INVESTIGATING THE ENVIRONMENT-DEPENDENT PHOTOPHYSICS OF CHLORINE DIOXIDE WITH RESONANCE RAMAN INTENSITIES

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The condensed-phase excited-state reaction dynamics of chlorine dioxide are investigated using resonance Raman intensity analysis. Absolute Raman intensities are measured on resonance with the ${}^2B_1 - {}^2A_2$ electronic transition and used to establish the excited-state structural evolution which occurs on the ${}^2A_2$ surface following photoexcitation. Analysis of the intensities demonstrates that excited-state relaxation occurs along all three normal coordinates; however, only modest evolution is observed along the asymmetric stretch. This limited relaxation stands in contrast to the extensive motion along this coordinate in the gas phase. It is proposed that the initial excited-state structural relaxation serves to define the symmetry of the reaction coordinate and thus the mechanism of Cl production following photolysis of OClO.

Keywords: Resonance Raman; chlorine dioxide; Raman intensities

INTRODUCTION

Understanding phase- and environment-dependent chemical reactivity is a central issue in environmental chemistry. This issue is nicely illustrated by the photochemistry of chlorine dioxide (OClO) (Fig. 1) [1]. Numerous investigations of OClO in the gas-phase have established that photoexcitation leads predominately to the formation

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FIGURE 1 Schematic of OCIO photochemistry. Photoexcitation of OCIO can lead to either the formation of ClO and O, or Cl + O₂.

of ClO and O. However, in low-temperature matrices the situation is reversed with photoexcitation leading exclusively to the formation of Cl + O₂. The mechanistic reasons for this phase-dependent reactivity are unknown. To address this question, we have employed absolute resonance Raman intensity analysis to elucidate the excited-state reaction dynamics which occur following photolysis and the influence of solvent on these dynamics [2].

EXPERIMENTAL AND RESULTS

Resonance Raman spectra of OCIO dissolved in cyclohexane were obtained throughout the photochemically relevant, ${}^2\text{B}_1 - {}^2\text{A}_2$ electronic transition (Fig. 2). The direct and hydrogen shifted output of a Nd:YAG laser operating at 30 Hz was focused onto a flowing sample jet. Pulse energies were $\leq 10 \mu\text{J}$ to minimize photolysis of OCIO. The Raman scattering was collected utilizing a back-scattering geometry and delivered to a 0.5 m spectrograph equipped with a LN₂ cooled CCD detector. Figure 3 presents the resonance Raman spectrum of OCIO obtained with 368.9 nm excitation. Intensity in transitions involving all three normal coordinates (the symmetric stretch (ν_1), bend (ν_2), and asymmetric stretch (ν_3)) is observed demonstrating that excited-state structural relaxation occurs along all three coordinates following photoexcitation. The electronic absorption spectrum and absolute resonance Raman intensities were modeled using the time-dependent formalism of Raman scattering. The details of which have been presented elsewhere [2, 3]. The excellent agreement between the predicted absorption and Raman cross-sections and the experimental results is shown in Figure 2. The picture of the excited state dynamics

FIGURE 2 (A) Electronic absorption spectrum of OClO (solid) and fit determined by resonance Raman intensity analysis (dashed). Details of this analysis are presented elsewhere [2]. (B) Resonance Raman intensities of the symmetric stretch fundamental transition (points) and fit (dashed). (C) Resonance Raman intensities of the asymmetric stretch overtone transition (points) and predicted intensity using the parameters determined in this study (solid) as well as from analysis of the gas-phase absorption spectrum (dashed) [4].

derived from this analysis is one where the structural evolution is dominated by motion along the symmetric stretch with only limited evolution occurring along the bend and asymmetric stretch.

The modest evolution along the asymmetric stretch in solution is the most intriguing result to emerge from this study. The asymmetric

FIGURE 3 Resonance Raman spectrum of chlorine dioxide dissolved in cyclohexane obtained with 368.9 nm excitation. Sample concentration is ~ 10 mM and pulse energy is $10 \mu\text{J}$. ν_1 , ν_2 , and ν_3 correspond to the symmetric stretch, bend, and asymmetric stretch, respectively. Solvent scattering has been subtracted in the expanded view of the spectrum.

stretch is non-totally symmetric with respect to the C_{2v} symmetry of ground-state OClO ; therefore, fundamental intensity is not expected on resonance [3]. However, if the excited-state frequency differs from that of the ground state, then overtone intensity may be observed. Figure 1 demonstrates that overtone intensity assignable to the asymmetric stretch is observed. Modeling of this intensity suggests that this coordinate undergoes a modest reduction in excited-state frequency to 750 cm^{-1} from the 1100 cm^{-1} frequency of the ground state. This result stands in contrast to gas-phase absorption studies in which the excited-state potential surface along the asymmetric stretch was determined to have an energetic double minimum and a saddle-point located at the Franck-Condon region [4]. Consistent with this, Figure 3C demonstrates that the gas-phase surface is not capable of reproducing the asymmetric stretch overtone intensity observed in cyclohexane.

DISCUSSION

The results presented above suggest that the geometry established on the optically-prepared, $^2A_2$ surface in cyclohexane is different than that in the gas phase. In particular, relaxation along the asymmetric stretch coordinate in the gas phase would result in a lowering of molecular symmetry from C_{2v} to C_s . However, the minimal evolution along this coordinate in cyclohexane results in preservation of the ground state symmetry. State correlation diagrams of OCIO indicate that if C_{2v} symmetry is preserved, $Cl + O_2$ can be directly produced [1]. However, the reaction coordinate under C_s symmetry should lead to the formation of ClOO which can subsequently decompose to form $Cl + O_2$. Therefore, the results presented here suggest that the dynamics which occur on the $^2A_2$ surface may define the mechanism by which Cl is produced.

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