretch fundamental transition in chloroform and cyclohexane are identical (938 cm^{-1}), but different from the frequency of this transition in water (945 cm⁻¹) consistent with intermolecular hydrogen bonding in water.⁴² Isotope splitting of the overtone band is evident with intensities consistent with the natural abundance of ³⁵Cl and ³⁷Cl. Finally, the expanded view of the overtone region presented in Fig. 3 demonstrates that intensity assignable to the overtone transition of the asymmetric-stretch coordinate is not observed. The absence of intensity assignable to this transition is consistent with limited evolution along this coordinate as discussed below.

Refinement of the excited-state potential energy surface parameters [Eq. (4)] was performed to reproduce the absorption and resonance Raman cross sections. The best reproduction of the absorption spectrum is presented in Fig. 1 (dotted line), with the excited-state parameters derived from this analysis presented in Table III. Inspection of Fig. 1 demonstrates that the agreement between the experimental spectrum and the model spectrum is good. Deviation between the data and model is observed on the red edge of the absorption spectrum. Similar deviations have been observed for other

TABLE III. ²A₂ excited-state potential energy surface parameters for chlorine dioxide in chloroform.^a

Transition ^b	$\omega_g \ (\mathrm{cm}^{-1})^{\mathrm{c}}$	$\omega_e (\mathrm{cm}^{-1})$	$\Delta^{\rm d}$	$\chi ~(\mathrm{cm}^{-1})^{\mathrm{e}}$	$\sigma_R \operatorname{Expt.}^{\mathrm{f}} (\times 10^{b 10} \mathrm{\mathring{A}}^2)$	σ_R Calc. (×10 ¹⁰ Å ²)
<i>v</i> ₁	938	695	5.62	-17.5	7.0 ± 1.0	8.5
v_2	450	267	0.45		1.9 ± 0.4	1.9
<i>v</i> ₃	1100	825	0		< 0.1	0
$2v_1$					6.1 ± 0.7	6.1
$2v_2$					0.5 ± 0.2	0.4
$2v_{3}$					≤0.18	0.18

^aCalculation performed with a Gaussian homogeneous linewidth. Best fit to the experimental cross sections resulted in $\Gamma = 95 \pm 15 \text{ cm}^{-1}$, inhomogeneous standard deviation $= 220 \pm 10 \text{ cm}^{-1}$, $M_{eg} = 0.38 \text{ Å}$, $E_{00} = 17.940 \text{ cm}^{-1}$, n = 1.444.

^bRaman transition for which the calculation is performed. The symbols v_1 , v_2 , and v_3 refer to the symmetric stretch, bend, and asymmetric stretch, respectively. The first three terms correspond to fundamental transitions and the latter three terms refer to overtone transitions.

 ${}^{c}\omega_{g}$ refers to the ground-state harmonic frequency, and ω_{e} is the excited-state harmonic frequency.

^dThe dimensionless displacement of the excited-state potential energy surface minimum relative to the ground state.

^eAnharmonicity prefactor for the cubic term in the series expansion of the potential energy surface. By comparison to the description of the Morse oscillator, this term is equal to $(\omega_e/2)^{1.5}/D_e^{0.5}$ in dimensionless units where ω_e is the excited-state harmonic frequency and D_e is the Morse dissociation energy given by $\omega_e^2/(4\omega_e x_e)$ where x_e is the anharmonicity parameter (Ref. 93).

^fExperimental Raman cross sections determined using 368.9 nm excitation.



FIG. 4. Raman excitation profiles for the symmetric stretch fundamental (A), the symmetric stretch overtone (B), the bend (C), and the asymmetric stretch overtone (D) transitions. The points represent the experimental data, and the error bars represent the standard deviation from the mean. The best fit to the data (solid lines) was obtained using the parameters reported in Table III. The fit using only homogeneous broadening (dashed lines) is presented.

systems when an exponential form for D(t) is employed, and this has lead to the incorporation of Gaussian and other functional forms for D(t).^{77,78} However, Fig. 1 demonstrates that a Gaussian functional form for D(t) still results in a noticeable deviations between the experimental spectrum and the model. Therefore, other functional forms for D(t) were studied in an attempt to better reproduce the absorption intensity at lower frequency. Previous studies of rotationally cooled gaseous OClO have shown that the homogeneous linewidth increases with excitation along the symmetric stretch.⁹ Therefore a level-dependent homogeneous linewidth was incorporated to reproduce the dependence of the excited-state decay rate on excitation along the symmetric stretch. In this approach, a slow Fourier transform of the absorption and Raman time correlators was performed with the homogeneous linewidth increasing as the energy over which the transformation was performed was increased. Level dependence of the homogeneous linewidth did not significantly improve the agreement beyond that evident in Fig. 1. A second attempt to improve agreement between the data and model involved application of the stochastic model for broadening developed by Kubo and adapted by Mukamel.⁷⁹ However, the best agreement was obtained in the slow-modulation limit of this formalism corresponding to a Gaussian functional form for D(t), identical to the phenomeno-logical model originally employed.

Figure 4 presents the Raman excitation profiles for the symmetric-stretch fundamental (A), symmetric-stretch overtone (B), bend (C), and asymmetric-stretch overtone transitions (D). Best reproduction of these intensities is presented as the solid line corresponding to the excited-state potentialenergy-surface parameters presented in Table III. Absolute resonance Raman cross sections are dependent on the magnitude of the homogeneous linewidth; therefore, these cross sections can be used to partition between homogeneous and inhomogeneous broadening.⁷¹ The dotted line presented in Fig. 4 corresponds to a model in which all broadening is incorporated as homogeneous. The figure demonstrates that the symmetric-stretch fundamental and overtone cross sections are modestly dependent on the homogeneous linewidth. However, the slower buildup of the Raman time correlator along the bend results in this fundamental transition along this coordinate being quite dependent on the extent of homogeneous broadening [Fig. 4(C)]. The measured cross section along this coordinate in combination with the symmetricstretch fundamental and overtone transitions were used to constrain the homogeneous linewidth to 95 ± 15 cm⁻¹.

The ground-state symmetry of OCIO is C_{2v} such that fundamental resonance Raman intensity along the asymmetric-stretch coordinate is not expected. However, overtone intensity along this coordinate can be observed if the excited-state potential-energy surface differs significantly from that of the ground state.⁸⁰ The paucity of asymmetricstretch overtone intensity (Fig. 3) suggests that excited state evolution along this coordinate is modest. Comparison to the intensity of the symmetric-stretch overtone transition and the signal-to-noise of the spectrum places an upper limit on the cross section of the overtone transition of $1.8 \times 10^{-11} \text{ Å}^2$. This modest cross section is consistent with a reduction in excited-state frequency along this coordinate to \geq 825 $\pm 20 \,\mathrm{cm}^{-1}$. As in our previous studies, the gas-phase potential Richard and Vaida and the ab initio surface of Peterson were not capable of reproducing the lack of intensity observed in the asymmetric stretch in chloroform.^{7,8}

Fluorescence results

Figure 5 shows the emission and absorption spectra of OCIO in cyclohexane. Measurements were also performed for OCIO dissolved in water; however, the fluorescence cross section in water was found to be essentially identical to that in cyclohexane such that the results in water are not presented. Inspection of the figure demonstrates that a broad background is observed under the sharper Raman features, with this background corresponding to OCIO fluorescence. The fluorescence intensity appears to be the mirror image of the absorption intensity consistent with the emission being relaxed; however, it must be noted that excitation wavelength dependence of the emission was not investigated to



FIG. 5. Fluorescence and absorption spectra of OCIO in cyclohexane. The absorption cross sections are displayed in units of $Å^2$, and the fluorescence spectra are scaled to approximately the same height in arbitrary intensity units. The fluorescence emission is the broad background under the sharper Raman transitions. The excitation wavelength (435.7 nm) is indicated.

ascertain if this is indeed the case. Etaloning effects from the back-thinned CCD employed in this study restricted the spectral region to that depicted in Fig. 5. This limitation required the generation of an accurate estimate for the fluorescence intensity at lower frequency. This was performed by fitting the entire emission envelope using the time-dependent formalism for fluorescence via the following equation:^{81,82}

$$I \propto v^3 \langle i | f(t) \rangle, \tag{9}$$

where v is the emission frequency, and $\langle i|f(t)\rangle$ is the overlap between the initial wave function in the excited state and the same wave function propagating under the influence of the ground state Hamiltonian. The parameters reported in our previous RRIA study of OCIO in cyclohexane were used in this analysis.^{40,42} Although this approach clearly compromises the quantitative determination of the fluorescence intensity, it does provide a reasonable estimate of the intensity at lower frequency. The area of the fluorescence band determined from this analysis was compared to area of the symmetric-stretch fundamental transition to determine the fluorescence cross section. This analysis provided a value for the fluorescence cross section of $5.7 \pm 2.8 \times 10^{-9} \text{ Å}^2$. Two separate measurements were performed, and the value for the cross section represents the average of these measurements. The difference between measurements was only 20%; however, the error estimate provided here is substantially greater than this value reflecting the possibility of systematic errors in the area determination as described above. The fluorescence and absorption cross sections were used to calculate the fluorescence quantum yield $(\Phi_F = \sigma_F / \sigma_A)$ resulting in $\phi_F \sim 1 \times 10^{-6}$. Elementary kinetics dictates that the fluorescence cross section is equal to $k_R/(k_R+k_{NR})$ where k_{NR} is the nonradiative-decay rate and k_R is the radiative-decay rate. Given this, Φ_F can be used to calculate the nonradiative rate assuming an estimate for the radiative rate is available. An estimate for this rate is provided by the following:⁸³

$$k_{R} = 2.88 \times 10^{9} n^{2} \langle v_{f}^{3} \rangle^{-1} \int \epsilon d \ln v, \qquad (10)$$

where ϵ is the extinction coefficient, *n* is the solvent refractive index, the term in brackets corresponds to the average frequency of the emission band, and the integration is done over the absorption band. For OCIO in cyclohexane, we calculated $k_R = 5 \times 10^6 \text{ s}^{-1}$. Combining the estimate for k_R with ϕ_F , a value for the nonradiative-decay rate of $k_{NR} = 5 \times 10^{12} \text{ s}^{-1}$ is obtained corresponding to an excited-state lifetime of ~200 fs. This estimate for the excited-state lifetime is in remarkable agreement with the ~200 fs decay time of the 2A_2 state measured by femtosecond pump-probe spectroscopy.⁵¹

DISCUSSION

OCIO excited-state structural evolution

The RRIA of OCIO dissolved in chloroform presented here demonstrates that the excited-state structural evolution in this solvent is similar to that observed in water and cyclohexane.40,42 The dominant structural change upon photoexcitation occurs along the symmetric-stretch (Table III), with the displacement along this coordinate in chloroform essentially identical to that in water ($\Delta = 5.62$ in CHCl₃ versus 5.63 in water). There is also modest evolution along the bend ($\Delta = 0.45$ in CHCl₃ versus 0.4 in water), and essentially no evolution along the asymmetric stretch. In our previous analysis of aqueous OClO, the dimensionless displacements were determined to reflect geometry changes corresponding to an increase in Cl-O bond length from 1.47 Å to 1.68 Å and a decrease in valence angle from 117.4° to 108.8° .⁴² The similarity of excited-state displacements observed between chloroform and water dictates that this evolution must also describe the excited-state structural relaxation of OCIO in chloroform.

Depolarization ratios

The resonance Raman depolarization ratio can be used to ascertain if the observed intensity is generated via resonance with a single electronic excited state.^{68,84} Specifically, a value of $\rho = 1/3$ indicates that the contribution to the scattering is from a single state. In our previous studies, the depolarization ratio for the symmetric-stretch fundamental transition was <1/3, and we have shown that contributions to the polarizability tensor from the nearby ${}^{2}A_{1}$ state were responsible for the deviation of ρ from 1/3.⁴¹ In contrast, the depolarization ratio of the symmetric stretch fundamental transition in chloroform is essentially 1/3, implying that the ${}^{2}A_{1}$ state is energetically shifted relative to the ${}^{2}A_{2}$ surface in this solvent relative to water or cyclohexane. This hypothesis can be tested by acquiring and analyzing the resonance Raman depolarization dispersion curves, and we are currently pursuing such a study. With respect to the current analysis, the closeness of the ρ to 1/3 indicates that the single state approximation employed in this analysis is reasonable.

Homogeneous and inhomogeneous broadening

Analysis of the absolute scattering intensities demonstrates that the homogeneous linewidth (Γ) in chloroform is 95 cm⁻¹, essentially identical to that determined in water or cyclohexane. The homogeneous linewidth contains contributions from both excited-state population decay and solventinduced pure dephasing:⁷⁷

$$\Gamma = \frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*}.$$
(11)

In the above expression, T_2 is the total dephasing time, T_1 is the excited-state lifetime, and T_2^* is the time scale for pure dephasing. The solvent independence of Γ could mean either that the contributions from T_1 and T_2^* are equal in all solvents studied to date, or that the solvent-dependent differences between T_1 and T_2^* cancel each such that the homogeneous linewidth simply appears to be solvent invariant. The fluorescence cross section of OCIO in cyclohexane and recent femtosecond pump-probe work⁵¹ establishes that T_1 is ~200 fs. Given a T_1 time of ~200 fs and the homogeneous linewidth of 85 cm⁻¹ corresponding to $T_2 \sim 60$ fs, Eq. (10) dictates that T_2^* is ~64 fs such that solvent-induced pure-dephasing processes must make the dominant contribution to the homogeneous linewidth.

Nonpolar solvation dynamics and solvent-induced dephasing

The question remains as to which solvent-solute interactions give rise to dephasing on the ~ 60 fs time scale, and why these interactions are apparently similar in all solvents studied to date. We propose that the origin of this dephasing is nonpolar or mechanical solvation in response to the substantial geometry changes accompanying OCIO photoexcitation. The motivation behind this hypothesis is as follows. Ab *initio* studies predict that the dipole moment (μ) of OCIO changes very little upon photoexcitation with $\mu = 1.71$ D and 1.85 D in the excited $({}^{2}A_{2})$ and ground $({}^{2}B_{1})$ states, respectively.⁸⁵ Furthermore, the direction of the dipole moment is relatively unchanged. Without a large change in the electronic distribution of the solute, one would expect the dielectric response of the solvent to be modest. In contrast, significant evolution occurs along the symmetric stretch and bend coordinates such that it is reasonable to assume that mechanical or nonpolar solvation dynamics dominate the solvent response to OClO photoexcitation.

Assuming that nonpolar solvation dynamics dominate the solvent response, do these dynamics occur on a similar time scale for the three substantially different solvents (water, cyclohexane, and chloroform)? Furthermore, is the time scale over which these interactions are operative sufficient to be responsible for dephasing on the ~ 60 fs time scale? There current theories describing several nonpolar are solvation;⁵²⁻⁶² however, we have focused our attention on the viscoelastic continuum theory (VCT) developed by Berg.^{52–54} This focus is largely motivated by the analytic nature of this theory, and by recent three-pulse photon echo studies of Fleming and co-workers which have demonstrated the ability of this theory to model nonpolar solvation.⁸⁶ The general theory and the key equations of VCT have been presented;^{53,87,88} therefore, only a brief overview describing the physics behind this model and the central results of this theory are presented here. The solute is approximated as a spherical cavity located within the solvent modeled as a viscoelastic continuum. Before excitation, a balance exists between the force applied by the continuum directed towards collapse of the solute cavity, and the restoring force applied to the continuum by the solute opposing cavity collapse. Photoexcitation of the solute initiates a change in molecular size, which results in a corresponding change in the force applied by the solute to the cavity boundary. The size of the solute cavity will therefore change to restore equilibrium between the solvent and solute forces. The solvent is modeled as isotropic, and the solvent response is separated into two components, one that occurs in the same direction of the applied force (known as the compressive strain) and another that occurs in directions perpendicular to the applied force (known as the shear strain). Correspondingly, the response of the solvent is described by the compressive and shear moduli denoted as K and G, respectively. For a force resulting in deformation of the material only in the same direction as the applied force, the ratio of the stress to the strain in that direction is called the wave modulus, M, and is given by

$$M = K + \frac{4}{3}G. \tag{12}$$

The moduli *G*, *K*, and *M* describing the viscoelastic response of the medium are in general time dependent. However, the dynamics of interest here occur on a relatively short time scale such that we consider only the short-time, solid like response of the medium, and only the high frequency moduli (G_{∞} , K_{∞} , and M_{∞}) are employed. By solving the appropriate viscoelastic equations of motion, Berg has used these moduli to calculate the solvent response, R(t):^{52,53}

$$R(t) = (1 - f) e^{-t/\tau_{\rm ph}} \left(\cos\left(\frac{t}{\beta \tau_{\rm ph}}\right) - \beta \sin\left(\frac{t}{\beta \tau_{\rm ph}}\right) \right) + f e^{-t/\tau_{\rm st}}$$
(13)

with

$$\beta^{2} = 3 \frac{M_{\infty} + (K_{s} - K_{\infty})}{M_{\infty} - 3(K_{s} - K_{\infty})},$$
(14)

$$f = \frac{4/3G_{\infty}}{K_s + 4/3G_{\infty}},$$
(15)

$$\tau_{\rm ph} = \frac{(1+\beta^2)}{2\beta^2} \tau_l, \qquad (16)$$

$$\tau_l = r_c \sqrt{\frac{\rho}{M_{\infty}}},\tag{17}$$

$$\tau_{\rm st} = \frac{\eta/G_{\infty}}{1-f}.\tag{18}$$

In the above equations, τ_1 is the time for longitudinal sound waves to travel a distance of one cavity radius, K_s is the effective compressive modulus of the solute, ρ is the solvent density, and r_c is the cavity radius taken to be 3 Å. Equation (13) is valid in the limit where phonon-induced solvation is

TABLE IV. Solvent-dependent parameters used in viscoelastic calculations.

Solvent	$\frac{G_{\infty}}{(\times 10^{-10} \mathrm{dyn/cm^2})}$	$\frac{K_{\infty}}{(\times 10^{-10} \mathrm{dyn/cm^2})}$	$\frac{K_s}{(\times 10^{-10} \mathrm{dyn/cm^2})}$	$ ho^{a}$ (g/cm ³)	η^{a} (cP)	$ au_{ m ph} \ ({ m fs})$	$\substack{\tau_{\rm st} \\ ({\rm fs})}$
Cyclohexane	0.8 ^b	4.4 ^b	3.9 ^b	0.778 ^c	1.02 ^c	85	1500
Water	8.5 ^d	11.4 ^d	11.4 ^d	0.997 ^c	0.89 ^c	40	200
Chloroform	1.5 ^e	4.2 ^e	2.5 ^e	1.483 ^c	0.56 ^c	130	670

^aAll values are interpolated for 25 °C.

^bValues are the average for benzene and toluene reported in Ref. 86.

^cValues are taken from Ref. 94.

^dValues are taken from Ref. 52.

^eValues are those reported for CCl₄ in Ref. 86.

rapid compared to the structural relaxation of the solvent such that the solvent response can be partitioned into a phonon-induced term [the term with the (1-f) prefactor in Eq. (13)] and a structural relaxation term. The validity of this limit for the solvents studied here deserves some comment. The time constants for phonon (τ_{ph}) and structural (τ_{st}) relaxation can be determined using Eqs. (16) and (18), respectively. With the viscoelastic parameters presented in Table IV, the predicted phonon relaxation times vary from 40 fs in water to 130 fs in chloroform while the structural relaxation time constants vary from 200 fs in water to 1500 fs in cyclohexane. These times are sufficiently different such that the separation of the solvent response into two separate components is assumed to be valid.

In the limit of linear response, R(t) can be equated to C(t), the normalized correlation function that describes the solvent-induced fluctuations in the energy gap between ground and excited state of the solute:

$$C(t) = \frac{\langle \delta U(t) \, \delta U(0) \rangle}{\langle \delta U^2 \rangle}.$$
(19)

In the above expression, U is the energy gap between ground and excited states, and $\delta U(t) = U - \langle U \rangle$ is the fluctuation of the energy gap from its equilibrium value. The assumption of linear response dictates that the post-perturbation relaxation of the system towards equilibrium is determined by the fluctuations that characterize the system at equilibrium.⁸⁹ Assuming linear response holds, then R(t) as described by VCT can be used to describe C(t). This term can subsequently be used to determine the functional form for homogeneous dephasing, D(t). The determination of D(t) follows closely the Brownian oscillator development presented by Mukamel and co-workers^{77,79} in which solvent-induced dephasing is incorporated into the expression for Raman or absorption cross section by $D(t) = e^{-g(t)}$ where

$$g(t) = \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \langle \, \delta U(\tau_2) \, \delta U(0) \rangle. \tag{20}$$

Thus, by knowing C(t) and equating the variance of the fluctuations to δ^2 , a functional form for g(t) and subsequently D(t) can be obtained. Using the R(t) provided in Eq. (13) and performing the integration prescribed by Eq. (20), we arrive at the following functional form for g(t):

$$g(t) = (1-f) \frac{\delta^2 \tau_{\rm ph}^2}{\hbar^2 \left(1 + \frac{1}{\beta^2}\right)} \times \left(1 - e^{t/\tau_{\rm ph}} \left(\cos\left(\frac{t}{\beta \tau_{\rm ph}}\right) + \beta \sin\left(\frac{t}{\beta \tau_{\rm ph}}\right)\right)\right) + f \frac{\delta^2 \tau_{\rm st}^2}{\hbar^2} \left(\frac{t}{\tau_{\rm st}} + e^{-t/\tau_{\rm st}} - 1\right).$$
(21)

The above expression was employed using only δ as an adjustable parameter in an attempt to reproduce the Gaussian function form of D(t) as determined in our RRIA studies. A comparison between D(t) as determined by our RRIA of OCIO dissolved in cyclohexane⁴⁰ and the VCT model is presented in Fig. 6(A). Specifically, the Gaussian form for D(t)with $\Gamma = 80 \text{ cm}^{-1}$ is given by the solid line and the shortdashed line is the VCT result with $\delta = 145 \text{ cm}^{-1}$. The corresponding solvent response function, R(t), is given by the short-dashed line in Fig. 6(B). The viscoelastic parameters used to calculate the VCT result correspond to the average values determined for benzene and toluene by three-pulse photon echo (Table IV).⁸⁶ The values for $\tau_{\rm ph}$ and δ are in reasonable agreement with the photon echo results where in benzene and toluene, a ~ 100 fs component of the solvent response having a reorganization energy of $\sim 50 \text{ cm}^{-1}$ was found to make a substantial contribution to the solvent response.⁸⁶ Inspection of Fig. 6(A) demonstrates that VCT is capable of reproducing the D(t) in cyclohexane consistent with mechanical solvation dynamics dominating the solvent response to OCIO photoexcitation in this solvent.

A more stringent test of the VCT model involves its ability to reproduce the solvent invariance of D(t). Figure 6(C) presents the comparison of D(t) determined in our RRIA study of OCIO dissolved in water ($\Gamma = 85 \text{ cm}^{-1}$) to the prediction of VCT with $\delta = 160 \text{ cm}^{-1}$ and other viscoelastic parameters as compiled by Berg (Table IV).⁵² The corresponding solvent response function for water using identical parameters is presented in Fig. 6(D). Figure 6(E) presents the corresponding comparison for chloroform with $\Gamma = 95 \text{ cm}^{-1}$ and $\delta = 150 \text{ cm}^{-1}$, and Fig. 6(F) shows the corresponding solvent response function. In these calculations, the viscoelastic parameters employed are those for CCl₄ reported by Fleming and co-workers.⁸⁶ As illustrated by Table IV, the viscoelastic parameters for these three solvents are markedly different; however, Fig. 6 demonstrates that the VCT model



FIG. 6. (A) Comparison between the Gaussian functional form for D(t) and the viscoelastic continuum theory (VCT) prediction [Eq. (21)] of D(t) for cyclohexane. The Gaussian form corresponds to $\Gamma = 80 \text{ cm}^{-1}$ (solid line), and the VCT result (dashed line) corresponds to $\delta = 145 \text{ cm}^{-1}$ and other viscoelastic parameters as provided in Table IV. (B) The solvent response function [Eq. (13)] predicted using VCT employing parameters identical to those used in part (A). (C) Comparison between the Gaussian functional form for D(t) and the VCT result for water. The Gaussian form corresponds to $\Gamma = 85 \text{ cm}^{-1}$ (solid line), and the VCT result (dashed line) corresponds to δ = 160 cm⁻¹ and other parameters as provided in Table IV. (D) The solvent response function predicted using VCT employing identical parameters to those used in part (C). (E) Comparison between the Gaussian functional form for D(t) and the VCT result for chloroform. The Gaussian form corresponds to $\Gamma = 95 \text{ cm}^{-1}$ (solid line), and the VCT result (dashed line) corresponds to $\delta = 150 \text{ cm}^{-1}$ and other parameters as provided in Table IV. (F) The solvent response function predicted from VCT employing parameters identical to those used in part (E).

is capable of reproducing D(t) in each case. It should be noted that this agreement is accomplished using a δ that is essentially solvent independent, a result that is consistent with the similarity of the OClO geometry change that occurs upon photoexcitation in these solvents.

The discussion presented above suggests that VCT description of the solvent response is consistent with both the functional form of the dephasing as well as the solvent invariance of homogeneous linewidth. However, the success of this approach is tempered by whether the assumptions made here are valid, most notably the continuum treatment of the solvent and the applicability of linear response. MD simulations of nonpolar solvation dynamics have shown that the mechanical response of the solvent is dominated by a subset of the molecules in the first solvent shell.^{57,61,62} This effect is directly related to the short-ranged nature of the repulsive interactions that dominate the mechanical response of the solvent. Clearly, the molecular aspects of nonpolar solvation are not reflected in the continuum treatment. Regarding linear response, Schwartz and co-workers have recently discussed the breakdown of linear response for several different changes in the solute upon electronic excitation and found substantial differences relative to the dynamics predicted by linear response.⁶² However, despite the lack of agreement between the equilibrium and nonequilibrium calculations, the end result of this study was that for spectroscopic applications, equilibrium approximations are still reasonable in the calculation of line shapes, especially for systems in which dielectric solvation dynamics are modest as is the case here.

One final question concerns the nature of the solventsolute interactions responsible for restricting evolution along the asymmetric-stretch coordinate. Previously, we had suggested that dielectric solvent-solute interactions were responsible for this behavior since the largest change in molecular dipole moment occurs with displacement along the asymmetric stretch.^{40,42} However, the discussion presented above indicates that nonpolar solvation dynamics dominate the initial solvent response to OCIO photoexcitation. This apparent discrepancy can be resolved if one assumes that dipolar solvent-solute interactions are operative on a time scale longer than that dictated by the homogeneous linewidth, an assumption that is supported by the increase in inhomogeneous linewidth accompanying an increase in solvent polarity. The contribution of these interactions to slower-time dynamics can be understood by considering the essential invariance of the molecular dipole moment to photoexcitation. We envision OCIO as a dipole located at center of an Onsager cavity, with the surrounding solvent described as a uniform dielectric. Reorientation of the molecular dipole moment will be accompanied by response of the surrounding dielectric, referred to as the solvent frictional force.^{90,91} In general, the dielectric relaxation will be frequency dependent, and related to the velocity of charge motion (i.e., dipole rearrangement) within the cavity. Optical methods have provided much insight into frequency dependent dielectric response,92 and these measurements typically employ probe molecules whose molecular dipole moment undergoes a substantial change in direction and/or magnitude upon photoexcitation. Rapid reorientation of the molecular dipole is expected to preferentially couple to high-frequency components of the dielectric response. OCIO represents the opposite extreme in which neither the magnitude nor direction of the molecular dipole moment changes significantly upon photoexcitation (see above). Correspondingly, one would expect significant coupling to lower-frequency components of the dielectric response. Both the presence of inhomogeneous broadening and the increase in inhomogeneous linewidth with an increase in solvent polarity are consistent with this conceptual picture, and suggest that dipolar interactions between OCIO and the solvent are largely responsible for the restricted evolution along the asymmetric-stretch coordinate in condensed media.

CONCLUSIONS

We have presented an absolute resonance Raman intensity analysis (RRIA) of OCIO dissolved in chloroform. Similar to our previous RRIA results in water and cyclohexane, the excited-state structural evolution in chloroform is dominated by motion along the symmetric stretch and bend coordinates, with little evolution occurring along the asymmetric stretch. This pattern of excited-state structural relaxation is consistent with the preservation of C_{2v} symmetry in the excited state, with this preservation of symmetry leading to enhanced Cl production in condensed environments. The homogeneous broadening determined in this study is similar in magnitude to that previously determined in cyclohexane and water suggesting that the vibronic-dephasing time for OCIO in solution is solvent independent. We have shown that this apparent solvent invariance is consistent with nonpolar or mechanical solvation dynamics dominating the solvent response to OCIO photoexcitation. Finally, we have proposed that the limited evolution along the asymmetric-stretch coordinate in condensed environments is due to dielectric solvent–solute interactions as evidenced by the increase in inhomogeneous linewidth with an increase in solvent polarity.

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