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Evidence for the ${}^{2}B_{1} - {}^{2}A_{1}$ electronic transition in chlorine dioxide from resonance Raman depolarization ratios

Philip J. Reid,^{a)} Anthony P. Esposito, Catherine E. Foster, and Robert A. Beckman *Department of Chemistry, Box 351700, University of Washington, Seattle, Washington 98195*

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The resonance Raman depolarization ratios of chlorine dioxide (OCIO) dissolved in cyclohexane are measured and analyzed to establish the existence of a ${}^{2}A_{1}$ excited state that is nearly degenerate with the optically stronger, ${}^{2}A_{2}$ excited state. The depolarization ratio of the symmetric stretch fundamental transition is measured at several excitation wavelengths spanning the lowest-energy electronic transition centered at ~360 nm. The depolarization ratio of this transition reaches a maximum value of 0.25 ± 0.04 directly on resonance suggesting that scattered intensity is not derived from a single excited state. The depolarization ratios are modeled utilizing the time-dependent formalism for Raman scattering. This analysis demonstrates that the observed Raman depolarization ratios are derived from contributions of two excited states of ${}^{2}A_{1}$ and ${}^{2}A_{2}$ symmetry to the observed scattering. The results presented here support the emerging picture of OCIO excited-state reaction dynamics in which photoexcitation to the ${}^{2}A_{2}$ excited state is followed by internal conversion from this state to the ${}^{2}A_{1}$ surface. Both the role of the ${}^{2}A_{1}$ state in the photochemistry of OCIO and the importance of this state in modeling resonance Raman intensities are discussed. (2007) (2000 + 2000

I. INTRODUCTION

The photochemical reaction dynamics of chlorine dioxide (OCIO) are of current interest due to the participation of this compound in the CIO_x atmospheric reservoir and its potential role in stratospheric ozone layer depletion.¹⁻⁴ The photochemistry of chlorine dioxide is illustrated in Scheme I:

$$OCIO \xrightarrow{hv} OCIO^* \xrightarrow{CIO (2\Pi) + O(3P_g)} CI (2P_u) + O_2 (1\Delta_g, 3\Sigma_g^-)$$

Photoexcitation of OCIO results in either bond cleavage to form CIO and O, or in the formation of molecular oxygen and atomic chlorine.^{1,5–38} The interesting aspect of this photochemistry is that photoproduct formation is phase dependent. The quantum yield for the Cl+O₂ production in the gas phase remains the subject of debate with values ranging from ~0 to 0.15.^{1,17,21–23} In contrast, photoexcitation of OCIO isolated in a variety of low temperature matrices results primarily in Cl production with a quantum yield approaching unity.^{32–36} Finally, the photochemical behavior in solution is intermediate between the gas- and solid-phase limits with the quantum yield for Cl formation in polar solvents being 0.1-0.2.¹²

Recent studies have attempted to quantitate the photochemical behavior of OCIO as reflected by the product quantum yields; however, the mechanistic origin of the phase dependent reactivity remains unclear. In an attempt to understand this pattern of reactivity, we recently reported the resonance Raman intensity analysis of OCIO dissolved in cyclohexane.³⁹ In this study, the resonance Raman intensities and electronic absorption spectrum of OCIO were measured and modeled to develop a description of the optically prepared, ${}^{2}A_{2}$ potential energy surface. One conclusion from this work was that the excited-state structural evolution which occurs following photoexcitation is significantly altered in solution relative to the gas phase. A second important result was that the optical dephasing time of the ${}^{2}B_{1}-{}^{2}A_{2}$ transition in cyclohexane is only ~60 fs with the paucity of fluorescence suggesting that the origin of this dephasing is internal conversion from the optically prepared excited state. This observation raises the following question, "Which states are populated from decay of the ${}^{2}A_{2}$ surface?" The work presented here seeks to address this question.

Determination of which excited states are formed by decay of the ${}^{2}A_{2}$ surface has been difficult. Both experimental studies^{8,27,28} and theoretical work^{37,38} suggest that a lower lying surface of either ${}^{2}A_{1}$ or ${}^{2}B_{2}$ symmetry may be populated by decay of the ${}^{2}A_{2}$ state. Unfortunately, a direct spectroscopic signature corresponding to either of these states has not been reported. Identification of those states formed by decay of the ${}^{2}A_{2}$ state and their energetic location is critical in understanding the photochemistry of OCIO. This point is well illustrated by the recent ab initio studies of Peterson and Werner.³⁸ In these studies, calculations were performed to determine the topography of the optically prepared ${}^{2}A_{2}$ state, the optically weak ${}^{2}A_{1}$ state, and the optically dark ${}^{2}B_{2}$ state (the ground electronic state of OCIO is of ${}^{2}B_{1}$ symmetry with all symmetry labels corresponding to the C_{2n} point group). One of the main conclusions of this work was that interaction of the ${}^{2}A_{1}$ and ${}^{2}B_{2}$ surfaces is of central importance in defining the products formed from OClO photolysis. The predictions obtained from this theoretical analysis are in good agreement with a recent gas-phase product analysis.²¹ However, identification of the energetic location of either the

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^{a)}Author to whom correspondence should be addressed.

 ${}^{2}A_{1}$ or ${}^{2}B_{2}$ surfaces would serve as a further test of the accuracy of this theoretical work.

In this paper, we present the measurement and analysis of the resonance Raman depolarization ratio of the symmetric stretch fundamental transition of OCIO dissolved in cyclohexane. The resonance Raman depolarization ratio is defined as the intensity of light scattered with polarization perpendicular to that of the incident radiation divided by the intensity of light scattered with polarization parallel to that of the incident radiation. It has been long recognized that on resonance, these ratios can serve as an extremely sensitive probe of optically weak states even in the presence of transitions to optically stronger states.^{40,41} In OCIO, transitions to either the ${}^{2}A_{2}$ or ${}^{2}A_{1}$ states are allowed by symmetry; therefore, one might expect the Raman depolarization ratios to reflect the presence of these transitions thereby providing information on the location of the ${}^{2}A_{1}$ surface. In our previous resonance Raman intensity analysis, the depolarization ratios obtained on resonance with the lowest energy absorption band were observed to reach a maximum value of only 0.25 ± 0.04 , significantly lower than the value of 0.33 expected if the scattering were derived from only the optically strong ${}^{2}A_{2}$ surface.³⁹ This observation suggests that another state must be participating in the scattering process. The modeling of these depolarization ratios and the information this analysis provides on the location of the ${}^{2}A_{1}$ surface is presented here. We demonstrate below that the depolarization ratios can only be modeled by including scattering contributions from a second electronic excited state of ${}^{2}A_{1}$ symmetry. This result demonstrates that an excited state ${}^{2}A_{1}$ symmetry exists and that it is nearly degenerate with the ${}^{2}A_{2}$ surface. Our experiments were performed in cyclohexane, a nonpolar, weakly associating solvent, in an attempt to connect our studies with the wealth of gas-phase spectroscopic and theoretical work on OClO. In this spirit, we have employed the parameters for the ${}^{2}A_{1}$ surface determined from the *ab initio* work in the analysis of the depolarization ratios. The results presented here demonstrate that the observed depolarization ratios are consistent with the state orderings and displacements of the ${}^{2}A_{1}$ surface reported by Peterson and Werner, thus supporting the picture of OCIO reactivity derived from this theoretical work.

II. MATERIALS AND METHODS

A. Materials

Chlorine dioxide (OClO) was synthesized as previously reported.³⁹ Briefly, 13.6 g of potassium chlorate (99+% reagent grade, Aldrich) and 11.1 g of oxalic acid dihydrate (reagent grade, J. T. Baker) were dissolved in 60 ml of 2.3 M sulfuric acid (98% reagent grade, J. T. Baker). The solution was continuously stirred and slowly heated in a water bath until the evolution of green, gaseous OCIO was observed. The OClO gas was passed through a drying tube containing phosphorus pentoxide (reagent grade, J. T. Baker), and bubbled through 250 ml of neat cyclohexane (spectrophotometric grade, J. T. Baker) cooled to ~ 5 °C. This procedure resulted in an OClO concentration of $\sim 100 \text{ mM}$ with concentration and prep purity determined by static vis-UV absorption.

B. Resonance Raman spectra

Excitation at 532, 435.7, 368.9, 355, 319.9, and 282.4 nm was provided by the direct and hydrogen shifted, secondand third-harmonic output of a Nd:YAG laser (Spectra-Physics GCR-170) operating at 30 Hz. The OCIO scattering at 368.9 nm was monitored and found to increase linearly with incident power up to 10 μ J/pulse. Pulse energies were kept to $<10 \,\mu$ J at 368.9 nm, and adjusted at other wavelengths with reference to the absorption cross section in order to maintain a homogeneous extent of photoalteration. A 135° backscattering geometry was employed with the incident light focused onto either a thin film, wire guided jet (368.9, 355, 319.9, and 282.4 nm) or glass capillary containing the OClO solution (532, 435.7, 368.9, and 355 nm) using a 100 mm focal length UV quality spherical lens. Sample flow rates were sufficient to replace the illuminated sample volume between excitation pulses. The sample temperature was maintained at 5 °C using an ice bath. The scattered light was collected and delivered to a 0.5 m spectrograph (Acton) using refractive, UV quality optics. A polarization scrambler was placed before the entrance of the spectrograph to minimize the polarization dependence of the spectrograph throughput. The scattered light was dispersed using either a 1200 g/mm classically ruled ($\lambda_b = 500$ nm) or a 2400 g/mm holographic grating and detected with a Princeton Instruments, liquid-nitrogen cooled CCD detector.

C. Depolarization ratios

The depolarization ratio is defined as the intensity of scattered light with polarization perpendicular to that of the excitation light divided by the intensity of scattered light with polarization parallel to that of the excitation light.⁴⁰ To measure this ratio, the polarization of the incident light was defined by passing the excitation light through a stack of five, air-spaced quartz microscope slides oriented at Brewster's angle resulting in a polarization contrast ratio >1000:1. The polarization of the scattered light was analyzed using a large aperture (1.5 cm) Glan-Taylor calcite polarizer placed before the polarization scrambler. Measurement of the depolarization ratio of the 801 cm⁻¹ line of cyclohexane at each wavelength was performed in order to correct for the nonideal extinction of the polarizer via the following equation:⁴²

$$\frac{I_{\text{per}}^{\text{measured}}}{I_{\text{per}}^{\text{measured}}} = \frac{I_{\text{per}}^{\text{ideal}} + cI_{\text{par}}^{\text{ideal}}}{I_{\text{per}}^{\text{ideal}} + cI_{\text{per}}^{\text{ideal}}},$$
(1)

where c is a constant representing the amount of the orthogonally polarized light which "leaks" through the polarizer. The measured depolarization ratio of the cyclohexane 801 cm⁻¹ transition and its known value of 0.08 ± 0.01 were used to determine c at each excitation wavelength.⁴³ This correction value was then used to calculate the depolariza-

tion ratios reported here. The OCIO and cyclohexane intensities were determined by both simple peak integration and by fitting the bands to a Gaussian function convolved with a Lorentzian instrument response. Either approach was found to produce identical results within the error of the measurement.³⁹ The spectra are corrected for the spectral response of the instrument using either a calibrated deuterium (Hellma) or quartz-tungsten-halogen (Oriel) lamp. The spectra are not corrected for chromatic aberration; however, the energetic proximity of the cyclohexane standard to the OCIO transition minimizes the effects of chromatic aberration in calculating the corrected depolarization ratios (see below).

D. Computational methods

To assist in the presentation of the computational approach taken in this study, a brief overview of Raman depolarization theory is presented. The complete expression for the Raman depolarization ratio of an isotropically oriented sample is given by the following:⁴⁰

$$\rho = \frac{I_{\text{per}}}{I_{\text{par}}} = \frac{5\Sigma^{1} + 3\Sigma^{2}}{10\Sigma^{0} + 4\Sigma^{2}},$$
(2)

$$\Sigma^{0} = \frac{1}{3} |\alpha_{xx} + \alpha_{yy} + \alpha_{zz}|^{2},$$
(2)

$$\Sigma^{1} = \frac{1}{2} \{ |\alpha_{xy} - \alpha_{yx}|^{2} + |\alpha_{xz} - \alpha_{zx}|^{2} + |\alpha_{yz} - \alpha_{zy}|^{2} \},$$
(3)

$$\Sigma^{2} = \frac{1}{2} \{ |\alpha_{xy} + \alpha_{yx}|^{2} + |\alpha_{xz} + \alpha_{zx}|^{2} + |\alpha_{yz} + \alpha_{zy}|^{2} \} + \frac{1}{3} \{ |\alpha_{xx} - \alpha_{yy}|^{2} + |\alpha_{xx} - \alpha_{zz}|^{2} + |\alpha_{yy} - \alpha_{zz}|^{2} \},$$

where α_{mn} (m, n = x, y, or z) are the polarizability tensor matrix elements defined in the molecular frame. On resonance with a single electronic excited state, only one diagonal tensor element is taken to be nonvanishing (for example, α_{xx}) such that the depolarization ratio in this limit is 0.33. However, rotational dynamics and/or the existence of more than one finite valued tensor element can result in deviation of the depolarization ratio from this value.^{40,41,44–57}

The symmetry of OCIO limits the number of polarizability matrix elements that must be considered in modeling the Raman depolarization ratio of the symmetric stretch fundamental transition on resonance. Ground state OCIO is of C_{2v} symmetry resulting in only the ${}^{2}B_{1}-{}^{2}A_{2}$ transition (*x* polarized) and the ${}^{2}B_{1}-{}^{2}A_{1}$ transition (*y* polarized) being allowed (the *z* axis is defined as oriented along the C₂ rotational axis of the molecule, the *x* axis is orthogonal to this axis and to the plane of symmetry bisecting the terminal oxygens). Since the vibrations of OCIO are of a_{1} or b_{2} symmetry, vibronic coupling of the ${}^{2}A_{2}$ and ${}^{2}A_{1}$ surfaces is not considered. However, it has been suggested that these surfaces are coupled via a spin-orbit interaction. We can estimate the magnitude of this coupling by the following procedure. Resonance Raman intensity analysis has established a Gaussian homoge-

neous linewidth of 80 cm⁻¹ corresponding to an optical dephasing time for the ${}^{2}B_{1} - {}^{2}A_{2}$ transition of ~60 fs.³⁹ If we assume that the exclusive origin of this linewidth is population relaxation, an upper limit of 0.033 fs^{-1} on the excitedstate decay rate is established. Employing a Fermi goldenrule rate description of the excited-state decay with an estimated final-state density of 5 states/cm⁻¹, the magnitude of the spin-orbit coupling between the ${}^{2}A_{2}$ and ${}^{2}A_{1}$ states is found to be only $\sim 2 \text{ cm}^{-1}$. Although this estimate is crude in that the Franck-Condon factors for states involved in the internal conversion are not explicitly considered, the small size of the coupling does suggest that separability of the transitions is a reasonable approximation. It should be noted that the vibronic linewidths observed in the absorption spectrum become larger for transitions to higher levels of the excited-state vibronic manifold; therefore, the estimate presented here can be viewed as approximate due to the "average" nature of the homogeneous linewidth. In the limit of this approximation, the transitions are modeled as separable with both the α_{xx} (transition to ${}^{2}A_{2}$) and α_{yy} (transition to ${}^{2}A_{1}$) tensor elements being nonvanishing on resonance. Utilizing the time-dependent approach, the polarizability tensor matrix elements corresponding to these transitions are given by the following:^{56,58,59}

$$\left[\alpha_{if}(E_L)\right]_{pp} = \frac{ie^2 M_{pp}^2}{\hbar} \int_0^\infty \langle f|i(t)\rangle e^{i(E_L + \epsilon_i)t/\hbar} e^{-\Gamma^2 t^2/\hbar^2} dt,$$
(4)

where E_L is the frequency of the incident light, ϵ_i is the energy of the initial vibrational state, M_{pp} is the electronic transition moment (p = x or y for the transition to the ${}^{2}A_{2}$ or ${}^{2}A_{1}$ state, respectively), Γ is the homogeneous linewidth, and $\langle f|i(t)\rangle$ represents the time-dependent overlap of the final state in the scattering process with the initial vibrational state propagating under the influence of the excited-state Hamiltonian. In this study, the final state for the fundamental transition involving the symmetric stretch corresponds to n=1along the symmetric stretch and n=0 along the bend and asymmetric stretch. The lowest frequency normal mode of OCIO is at 450 cm^{-1} ; therefore, the initial vibrational state for all degrees of freedom was taken to be the ground vibrational level. The homogeneous linewidth is a composite of both radiative and nonradiative vibronic dephasing processes corresponding to both population decay (T_1) and pure dephasing (T_2^*) . Consistent with our previous analysis, the homogeneous linewidth is modeled as Gaussian.³⁹ The absorption cross section (σ_A) at the same level of approximation is:56,58,59

$$[\sigma_A(E_L)]_{pp}$$

$$= \frac{4\pi e^2 E_L M_{pp}^2}{6\hbar^2 cn} \int_{-\infty}^{\infty} \partial E_{00} H(E_{00})$$
$$\times \int_{-\infty}^{\infty} \langle i|i(t)\rangle e^{i(E_L + \epsilon_i)t/\hbar} e^{-\Gamma^2 t^2/\hbar^2} dt, \qquad (5)$$

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where $\langle i | i(t) \rangle$ is the time-dependent overlap of the initial ground vibrational state with this same state propagating on the excited-state potential energy surface. The product of this overlap with the homogeneous broadening terms is Fourier transformed to the frequency domain.⁵⁹ The result of this transformation is convolved with a Gaussian function to model the effect of inhomogeneous broadening on the absorption spectrum. This broadening originates from static solvent environments which alter the energy gap between the ground and excited state (E_{00}) . The inhomogeneous linewidth reported here corresponds to the standard deviation of this distribution. The magnitude of this broadening for the ${}^{2}A_{2}$ state has been determined by resonance Raman intensity analysis; however, corresponding information for the ${}^{2}A_{1}$ state is not available. Therefore, the inhomogeneous distributions for both the ${}^{2}B_{1} - {}^{2}A_{2}$ and ${}^{2}B_{1} - {}^{2}A_{1}$ transitions are assumed to be equivalent such that the absorption cross sections for either transition are convolved with identical Gaussian functions. In doing so, the approximation is made that the energy shifts which characterize the inhomogeneous distributions are identical, and that the shifts for both transitions are correlated. At this level of approximation, the expression for the Raman cross section (σ_R) averaged over all molecular orientations when two uncoupled, orthogonally polarized states contribute to the observed scattering is:44,59

$$\sigma_{R}(E_{L}) = \frac{8\pi E_{S}^{3} E_{L}}{9\hbar^{4} c^{4}} \left[\left(\int_{-\infty}^{\infty} \partial E_{00} H(E_{00}) |\alpha_{xx}(E_{00})|^{2} \right) + \left(\int_{-\infty}^{\infty} \partial E_{00}' H(E_{00}') |\alpha_{yy}(E_{00}')|^{2} \right) \right].$$
(6)

Finally, inhomogeneous broadening is included in calculation of the depolarization ratio as follows:

$$\rho(E_L) = \left(\frac{\int_{-\infty}^{\infty} \partial E_L H(E_L) (5\Sigma^1 + 3\Sigma^2)}{\int_{-\infty}^{\infty} \partial E_L H(E_L) (10\Sigma^0 + 4\Sigma^2)}\right),\tag{7}$$

where the rotational invariants (Σ^n) are given in Eq. (3). The rotational invariants are derived from polarizability terms which originate from transitions with different E_{00} energies such that the invariants are not characterized by a single E_{00} . Therefore, inhomogeneous broadening is incorporated by convolving with respect to excitation energy using an identical Gaussian distribution to that employed in calculating the absorption and Raman cross sections.

Consistent with our previous study, anharmonicity was included in the description of the ${}^{2}A_{1}$ and ${}^{2}A_{2}$ excited states. Specifically, the excited-state potential energy surfaces described in the ground-state dimensionless coordinate basis are as follows:

$$V_{e} = \frac{1}{2} \frac{\omega_{e1}^{2}}{\omega_{g1}} (q_{1} - \Delta_{1})^{2} + \frac{1}{6} \chi_{111} \left(\frac{\omega_{e1}}{\omega_{g1}}\right)^{3/2} (q_{1} - \Delta_{1})^{3} + \frac{1}{2} \frac{\omega_{e2}^{2}}{\omega_{g2}} (q_{2} - \Delta_{2})^{2} + \frac{1}{2} \frac{\omega_{e3}^{2}}{\omega_{g3}} (q_{3})^{2}, \qquad (8)$$

where the subscripts 1, 2, and 3 refer to the symmetric stretch, bend, and asymmetric stretch, respectively. In addi-

tion, ω_e and ω_g denote the excited- and ground-state harmonic frequencies, respectively. In the above potential, the symmetric stretch is modeled with both harmonic and cubic anharmonic terms. The potential along the bend and asymmetric stretch contains only the harmonic terms given the limited displacement along the bend coordinate and absence of displacement along the asymmetric stretch coordinate.³⁹ Anharmonic coupling between the symmetric and asymmetric stretch coordinates is not included; however, calculations in which this coupling was included were performed to quantify the error in this approximation. It was found that the inclusion of off-diagonal anharmonicity lowered the cross sections by $\sim 15\%$ and had a negligible (<5%) effect on the depolarization ratios reported below. The ground electronic state along all three coordinates was modeled as harmonic. In the limit of this description for the excited-state potential energy surface, the three vibronic degrees of freedom can be modeled as separable such that the multidimensional, time-dependent overlaps in the above equations are decomposed into products involving one-dimensional overlaps:

$$\langle i|i(t)\rangle = \prod_{k=1}^{3} \langle i_{k}|i_{k}(t)\rangle, \qquad (9)$$

$$\langle f|i(t)\rangle = \langle f_1|i_1(t)\rangle \prod_{k=2}^3 \langle i_k|i_k(t)\rangle, \tag{10}$$

where the subscript 1 denotes the Raman active coordinate (the symmetric stretch for the transition of interest in this study). The time-dependent overlaps involving harmonic surfaces with frequency change were calculated using the method of Mukamel and co-workers.⁶⁰ Time-dependent overlaps for the anharmonic potentials were calculated using the approximate time-propagator method of Feit and Fleck.^{61,62} In this approach, $|i(t)\rangle$ is given by:

$$|i(t)\rangle = e^{i(\Delta t)\nabla^2/4M} e^{-i(\Delta t)V} e^{i(\Delta t)\nabla^2/4M} |i(0)\rangle + \vartheta(\Delta t^3),$$
(11)

where ∇^2 is the Laplacian in position space, *V* is the excitedstate potential, and Δt is the size of the propagation time step. The error in this approach scales as the cube of the time step; therefore, the step size was kept to a minimum (0.2 fs) with propagations employing 2000 time steps. The calculated intensities did not change with further increase in the number of time steps or a reduction in the step size.

III. RESULTS

A. Experimental results

Figure 1 presents the polarization dependent resonance Raman spectrum of OCIO dissolved in cyclohexane obtained with excitation at 319.9 nm. The upper spectrum is obtained when the polarization of the scattered light is selected to be parallel to that of the incident field (the parallel spectrum), and the lower spectrum corresponds to scattering when the polarization is selected to be perpendicular to the polarization of the incident field (the perpendicular spectrum). The 8266



FIG. 1. Resonance Raman spectrum of chlorine dioxide dissolved in cyclohexane obtained with excitation at 319.9 nm. The spectra correspond to experiments in which the polarization of the scattered light is selected to be parallel (||) or perpendicular (\perp) to that of the incident light. The fundamental transition involving the symmetric stretch is at 937 cm^{-1} , with transitions due to the cyclohexane solvent denoted with an asterisk. The perpendicular spectrum has been multiplied by a factor of 2 for clarity.

fundamental transition involving the symmetric stretch is at 937 cm^{-1} and the cyclohexane transition used as an internal depolarization standard is at 801 cm⁻¹. The figure demonstrates that the intensity of the perpendicular spectrum is less than that observed in the parallel spectrum, with the depolarization ratio calculated by dividing the intensity observed in the perpendicular spectrum by that observed in the parallel spectrum.

Figure 2 presents the experimentally determined Raman depolarization ratios of the symmetric stretch fundamental transition of chlorine dioxide (OClO) dissolved in cyclohexane. The values for the ratios are reported in Table I. In addition to the various excitation wavelengths studied here, the previously reported depolarization ratios for the symmetric stretch fundamental transition of OCIO dissolved in CFCl₃ are also shown in Fig. 2.⁶³ The absorption spectra of OCIO in both CFCl₃ and cyclohexane are similar, and the polarizability of both solvents is roughly the same $(CFCl_3:9.5 \text{ Å}^3, C_6H_{12}:11 \text{ Å}^3)^{64}$ such that simultaneous analysis of both data sets is reasonable.

If only a single electronic excited-state surface contributes to Raman scattering on resonance, a depolarization ratio of 1/3 is expected. Figure 2 demonstrates that although the depolarization ratio increases towards this value on resonance, the entire depolarization dispersion curve is significantly lower than what would be expected if the scattering originated from a single excited state. There are two possible explanations for this behavior. First, rotation of the molecule during the Raman scattering process can result in deviation of the depolarization ratio from 1/3 even if only a single electronic surface is involved in the scattering process.^{40,51–56}



FIG. 2. Absorption spectrum of chlorine dioxide in cyclohexane (solid line) and the Raman depolarization ratios for the symmetric stretch fundamental transition (points). The square points represent the depolarization ratios determined in this study, and the circles correspond to previously reported values for chlorine dioxide in CFCl₃ (Ref. 67).

Second, the presence of multiple electronic states with nonaligned electronic transition moments can result in more than one matrix element of the polarizability tensor being nonzero.40,41,44,50 For example, the expected resonance Raman depolarization ratio for a totally symmetric mode measured on resonance with two orthogonally polarized degenerate excited states with equal transition moments is 1/8 [as can be verified by substitution in Eqs. (2) and (3) with α_{xx} $= \alpha_{yy}$ and all other elements equal to zero]. As this example illustrates, resonance Raman depolarization ratios can be used as a probe for the presence of multiple excited states. As will be shown below, the experimental depolarization dis-

TABLE I. Depolarization ratios of the symmetric stretch fundamental transition of chlorine dioxide.

Excitation energy ($\times 10^{-3}$ cm ⁻¹)	$ ho(\nu_1)^{\mathrm{a}}$	
15.4 ^b	0.15 ± 0.01	
18.8 ^c	0.12 ± 0.01	
19.4 ^b	0.16 ± 0.01	
20.5 ^b	0.18 ± 0.011	
21.4 ^b	0.21 ± 0.011	
22.9 ^c	0.20 ± 0.02	
27.1 ^c	0.25 ± 0.04	
28.2 ^c	0.21 ± 0.03	
31.3 ^c	0.19 ± 0.02	
35.4 ^c	0.18 ± 0.02	

^aThe depolarization ratio (ρ) is defined as the intensity of Raman scattering observed polarized perpendicular to the polarization of the excitation light divided by the observed scattering with polarization parallel to the polarization of the excitation light.

^bValues are from the previous study of Eysel and Bernstein of OCIO in CFCl3 (Ref. 63).

^cValues are from the measurements performed in the study.

persion curves for OClO are consistent with the presence of an optically weak transition to a ${}^{2}A_{1}$ excited state which is nearly degenerate with the optically strong ${}^{2}B_{1} - {}^{2}A_{2}$ transition; however, the contribution of rotational dynamics must be evaluated, as illustrated in the next section. This is followed by an analysis in which the scattering contribution from the ${}^{2}A_{1}$ excited state is incorporated into the description of the Raman depolarization ratios.

B. Rotational dynamics and Raman depolarization

The dependence of Raman depolarization ratios on molecular rotation during the Raman scattering process is well documented.51-54,56 This effect has been typically observed in the gas phase where unhindered rotation of the molecule is coupled with a decrease in the homogeneous linewidth due to the absence of solvent-induced dephasing. The effect of rotational dynamics on resonance Raman depolarization ratios is illustrated by the time-dependent expression for Raman anisotropy:⁵⁴

$$r_{if} = \frac{\int_0^\infty e^{-2\Gamma t/\hbar} |\langle f|i(t)\rangle|^2 R(t) dt}{\int_0^\infty e^{-2\Gamma t/\hbar} |\langle f|i(t)\rangle|^2 dt},$$
(12)

where R(t) represents the time-dependent anisotropy factor of 0.4 $\langle P_2[\mu(0) \cdot \mu(t)] \rangle$ where P_2 is the second Legendre polynomial and μ is the electronic transition dipole moment. The above expression is appropriate in the limit of large inhomogeneous linewidth and population of high rotational quantum states. As determined by resonance Raman intensity analysis, inhomogeneous effects represent the largest contribution to the broadening evident in the electronic absorption spectrum, and the experiments reported here are performed at 5 °C such that the high-temperature limit for rotational states is applicable.³⁹ This equation dictates that if the product of the vibronic time correlator and homogeneous linewidth decays more rapidly than the evolution of the rotational anisotropy, then a Raman anisotropy of 0.4 should be observed corresponding to a Raman depolarization ratio of 1/3.65 For OCIO dissolved in cyclohexane, the homogeneous broadening is modest (80 cm^{-1}) and the majority of the excited-state nuclear evolution occurs along the symmetric stretch coordinate.³⁹ Furthermore, the rotational constants of OCIO are relatively large $(A = 1.05633 \text{ cm}^{-1}, B)$ $= 0.30950 \text{ cm}^{-1}$, and $C = 0.23815 \text{ cm}^{-1}$) such that rotational contributions to Raman depolarization cannot be obviously neglected.^{26,29,66} In the analysis presented here, we approximate OClO as a prolate symmetric top with A $= 1.05633 \text{ cm}^{-1}$ and $B = C = 0.30950 \text{ cm}^{-1}$. With this approximation and knowledge that the ${}^{2}B_{1} - {}^{2}A_{2}$ transition is orthogonal to the C₂ symmetry axis of OClO,⁹ the rotational correlation function is given by the following:⁵³

$$R(t) = \left\{ \sum_{JK} JP_{JK} \right\}^{-1} \left\{ \sum_{JK} JP_{JK} \left[\frac{1}{40} \left[1 - 3(K')^2 \right]^2 + \frac{3}{10} (K')^2 \left[1 - (K')^2 \right]^2 \cos(\omega J t) + \frac{3}{40} \left[1 - (K')^2 \right]^2 \cos(2\omega J t) \right. \\ \left. + \frac{9}{80} \left[1 - (K')^2 \right]^2 \cos(2\Omega K t) + \frac{3}{20} \left[1 - (K')^4 \right] \cos(\omega J t) \cos(2\Omega K t) + \frac{3}{80} \left[1 + 6(K')^2 + (K')^4 \right] \cos(2\omega J t) \cos(2\Omega K t) \right] \right\},$$

$$\left. + (K')^4 \left[\cos(2\omega J t) \cos(2\Omega K t) \right] \right\},$$

$$\left. (13)$$

1

where K' = K/J, $\omega = 2B/\hbar$, $\Omega = 2(A-B)/\hbar$, and P_{JK} represents the population of the $|JK\rangle$ rotational state as dictated by Boltzmann statistics. Figure 3(A) presents the rotational correlation function for OCIO calculated using Eq. (11). This calculation was performed by discrete summation over all J and *K* states for which the energy was $\leq 6 \text{ kT}$ resulting in the incorporation of 98% of the population. The correlation function depicted in the figure corresponds to the rotational dynamics of gas-phase OCIO with the corresponding dynamics in solution expected to be slower. Therefore, the calculation presented here establishes an upper limit on the effect of rotational dynamics on the resonance Raman depolarization ratios. Figure 3(B) presents the product of the vibronic time correlator and the homogeneous dephasing term calculated using the parameters in Table II for the ${}^{2}A_{2}$ potential energy surface. This product undergoes the majority of its decay in the first 50 fs, a time scale which is rapid compared to rotational dynamics. Consistent with this, the Raman anisotropy

is found to be 0.39 corresponding to a Raman depolarization ratio of 0.34. Therefore, rotational dynamics are too slow to play a significant role in defining depolarization ratios. In addition, the effect of rotation on this transition is to elevate the depolarization ratio above 1/3; however, the experimental values are all below this value suggesting that factors other than rotational dynamics are of importance.

C. Preresonant intensity of UV states and Raman depolarization ratios

Previous analysis of the preresonant Raman depolarization ratios of OCIO suggested that the preresonant contributions from transitions to electronic states located in the far-UV (<200 nm) were important in establishing the depolarization ratios of OClO.67 High-resolution absorption and electron-energy loss spectroscopy have been used to characterize these higher energy transitions.^{68,69} These studies have demonstrated the presence of four bands which are denoted



FIG. 3. (A) Rotational correlation function $(0.4\langle P_2[\mu(0),\mu(t)]\rangle)$ of the ${}^2B_1{-}^2A_2$ transition of chlorine dioxide. Calculation was performed by approximating chlorine dioxide as a prolate symmetric top with rotational constants of $A = 1.056 \text{ cm}^{-1}$ and $B = 0.310 \text{ cm}^{-1}$ (Ref. 29). (B) The multidimensional time-dependent overlap function $\langle fli(t) \rangle$ multiplied by exp $(-2\Gamma/t)$ where Γ is the homogeneous linewidth determined from resonance Raman intensity analysis (80 cm⁻¹) (Ref. 39). The rapid decay of this function combined with the relatively slow rotational dynamics results in a negligible contribution of rotational dynamics to the resonance Raman depolarization ratios.

as follows (with band origin in parentheses): *C* band (183.08 nm), *D* band (162.66 nm), *E* band (~156.7 nm), and *F* band (144.29 nm). Of these transitions, the absorption cross section of the *F* band is largest (~4 times larger than the ${}^{2}B_{1}-{}^{2}A_{2}$ transition).⁶⁸ These transitions are assigned as Rydberg progressions with the *C* and *D* band transition moments being perpendicular to the ${}^{2}B_{1}-{}^{2}A_{2}$ transition.^{68–72}

The presence of transitions at higher energy than the ${}^{2}B_{1}-{}^{2}A_{2}$ transition, and polarized perpendicular to this transition, may result in deviation of the depolarization ratio from 1/3. The behavior of resonance Raman depolarization ratios when two orthogonal transitions contribute to the scattering process has been presented by Shang and Hudson, and the arguments presented in their paper are revisited here for completeness.⁴¹ In the limit where only two orthogonally polarized transitions contribute to resonance Raman scattering, and coupling between excited states is negligible, two diagonal elements of the polarizability tensor will be nonzero (for example, α_{xx} and α_{yy}). The expressions for the rotational invariants and Raman depolarization ratio [Eqs. (2) and (3)] reduce to:

TABLE II. Parameters for the example depolarization ratio calculation.

	State 1	State 2
$\nu ({\rm cm}^{-1})^{\rm a}$	1000	1000
Δ^{b}	0.1	0.1
$\Gamma (cm^{-1})^{c}$	200	200
$\Theta (\mathrm{cm}^{-1})^{\mathrm{d}}$	0	0
M_{eg} (Å) ^e	1.0	1.0
E_{00} (cm ⁻¹) ^f	30000	31000

^aThe ground and excited-state frequencies are equal.

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

^cThe homogeneous linewidth. A Lorentzian functional form was employed in this calculation.

^dThe standard deviation of the inhomogeneous linewidth.

^eThe transition length.

^fThe energy gap between the ground and excited electronic states.

$$\Sigma^{0} = \frac{1}{3} |\alpha_{xx} + \alpha_{yy}|^{2}, \quad \Sigma^{1} = 0$$

$$\Sigma^{2} = \frac{1}{3} \{ |\alpha_{xx} - \alpha_{yy}|^{2} + |\alpha_{xx}|^{2} + |\alpha_{yy}|^{2} \}$$

$$\rho = \frac{3\Sigma^{2}}{10\Sigma^{0} + 4\Sigma^{2}}.$$
(14)

We have performed a sample calculation to illustrate the dependence of the depolarization ratio on the relative sign and amplitudes of α_{xx} and α_{yy} . The results of this calculation are presented in Fig. 4 with the parameters for the calculation documented in Table II. The "gedanken" system consists of two orthogonally polarized transitions with equal transition lengths. There is a single vibronic degree of freedom, with the frequency and excited-state displacement of this mode being identical for both transitions. The only difference between the transitions is the E_{00} energy which differs by 1000 cm^{-1} (30 000 vs 31 000 cm⁻¹). Since the polarizability tensor elements are complex quantities, Figures 4(A) and 4(B) present the real and imaginary parts of α_{xx} and α_{yy} , respectively. Figure 4(C) presents the values of the rotational invariants [Eq. (14)], and the Raman depolarization ratio is presented in Fig. 4(D). Figure 4 illustrates the dependence of the depolarization ratio on the amplitudes of the tensor elements with this dependence consisting of three separate regions, preresonance, resonance, and postresonance. First, preresonant with either transition, the real part of the polarizability dominates such that a depolarization ratio of 1/8 is observed due to the equal amplitude of the real part of the polarizability for both states. As resonance with the lowerenergy state is approached, the depolarization ratio increases in value reaching a single-state value of 1/3 when the lowerenergy transition dominates the polarizability. At excitation wavelengths which are postresonant with the lower-energy transition yet preresonant with the higher energy transition, both the real and imaginary parts of α_{xx} can differ in sign relative to α_{yy} . Due to this evolution in sign, the depolarization ratio becomes larger than 1/3 approaching a limiting value of 3/4. Finally, at frequencies which are postresonant with both states, the depolarization ratio decreases and even-



FIG. 4. Sample calculation of the Raman depolarization ratio arising from two orthogonally polarized transitions. The parameters for the calculation are given in Table II. (A) The real part of the polarizability arising from state 1 (solid line) and state 2 (dashed line). (B) The imaginary part of the polarizability arising from state 1 (solid line) and state 2 (dashed line). (C) Rotational invariants used in calculation of the Raman depolarization ratio [Eq. (12)]: Σ_0 (solid line) and Σ_2 (dashed line). (D) The Raman depolarization ratio.

tually reaches 1/8 similar to the preresonance case. This example serves to illustrate that due to the evolution in sign of the real and imaginary parts of the polarizability, the presence of an orthogonally polarized state in energetic proximity to the electronic transition of interest can have a pronounced effect on the resonance Raman depolarization ratio.

To ascertain the importance of preresonance contributions of the far-UV transitions, the first depolarization ratio model employed was with α_{xx} and α_{yy} corresponding to the ${}^{2}B_{1}-{}^{2}A_{2}$ transition and preresonant contributions of the higher energy transitions, respectively. Given that the higherenergy states are located in the far-UV and that the slowly varying real part of the polarizability dominates far from resonance (Fig. 4), it is reasonable to model α_{yy} as a constant. This was the approach previously taken in analyzing the preresonant OCIO depolarization ratios in CFCl₃.⁶⁷ Figure 5 presents a comparison of the calculated Raman depo-



FIG. 5. Measured depolarization ratios for the symmetric stretch fundamental transition of chlorine dioxide, and calculated depolarization dispersion curves. The curves were determined by modeling α_{xx} and α_{yy} as originating from the ${}^{2}A_{2}$ and excited-states located in the far-ultraviolet, respectively. Parameters for the ${}^{2}A_{2}$ state are presented in Table III. The preresonance contribution of the far-UV states is modeled as a constant with values of 0.06 (short-dash line), 0.2 (solid line), and 0.4 Å³ (long-dash line). Although the depolarization ratios at lower excitation energies can be reproduced, the depolarization ratios measured directly on resonance are not well modeled by this approach.

larization dispersion curves where α_{xx} was calculated utilizing the parameters for the ${}^{2}A_{2}$ potential-energy surface determined in resonance Raman intensity analysis (Table III) and values for α_{yy} ranging from 0.06 to 0.4 Å.³ The comparison of the calculated Raman depolarization to the experimentally determined depolarization ratios (Fig. 5) demonstrates that although the ratios at preresonant wavelengths (15 000–20 000 cm⁻¹) can be reproduced, the ratios observed on resonance are significantly overestimated.

The Raman depolarization ratios measured directly on resonance demonstrate that preresonant contributions from electronic transitions located in the far-UV are not entirely responsible for the deviation of the ratios from 1/3. The interesting aspect of this calculation is that as α_{yy} is increased, the predicted Raman depolarization ratio directly on resonance increases beyond 1/3; however, the experimental values are always below this value. As demonstrated in Fig. 4, the calculated depolarization ratio values above 1/3 originate from the evolution in the sign of α_{xx} relative to α_{yy} with excitation throughout the ${}^{2}B_{1} - {}^{2}A_{2}$ transition. Since the depolarization ratios are all less than 1/3, the sign of α_{yy} must be similar in sign to α_{xx} at all excitation wavelengths. This can only occur if the orthogonally polarized transition is either degenerate or nearly degenerate with the ${}^{2}B_{1} - {}^{2}A_{2}$ transition.

D. Near-degenerate ${}^{2}B_{1} - {}^{2}A_{1}$ transition and resonance Raman depolarization ratios

The above analysis suggests that in addition to the ${}^{2}B_{1}-{}^{2}A_{2}$ transition, an energetically close, orthogonally polarized transition is participating in the scattering process.

TABLE III. ${}^{2}A_{2}$ and ${}^{2}A_{1}$ excited-state potential energy surface parameters.

${}^{2}A_{2}$ potential energy surface ^a						
Transition ^b	$(\mathrm{cm}^{-1})^{\mathrm{c}}$	ω_e (cm ⁻¹)	Δ^{d}	χ_{111}^{e}		
ν_1	937	675	6.1	-137		
ν_2	450	284	0.3	0		
ν_3	1100	750	0	0		
${}^{2}A_{1}$ potential energy surface ^{f.g}						
ν_1	937	650	6.6	-137		
ν_2	450	311	0.05	0		
<i>ν</i> ₃	1100	1474	0	0		

^aParameters were determined from the resonance Raman intensity analysis of chlorine dioxide (Ref. 39). Calculation was performed employing a Gaussian homogeneous linewidth (Γ) of 75 cm⁻¹, inhomogeneous standard deviation of 140 cm⁻¹, $E_{00} = 17450$ cm⁻¹, $M_{eg} = 0.32$ Å, and n = 1.42. ^bThe symbols ν_1 , ν_2 , and ν_3 refer to the symmetric stretch, bend, and asymmetric stretch, respectively.

 $^{c}\omega_{e}$ and ω_{e} correspond to the ground- and excited-state harmonic frequencies, respectively.

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

eAnharmonicity prefactor for the cubic term in the expression for the excited-state potential energy surface as given in Eq. (7).

^fPotential energy surface parameters were obtained from the *ab initio* theoretical analysis of Peterson and Werner (Ref. 38). Calculation was performed with the following additional parameters for the ${}^{2}A_{1}$ state: Gaussian homogeneous linewidth $(\Gamma) = 240 \text{ cm}^{-1}$, inhomogeneous standard deviation=160 cm⁻¹, E_{00} =16 400 cm⁻¹, M_{eg} =0.16 Å, n=1.42.

^gCalculation involving an additional preresonance contribution from states located in the far-UV was accomplished by adding a constant contribution of 0.2 Å³ to the polarizability determined using the ${}^{2}A_{1}$ state parameters reported here.

Experimental support for the presence of a ${}^{2}B_{1} - {}^{2}A_{1}$ transition, orthogonal to the ${}^{2}B_{1} - {}^{2}A_{2}$ transition, in this spectral region is modest at best. High-resolution absorption studies have failed to observe any intensity assignable to a transition involving a state of ${}^{2}A_{1}$ symmetry.⁸ However, the increase in linewidth for higher-energy vibronic transitions in ${}^{2}B_{1} - {}^{2}A_{2}$ absorption spectrum was interpreted as arising from an increase in the depopulation rate of the ${}^{2}A_{2}$ surface at higher energies.⁹ The rotational structure of the ${}^{2}B_{1} - {}^{2}A_{2}$ transition has also been used to argue for internal conversion of the ${}^{2}A_{2}$ state.²⁶⁻²⁸ In the gas-phase absorption study of Hubinger and Nee, a nonvanishing cross section between the ${}^{2}B_{1} - {}^{2}A_{2}$ transition and the C band was observed and suggested to arise from a transition involving the ${}^{2}A_{1}$ state.⁶⁸ The strongest support for the presence of a ${}^{2}B_{1} - {}^{2}A_{1}$ transition nearly degenerate with that to the ${}^{2}A_{2}$ state is found in *ab initio* studies.37,38 These calculations predict that three excited states of ${}^{2}A_{2}$, ${}^{2}A_{1}$, and ${}^{2}B_{2}$ symmetry are all nearly degenerate in the Franck–Condon region of the ${}^{2}A_{2}$ surface accessed by optical excitation from the ground state. Recall, the ${}^{2}B_{2}$ state cannot directly contribute to the observed scattering since the ${}^{2}B_{1} - {}^{2}B_{2}$ transition is optically dark by symmetry.

To explore the possibility of a ${}^{2}B_{1} - {}^{2}A_{1}$ transition contributing to the Raman depolarization ratios, the contribution of the ${}^{2}A_{1}$ surface was modeled using the parameters reported in the ab initio study of Peterson and Werner with these values reported in Table III.38 The ab initio results predict that not only is the transition to the ${}^{2}A_{1}$ state nearly degenerate with that to the ${}^{2}A_{2}$ surface, but that the displacements and anharmonicities along the symmetric stretch coordinate are also similar. The ${}^{2}A_{1}$ surface is predicted to be only slightly displaced along the bend, and not displaced along the asymmetric stretch. Frequency differences exist between the ground and excited state along all coordinates. To constrain the calculation, the ab initio determined displacements of the ${}^{2}A_{1}$ state along each normal coordinate were used as reported with only the transition length and the E_{00} energy for the ${}^{2}A_{1}$ state adjusted in an attempt to reproduce the depolarization ratios. The inhomogeneous broadening determined from resonance Raman intensity analysis of the ${}^{2}B_{1} - {}^{2}A_{2}$ transition was applied to transitions involving both the ${}^{2}A_{2}$ and ${}^{2}A_{1}$ states; however, the amount of homogeneous broadening to include in modeling the ${}^{2}A_{1}$ transition is not well defined. If the homogeneous linewidth were similar to that of the ${}^{2}A_{2}$ state, then vibronic structure in the ${}^{2}B_{1} - {}^{2}A_{1}$ transition would be expected. However, all observed structures in the electronic absorption spectrum observed in this spectral region are accounted for by the ${}^{2}B_{1} - {}^{2}A_{2}$ transition.⁸ Therefore, the homogeneous linewidth was increased until an unstructured spectrum was obtained. It should be noted that a factor of two increase in the linewidth had a negligible effect on the calculated depolarization dispersion curves such that the ambiguity in the homogeneous linewidth does not significantly impact the results and conclusions reported here.

Figure 6(A) presents the calculated absorption spectra arising from the ${}^{2}A_{2}$ and ${}^{2}A_{1}$ states. The figure demonstrates that the transition to the ${}^{2}A_{1}$ state is shifted to higher energies due to the larger displacement along the symmetric stretch coordinate (Table III) combined with similar E_{00} energy relative to the ${}^{2}A_{2}$ state. However, the entire ${}^{2}A_{1}$ band profile is expected to reside under the stronger ${}^{2}B_{1} - {}^{2}A_{2}$ transition. Figure 6(B) presents the sum of the individual absorption bands and the experimental absorption spectrum. As the figure demonstrates, the agreement between the calculated and measured absorption spectra is good. Figure 6(C)presents the calculated Raman depolarization dispersion curve for this two-state model using the parameters reported in Table III. Although the predicted depolarization dispersion curve remains significantly below 1/3 at all excitation wavelengths, the preresonance depolarization ratios are not well reproduced. Better overall agreement can be achieved by increasing the ${}^{2}B_{1} - {}^{2}A_{1}$ transition length; however, this would result in rather large intensity for this transition, a result which is not supported by experiment.

To improve upon this two-state model, a hybrid model which incorporates both the resonance and preresonance aspects of the above models was created. In this approach, the α_{yy} tensor element consists of two parts: the ${}^{2}B_{1} - {}^{2}A_{1}$ transition, and a constant term representing preresonant scattering from higher-energy states. The contribution to α_{yy} from the ${}^{2}B_{1} - {}^{2}A_{1}$ transition was identical to the calculation pre-



FIG. 6. (A) Calculated electronic absorption spectra corresponding to the ${}^{2}B_{1}-{}^{2}A_{2}$ (solid line) and ${}^{2}B_{1}-{}^{2}A_{1}$ (dashed line) transitions, respectively. Calculations were performed as outlined in the text with parameters for the ${}^{2}A_{2}$ state determined from resonance Raman intensity analysis (Ref. 39) and parameters for the ${}^{2}A_{1}$ state obtained from previous *ab initio* theoretical work (Ref. 38). (B) The sum of the calculated absorption spectra (dashed) and measured (solid) absorption spectrum of chlorine dioxide in cyclohexane. (C) Comparison of the measured (points) and calculated (solid line) Raman depolarization ratios. (D) Comparison of the measured (points) and calculated (solid line) Raman depolarization ratios. The tensor element corresponding to the ${}^{2}A_{1}$ transition also includes a constant term of 0.2 Å³ representing the preresonance contribution of states located in the farultraviolet.

sented above. To incorporate the preresonant contribution, a constant term of 0.2 Å³ was also added to α_{yy} . Figure 6(D) presents the calculated resonance Raman depolarization dispersion curve with the inclusion of preresonance effects. The combination of both resonant and preresonant contributions to α_{yy} results in a model which is capable of reproducing the experimental depolarization ratios. The important result of this analysis is that even if preresonant scattering contributions are included, the resonance Raman depolarization ratios can only be modeled by including a transition which is both nearly degenerate with and orthogonal to the ${}^{2}A_{2}$ state. Symmetry constraints dictate that the character of this state must be ${}^{2}A_{1}$.

IV. DISCUSSION

A. The ${}^{2}A_{1}$ state and the photochemistry of OCIO

The experimental results and analysis presented here demonstrate that in OClO, a ${}^{2}A_{1}$ electronic excited state exists and is nearly degenerate with the ${}^{2}A_{2}$ excited state. This represents the first spectroscopic study to establish both the presence and the symmetry of a second electronic excited state in energetic proximity to the ${}^{2}A_{2}$ surface. Previous studies have suggested the importance of a ${}^{2}A_{1}$ state in the photochemistry of OClO.^{8,9} As mentioned above, high resolution absorption spectra of OCIO have demonstrated that the linewidth of vibronic progressions involving the symmetric stretch increases with excitation into higher-energy levels of the ${}^{2}A_{2}$ vibronic manifold.⁸ Analysis of these linewidths suggests that the general time scale for decay of the ${}^{2}A_{2}$ excited state in the gas phase is <1 ps. Furthermore, transitions involving excitation of both the symmetric stretch and the bend or asymmetric stretch are significantly broader in comparison to transitions involving excitation of the symmetric stretch only, suggesting that evolution along either the bend or asymmetric stretch serves to promote the decay of the ${}^{2}A_{2}$ excited state. This conclusion is supported by recent gas-phase photofragment translational energy studies.²¹ In the condensed phase, resonance Raman intensity analysis has established a homogeneous linewidth of 80 cm⁻¹ for the ${}^{2}A_{2}$ surface corresponding to an optical T_2 of ~60 fs.³⁹ The origin of this rapid dephasing was tentatively assigned to decay of the ${}^{2}A_{2}$ surface.

Given that the structural evolution and rapid decay of the optically prepared ${}^{2}A_{2}$ state in both the gas phase and in cyclohexane has been established, knowledge of the electronic state or states populated by decay of the ${}^{2}A_{2}$ state is the next issue to be addressed in describing OCIO photochemistry. The results presented here suggest that the ${}^{2}A_{1}$ excited state participates in decay of the optically prepared excited state. However, the majority of attention to date has been paid to the ${}^{2}B_{2}$ surface. The main reason for interest in the ${}^{2}B_{2}$ surface is that in the limit of a linear OCIO geometry, the ${}^{2}A_{2}$ and ${}^{2}B_{2}$ excited states will be degenerate.⁹ However, the bent geometry of OCIO combined with the limited evolution along the bend coordinate on the ${}^{2}A_{2}$ excited state surface dictates that the coupling between these states should be weak.^{9,39} In addition, a mode of b_1 symmetry is not present; therefore, vibronic coupling of the ${}^{2}A_{2}$ and ${}^{2}B_{2}$ states is not possible. Therefore, the ${}^{2}B_{2}$ state is probably not produced directly by decay of the ${}^{2}A_{2}$ state. In contrast, the ${}^{2}A_{1}$ excited state may be populated by ${}^{2}A_{2}$ state decay. Analysis of the rotational transitions in the highresolution electronic absorption spectrum of gas-phase OCIO have suggested that spin-orbit coupling of the ${}^{2}A_{2}$ and ${}^{2}A_{1}$ states is the primary mechanism through which the ${}^{2}A_{2}$ state decays.^{27,28} The results presented here are consistent with this hypothesis in that the near-degeneracy of the ${}^{2}A_{2}$ and ${}^{2}A_{1}$ excited states should result in facile depopulation of the ${}^{2}A_{2}$ surface. Subsequent reactivity of the ${}^{2}A_{1}$ state probably involves internal conversion to the ${}^{2}B_{2}$ state via vibronic coupling through the asymmetric stretch.⁹ Therefore, the re-



FIG. 7. (A) Calculated Raman excitation profiles of the symmetric stretch fundamental transition arising from the ${}^{2}A_{2}$ (solid line) and ${}^{2}A_{1}$ (dashed line) excited states. Parameters for the calculation are presented in Table III. (B) Comparison of the measured absolute resonance Raman cross section of the symmetric stretch fundamental transition (points) and the sum of intensities depicted in A (solid line).

sults and discussion presented here support the emerging picture of OCIO photochemistry in which photoexcitation results in the population of the ${}^{2}A_{2}$ state which decays to form the ${}^{2}A_{1}$ state with further relaxation on this surface resulting in population of the ${}^{2}B_{2}$ state. The next question to be addressed in OClO photochemistry is, "Which of these excited states is involved in photoproduct formation?" Ab initio work has suggested that the dynamics which occur on the ${}^{2}B_{2}$ state are critical in determining product formation.³⁸ The hypothesis and predictions of reactivity generated by the theoretical work is in agreement with the product analysis studies of Davis and Lee.²¹ In the condensed phase, the situation is not as well understood. Towards this end, time-resolved studies which directly monitor photoproduct formation will be extremely useful in unraveling the complex photochemistry of OClO.^{11,73}

B. The ${}^{2}A_{1}$ state and resonance Raman intensities

In our resonance Raman intensity analysis of OClO, the electronic absorption and Raman cross sections were modeled assuming that only the ${}^{2}B_{1} - {}^{2}A_{2}$ transition participated in the scattering process.³⁹ Given the results presented here, this assumption needs to be reevaluated. In Fig. 7(A), the calculated Raman excitation profiles for the symmetric stretch fundamental transition with intensity derived exclusively from the ${}^{2}A_{2}$ and the ${}^{2}A_{1}$ excited states are shown. Figure 7(B) presents a comparison of the calculated cross sections [Eq. (6)] to the integrated cross section for the symmetric-stretch-fundamental transition. The experimentally observed intensities can be used to calculate the integrated Raman cross section by the following equation:

$$\frac{\sigma_{\rm OCIO}}{\sigma_{\rm CXN}} = \frac{(I_{\rm OCIO})(c_{\rm CXN})}{(I_{\rm CXN})(c_{\rm OCIO})} \frac{[(1+2\rho)/(1+\rho)]_{\rm OCIO}}{[(1+2\rho)/(1+\rho)]_{\rm CXN}},$$
(15)

where σ is the integrated Raman cross section, I is the experimental intensity summed over both parallel and perpendicular polarizations, c is the concentration, ρ is the Raman depolarization ratio, and the subscripts OClO and CXN refer to chlorine dioxide and the 801 cm⁻¹ line of cyclohexane, respectively. This figure demonstrates that although the effect of the ${}^{2}A_{1}$ state on the resonance Raman depolarization ratios is significant, the corresponding contribution of this state to the observed Raman cross sections is not as dramatic. There are two reasons for this behavior. First, the Raman cross section depends on the fourth power of the electronic transition length. In the analysis presented above, the best fit to the measured depolarization ratios results in a length of the ${}^{2}B_{1} - {}^{2}A_{1}$ transition that is roughly 1/2 that of the ${}^{2}B_{1} - {}^{2}A_{2}$ transition such that the contribution of the ${}^{2}A_{1}$ state to the resonance Raman cross section will only be 1/16 that of the ${}^{2}A_{2}$ state. Second, resonance Raman cross sections are not normalized with respect to the homogeneous linewidth such that an increase in linewidth results in a decrease in scattering intensity.⁵⁹ Since the homogeneous linewidth of the ${}^{2}B_{1} - {}^{2}A_{1}$ transition was taken to be roughly three times larger than that of the corresponding transition to the ${}^{2}A_{2}$ state, the effect of this difference is to significantly reduce the contribution of the ${}^{2}A_{1}$ state to the observed scattering. Although the Raman depolarization ratios can be significantly altered by the presence of secondary excited states, effects of similar magnitude involving the Raman cross section do not necessarily occur. Consistent with this behavior, modification of the parameters for the ${}^{2}A_{2}$ surface obtained from our previous intensity analysis are slight with the transition length (0.35–0.32 Å) and homogeneous linewidth $(80-75 \text{ cm}^{-1})$ being reduced from their original values. Any remaining discrepancy between the calculated and measured Raman cross sections likely resides in the omission of preresonance contributions from states located in the far-UV. Quantitative incorporation of preresonance contributions from these states is difficult since their normal mode displacements are unknown and essentially impossible to determine in cyclohexane given the spectral region in which these transitions are located. In summary, resonance Raman depolarization ratios represent a sensitive test for the presence of optically weak excited states; however, the effect of optically weak states on the Raman cross sections may or may not be important. It should be noted that OCIO may be a relatively special case where the minimal intensity derived from the optically weaker ${}^{2}A_{1}$ state does not represent a general truism.

V. CONCLUSION

In this paper, we have reported the resonance Raman depolarization ratios of chlorine dioxide (OClO) dissolved in cyclohexane. The depolarization ratios of the symmetric stretch fundamental transition were modeled by including a transition to an excited state of ${}^{2}A_{1}$ symmetry which is nearly degenerate with the optically strong ${}^{2}A_{2}$ excited state. The energetic proximity of the ${}^{2}A_{1}$ state combined with the results of previous spectroscopic studies suggests that the internal conversion of the optically prepared ${}^{2}A_{2}$ state results in population of the ${}^{2}A_{1}$ surface in agreement with the emerging picture of OCIO photochemistry. The results presented here illustrate the utility of resonance Raman depolarization ratios in elucidating the energetics of weak optical states which may be obscured by transitions to optically strong surfaces. The combination of both resonance Raman intensity analysis and resonance Raman depolarization ratios in determining excited-state reaction dynamics and energetics should prove useful in unraveling the phase-dependent reactivity of chlorine dioxide.

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