Photodissociation of Cl\(_2\)O at 248 and 308 nm

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INTRODUCTION

Studies of the photodissociation dynamics of Cl\(_2\)O (dichlorine monoxide) can aid in understanding the photochemistry of the more complex chlorine oxides which play a major role in stratospheric ozone depletion. As we reported in a previous publication,\textsuperscript{1} the formation of Cl\(^+\)+ClO products (\(\Delta H^\circ_\text{\textit{f}}=33.8\) kcal/mol)\textsuperscript{2} is the only channel observed for Cl\(_2\)O photolysis at 308 nm and is the major channel at 248 nm. We have repeated the Cl\(_2\)O photolysis experiment at 248 and 308 nm and present here a refinement of the analysis for the Cl\(^+\)+ClO channel. At 248 nm, three distinct dissociation pathways that led to Cl\(^+\)+ClO products were resolved. At 308 nm, the angular distribution is slightly more isotropic than previously reported.

The new data were recorded on the same apparatus under similar conditions that differed primarily in source conditions and laser polarization. For the new experiment, a continuous molecular beam of Cl\(_2\)O was formed by passing a gas mixture of 2% SF\(_6\) in helium over the surface of liquid Cl\(_2\)O at \(-73^\circ\text{C}\) and expanding the mixture through a 0.1 mm quartz nozzle held at or below \(-60^\circ\text{C}\) with a stagnation pressure of 190 Torr. In all experiments, the laser beam was nearly randomly polarized in a plane perpendicular to the scattering plane and parallel to the molecular beam axis. In the current experiment, there was a slight net polarization (<58%) perpendicular to the scattering plane, whereas previously there was a slight net polarization parallel to that plane. The differences in the beam conditions and the laser polarization were taken into account in the analysis.

Analysis of product TOF and angular distributions were carried out by the forward convolution technique used previously. For each channel, center of mass (c.m.) translational energy \(P(E_T)\) and angular \(\psi(\theta)\) distributions were transformed to the LAB frame and adjusted iteratively until the predicted LAB TOF distributions agreed with the observed distributions at all LAB angles. The c.m. angular distributions were fit to \(\psi(\theta) \propto 1 + \beta P_2(\cos \theta)\), where the anisotropy parameter \(\beta\) varies from \(-1\) to \(2\) for dissociation with the recoil vector perpendicular and parallel to the transition dipole, respectively.

248 nm

Representative TOF distributions of products from 248 nm photolysis are shown in Fig. 1. The \(m/z=51\) (ClO\(^+\)) data could not be fit at all angles with a single \(P(E_T)\) distribution as was done in the previous work. Instead, the three observed peaks at \(m/z=51\) were fit with three separate components in the \(P(E_T)\) distribution (Fig. 2), each with different anisotropy parameters. The fastest component had a large translational energy release with a maximum at 49 kcal/mol \((E_{\text{int}}=33\) kcal/mol). The angular distribution was fit by \(\beta=0.7\pm0.2\), indicating a prompt, parallel dissociation. The middle component had an average translational energy release of \(\langle E_T \rangle=36\) kcal/mol \((\langle E_{\text{int}} \rangle=46\) kcal/mol\) and anisotropy of \(\beta=1.5\pm0.2\). A fit to the slowest component gave \(\beta=1.2\pm0.2\) and a \(P(E_T)\) distribution with a sharp cutoff.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure1.jpg}
\caption{TOF number density distribution \(N(t)\) from Cl\(_2\)O photolysis at 248 nm for (A) Cl\(^+\) products collected at a detector angle of 30\(^\circ\), (B) ClO\(^+\) products at 30\(^\circ\), (C) Cl\(^+\) products at 50\(^\circ\), and (D) ClO\(^+\) products at 50\(^\circ\). The solid line is the overall fit to the data. The dashed, dotted, and dot--dashed lines correspond to the three components in the c.m. \(P(E_T)\) distribution (Fig. 2). The long-dashed line in (A) and (C) is a hypothetical fit based on photolysis of Cl\(_2\)O clusters in the beam. The dot--dotted--dashed line in (A) and (C) corresponds to the spontaneous secondary dissociation of ClO. Stimulated secondary dissociation of ClO is not included.}
\end{figure}
In summary, we have now resolved three components in the \( P(E_T) \) distribution with differing anisotropies, each leading to Cl+ClO products. These results support our conjecture that the formation of Cl+ClO products involves several excited state potential energy surfaces.

### 308 nm

At 308 nm, the \( m/z = 51 \) (ClO\(^+\)) TOF spectra were fit by a \( P(E_T) \) distribution very similar to the one published previously, with a peak at 33 kcal/mol and a slow shoulder extending down to 6.5 kcal/mol. The angular distribution, fit with \( \beta = 0.4 \pm 0.3 \), was slightly less anisotropic than previously reported.

A long-lived excited state of Cl\(_2\)O was recently proposed by Nickolaisen et al.\(^6\) to explain quenching at high pressures of the ClO yield from Cl\(_2\)O photolysis at \( \lambda > 300 \) nm in flow tube studies. They postulated a metastable excited state which must live longer than the mean collision time at 5 Torr of \(~50\) ns. Such a lifetime would lead to complete rotational averaging of the anisotropic angular distribution, resulting in \( \beta \leq 0.19 \) if Cl\(_2\)O dissociates from its ground state geometry.\(^7\) This value of \( \beta \) is half of the observed value, but within our uncertainty. Our results thus indicate that \( \tau < 9 \) ps at 308 nm, but our uncertainties preclude us from ruling out a longer-lived state.

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