The UV photodissociation dynamics of ClO radical using velocity map ion imaging

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We have studied the wavelength-dependent photodissociation dynamics of jet-cooled ClO radical from 235 to 291 nm using velocity map ion imaging. We find that Cl(2P\(3/2\)) + O(1D\(2\)) is the dominant channel above the O(1D\(2\)) threshold with minor contributions from the Cl(2P\(1/2\)) + O(1D\(2\)) and Cl(2P\(1/2\)) + O(1D\(2\)) channels. We have measured the photofragment angular distributions for each dissociation channel and find that the A 2\(\Pi\) state reached via a parallel transition carries most of the oscillator strength above the O(1D\(2\)) threshold. The formation of O(3P) fragments with positive anisotropy is evidence of curve crossing from the A 2\(\Pi\) state to one of several dissociative states. The curve crossing probability increases with wavelength in good agreement with previous theoretical calculations. We have directly determined the O(1D\(2\)) threshold to be 38 050±20 cm\(^{-1}\) by measuring O(1D\(2\)) quantum yield in the wavelength range of 260–270 nm. We also report on the predissociation dynamics of ClO below the O(1D\(2\)) threshold. We find that the branching ratio of Cl(2P\(3/2\))/Cl(2P\(1/2\)) is 1.5±0.1 at both 266 and 291 nm. The rotational depolarization of the anisotropy parameters of the Cl(2P\(3/2\)) fragments provides predissociation lifetimes of 1.5±0.2 ps for the 9-0 band and 1.0±0.4 ps for the 8-0 band, in reasonable agreement with previous spectroscopic and theoretical studies. © 2005 American Institute of Physics.

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I. INTRODUCTION

The role of photodissociation of chlorine compounds in the stratosphere is critical in understanding stratospheric ozone depletion.\(^1\) Chlorine monoxide is a radical intermediate that plays an important role in the stratospheric ozone depletion via the photodissociation as well as bimolecular reactions.\(^2\)\(^,\)\(^3\) The UV photodissociation of ClO is estimated to be responsible for 2%–3% of the total ozone loss in the stratosphere.\(^4\) In addition, since ClO is produced as a primary photoproduct of ClONO\(_2\), an understanding photodissociation dynamics of ClO is critical for modeling recent ClONO\(_2\) photodissociation experiments.\(^5\)\(^,\)\(^6\)

The ClO absorption spectrum is characterized by a continuum that spans from 220 to near 263 nm and the subsequent rovibrational-resolved structure that terminates at 316 nm.\(^7\) Details of the electronic transitions responsible for the ClO absorption spectrum can be explained considering electronic configurations of ClO. The ground state of ClO has the configuration (\(\alpha\))\(^2\)(\(\pi\))^4(\(\pi^*\))^3(\(\alpha^*\))^0 and the term symbol X 3\(\Pi_\Omega\) which correlates to ground-state atoms. Promotion of an electron from a \(\pi\) orbital to a \(\pi^*\) orbital results in the (\(\alpha\))^2(\(\pi\))^3(\(\pi^*\))^3(\(\alpha^*\))^0 configuration and the term symbol A 3\(\Pi_\Omega\) and correlates to Cl(2P\(j\)) + O(1D\(2\)) fragments based on the Wigner-Witmer correlation rule.\(^8\) There are four electronic pathways for ClO photodissociation which are energetically accessible in the UV region:

\[\text{ClO}(X 3\Pi_\Omega) \rightarrow \text{Cl}(2P_{3/2}) + O(3P_{2,1,0}) \] (1)
\[\rightarrow \text{Cl}(2P_{1/2}) + O(3P_{2,1,0}) \] (2)
\[\rightarrow \text{Cl}(2P_{3/2}) + O(1D_2) \] (3)
\[\rightarrow \text{Cl}(2P_{1/2}) + O(1D_2) \] (4)

Channels (1) and (2) are accessible at wavelengths between 316 and 263 nm and all four channels are accessible at wavelengths shorter than 263 nm. The high-resolution absorption spectrum ClO was first studied by Durie and Ramsay.\(^9\) The authors predicted that only Cl(2P\(3/2\)) and O(1D\(2\)) fragments [channel (3)] were produced as a result of photodissociation in the continuum region based on a comparison with IO. Analysis of the convergence of the vibronic transitions resulted in the onset wavelength for Cl(2P\(3/2\))+O(1D\(2\)) of 263.01±0.1 nm (38 052 cm\(^{-1}\)).\(^10\) McLoughlin et al. studied the high-resolution absorption spectrum of ClO using laser absorption spectroscopy.\(^11\) The authors estimated the onset wavelength for Cl(2P\(3/2\)) + O(1D\(2\)) to be 262.90±0.05 nm.

Photodissociation at wavelengths longer than the O(1D\(2\)) threshold involves predissociation of the bound A 3\(\Pi_\Omega\) state via several repulsive states. Predissociation lifetimes for specific vibrational levels of the A 3\(\Pi_\Omega\) state predissociation based on spectral linewidths have been previously reported.\(^11\)\(^–\)\(^13\) A theoretical treatment of the predissociation was first made by Bunker and Klein.\(^14\) The authors neglected a rotational contribution to the predissociation lifetime and predicted predissociation rates using the spin-orbit interaction between A 3\(\Pi_\Omega\) state and a single repulsive state corre-
lating to ground-state atoms. The authors concluded that more than a single repulsive state must be involved to explain the observed oscillatory pattern of predissociation lifetimes with wavelength. Recently, Toniolo et al. and Lane et al. performed high-level \textit{ab initio} calculations of the excited states of ClO and identified several states involved in predissociation of $A^2\Pi_\Pi$ state.\textsuperscript{15,16} Both studies concluded that the 1 $\Sigma^+$, 2 $\Sigma^–$, and 3 $\Pi^\Pi$ states were the principal states responsible for the predissociation of the $A^2\Pi_\Pi$ state. Lane et al. predicted predissociation lifetimes ranging from 0.5 to 10 ps depending on the $A^2\Pi_\Pi$ vibrational level.

In contrast to the numerous spectroscopic studies, there have been a limited number of direct experimental studies of ClO photodissociation. Davis and Lee investigated the photodissociation of ClO at 248 nm using photofragment translational spectroscopy and concluded that channel (3) was the dominant channel (97%) with a minor contribution from channels (1) and (2).\textsuperscript{17} The measured nonlimiting anisotropy parameter of 1.2±0.2 for channel (3) suggested that one or more perpendicular transitions contribute significantly (30%) to the oscillator strength at this wavelength. Zou et al. studied the photodissociation of ClO near 235 nm using 2+1 resonance-enhanced multiphoton ionization (REMPI) with time-of-flight mass spectrometry (TOFMS).\textsuperscript{18} The authors reported that channel (3) was the dominant channel with anisotropy parameter of 1.2±0.2, suggesting that the photodissociation dynamics of ClO at 230–250 nm is not strongly wavelength dependent. Schmidt et al. investigated photodissociation of ClO over the wavelength range of 205–270 nm employing 2+1 REMPI detection of O$(^1D_2)$.\textsuperscript{19} Only the sum of channels (3) and (4) in the continuum region was reported since the authors were unable to distinguish between the coincident Cl$(^2P_{3/2})$ and Cl$(^2P_{1/2})$ fragments due to insufficient velocity resolution of the mass spectrometer. They also determined the wavelength corresponding to the onset of the continuum to be $263.4\pm0.2$ nm based on the wavelength-dependent O$(^1D_2)$ yield near threshold. Recently, Flesch et al. employed single-photon ionization in the wavelength range of 262–265 nm and determined the O$(^1D_2)$ threshold to be $263.71\pm0.01$ nm.\textsuperscript{20}

In this paper, we report the wavelength-dependent photodissociation dynamics of ClO from 235 to 291 nm corresponding to the wavelengths above, near, and below the O$(^1D_2)$ formation threshold using velocity map ion imaging. In Sec. III A, photodissociation of ClO above the O$(^1D_2)$ threshold is addressed. Here we focus on the identification of photoproducts and angular distributions to unravel the role of excited states other than the $A^2\Pi_\Pi$ state and the role of nonadiabatic curve crossing of ClO. Our discussion relies heavily on the recent theoretical work of Persico. In Sec. III B, we present an accurate determination of the O$(^1D_2)$ formation threshold wavelength and discuss the observed breakdown of the axial recoil approximation. In Sec. III C, we examine the state-selected predissociation lifetimes based on the analysis of the photofragment angular distributions and discuss the Cl$(^2P_{3/2})$/Cl$(^2P_{1/2})$ branching ratio below the O$(^1D_2)$ threshold.

II. EXPERIMENT

A pulsed ClO molecular beam, collimated by a conical skimmer, was intersected at 90° by two copropagating linearly polarized laser beams. The dissociation beam was generated using a 10 Hz Nd:yttrium aluminum garnet (YAG) Spectra Physics GCR-150-10 pumped dye laser (LAS LDL 2051) operating on the dye Coumarin 500 followed by a frequency doubling crystal [beta-barium borate (BBO)]. The fundamental dye outputs were accurately calibrated using a Ne-filled hollow cathode lamp. The probe beam wavelengths were provided by mixing 1064 nm with the frequency-doubled dye output from a second dye laser (Quantel TDL-51) running on the dye mixture of Rhodamin 610 and 640. A photoelastic modulator (PEM-80, HINDS) was used to rotate the polarization of the probe beam. Typical dissociation and probe pulse energies were 30 and 50 $\mu$J, respectively. The time delay between the dissociation and the probe beam was set to 10 ns in order to detect fast fragments traveling perpendicular to the laser propagation direction. The chlorine atoms [Cl$(^2P_{3/2})$/Cl$(^2P_{1/2})$] were probed using 2+1 REMPI transitions at 235.336 nm (4$p^3^2P_{3/2}^\Pi \rightarrow 3p^3^2P_{3/2}^\Pi$) and 235.205 nm (4$p^5^2P_{1/2}^\Pi \rightarrow 3p^3^2P_{1/2}^\Pi$), respectively.\textsuperscript{21} The oxygen atoms were probed using 2+1 REMPI transitions near 226 nm (3$p^5^2P_{1/2}^\Pi \rightarrow 3^2P_{1/2}^\Pi$).\textsuperscript{22} The resulting chlorine and oxygen ions were accelerated by velocity mapping ion optics pioneered by Eppink and Parker, a variant of traditional ion imaging developed by Chandler and Houston,\textsuperscript{23} before entering the 50-cm-long field-free flight tube along the axis defined by the molecular beam.\textsuperscript{24} The voltages of ion optics were adjusted until the speed resolution of the fragment was maximized. The ions were projected on the position-sensitive microchannel plate phosphor assembly gated to detect the mass of interest. A photomultiplier (PMT) positioned off-axis was used to record mass spectra and establish proper timing. A charge-coupled device (CCD) camera (Mintron MS-2821E/C) acquired images of the phosphor screen and sent raw images to a frame grabber controlled by commercial software (CODA32) which involved centroiding and event counting.\textsuperscript{25} The final images were obtained by repeatedly scanning Doppler profiles of Cl$(^2P_{3/2})$/Cl$(^2P_{1/2})$ to achieve homogeneous detection efficiency. Since cylindrical symmetry with respect to the electric field was maintained throughout the experiments, the two-dimensional projections were reconstructed to the original three-dimensional ion spheres by applying the basis-set expansion (BASEX) method developed by Drinbinski et al.\textsuperscript{26}

In our previous work on ClO photodissociation the radicals were generated using a pulsed electric discharge\textsuperscript{27,28} similar to the approach of Cooper et al.\textsuperscript{16,29} We find that an intense molecular beam of ClO radicals can be generated using the flash pyrolysis of a Cl$_2$O/He mixture. The active region of the pyrolysis source consists of a 3 cm alumina tube wrapped with nickel-chrome alloy wire which is resistively heated to approximately 800 K.\textsuperscript{30} Figure 1 demonstrates the production of ClO radicals using the pyrolytic source. The images were collected using one color near 235 nm to probe the Cl$(^2P_{3/2})$ fragments. At room temperature the Cl$(^2P_{3/2})$ image is consistent with Cl$_2$O photodissoc-
cation at 235 nm. As the nozzle is heated, features associated with Cl₂O decrease in intensity and are replaced by a sharp ring consistent with diatomic photodissociation. At higher temperatures there is little evidence of Cl₂O photodissociation and a bright spot in the center image from entrained Cl atoms is observed. Although the pyrolysis of Cl₂O should, by simple stoichiometry, provide a 1:1 yield of ClO and Cl in the expansion, we find that the relative signals associated with these two species vary greatly depending on the experimental conditions. This is due, in part, to the difference in the rate constants for the reaction of these species with Cl₂O. The reaction of Cl₂O with Cl is rapid (k = 7.3 × 10⁻¹¹ cm³ s⁻¹ at 800 K),

\[ \text{Cl}_2\text{O} + \text{Cl} \rightarrow \text{Cl}_2 + \text{ClO}, \]

and results in a net loss of Cl and net production of ClO, while the reaction of ClO with Cl₂O is considerably slower. In addition, since the entrained Cl atoms are limited to a few pixels in the center of the image, intense signals can result in attenuation using ion-counting techniques. We find that the formation of hot ClO radicals is significantly reduced by using a water-cooled endcap located at the nozzle tip prior to expansion. Based on images taken near the threshold for O¹(D) production from ClO \textit{(vide infra)} we estimate that the ClO radicals can be characterized by \( T_{\text{rot}} < 100 \text{ K}, \) \( T_{\text{vib}} < 200 \text{ K}, \) and \( T_{\text{elec}} < 200 \text{ K}. \)

Cl₂O was synthesized by the method of Cady. Cl₂ was collected on prebaked H₂O (Aldrich) powder and the reaction was allowed to run overnight at 195 K. The product was then purified by vacuum distillation, and the purity (>90%) was checked by UV absorption spectroscopy.

### III. RESULTS AND DISCUSSION

#### A. Photodissociation of ClO above the O¹(D) threshold

The one-color photodissociation of ClO at 235 nm resulted in Cl(²P₃/₂) and Cl(²P₁/₂) images, as shown in Fig. 2. The speeds of the atomic fragments corresponding to each asymptotic channel can be obtained from the total translational energy of the photofragments by energy conservation

\[ E_{\text{trans}} = h \nu + E_{\text{e CL}} - D_0(\text{ClO}) - E_{\text{e Cl}} - E_{\text{e O}}, \]

where \( h \nu \) is the energy of dissociation photon, \( D_0(\text{ClO}) \) is the bond energy of ClO, \( E_{\text{e Cl}} \) and \( E_{\text{e O}} \) are the electronic energy of Cl and O, and \( E_{\text{e CL}} \) is the initial energy of the ClO prior to dissociation which is a function of both Franck-Condon factors and the internal temperature. The accurate determination of the ClO internal temperature and bond dissociation energy will be discussed in the following section. The Cl(²P₃/₂) image in Fig. 2 shows a single ring with a speed consistent with the Cl(²P₃/₂)+O(¹D₂) channel. No evidence for the Cl(²P₁/₂)+O(¹P₁) channel is observed, consistent with the earlier work of Zou et al. In contrast, the Cl(²P₃/₂) image shows two rings with speeds consistent with the Cl(²P₃/₂)+O(¹D₂) and Cl(²P₁/₂)+O(¹P₁) channels. The signals associated with Cl(²P₁/₂) are weak, indicating that the contributions of the Cl(²P₁/₂)+O(¹D₂) and Cl(²P₁/₂)+O(¹P₁) channels at 235 nm are minor. We obtained a quantitative branching ratio of Cl(²P₃/₂) and Cl(²P₁/₂) at 235 nm by integrating Doppler profiles of 2+1 REMPI transitions collected at the identical laser power. The integrated signals are calibrated by using the detection efficiency of Cl(²P₃/₂) and Cl(²P₁/₂). We find a Cl(²P₁/₂)/Cl(²P₃/₂) ratio of 0.02±0.01 in good agreement with our previous work.

We have measured two-color images for ClO photodissociation at several wavelengths from 235 to 262 nm. Figure 3 shows the speed distributions of Cl(²P₃/₂) (bottom panel) and Cl(²P₁/₂) (top panel) derived from images acquired at 255 nm. The solid lines represent forward-convolution simulations to the data (circles) and the arrows in the figure indicate the speeds associated with the various dissociation channels. We do not observe the Cl(²P₁/₂)+O(¹D₂) channel at 255 nm but observe a small yield of Cl(²P₁/₂)+O(¹P₁). We have not attempted to measure the relative yields of the oxygen spin-orbit states. The measured Cl(²P₂/₃) and Cl(²P₁/₃) speed distributions provide accurate relative branching ratios between the O¹(D₂) and O¹(P₁) channels coincident with either Cl(²P₃/₂) or Cl(²P₁/₂). Determination of the relative branching between Cl(²P₃/₂) and Cl(²P₁/₂) channels proved more difficult since the Cl(²P₁/₂) channels are produced in minor yield (∼1%–3%). We do not observe a significant variation in this yield with wavelength above the O¹(D₂) threshold based on a comparison of features associated with the photodissociation at a given wavelength with features associated with dissociation by the 235 nm probe in the Cl(²P₃/₂) and Cl(²P₁/₂) images. We have fixed this value at 0.02 based on our measurements at 235 nm for the results presented in Table I. A comparison to the work of Davis and Lee at 248 nm, where the neutral TOF technique permits an accurate measurement of the O¹(D₂)/O¹(P₁) branching ratio, demonstrates that a wavelength-independent Cl(²P₁/₂)/Cl(²P₃/₂) branching ratio is reasonable. There are several conclusions regarding the relative product yields, however, that do not depend on the absolute Cl(²P₁/₂)/Cl(²P₃/₂) branching ratio: (1) The yield of O¹(P₁) is nonzero above the O¹(D₂) threshold, decreasing from a maximum value of 0.06 at 262 nm to 0.01 at 235 nm. (2) The Cl(²P₃/₂)+O¹(P₁) channel is not observed at wavelengths shorter than 248 nm and the relative yield of this
channel increases with wavelength. (3) The Cl(\(^{2}\text{P}_{{1/2}}\))
+O(\(^{1}\text{D}_{{2}}\)) channel is not observed at wavelengths longer than
248 nm and the relative yield of this channel decreases with
wavelength.

The angular distributions of the Cl(\(^{2}\text{P}_{{3/2}}\)) and Cl(\(^{2}\text{P}_{{1/2}}\))
fragments at 235 nm are shown in the lower panel of Fig. 2
and the experimental angular distributions are fitted to the
following equation: \(^{37}\)

\[
I(\theta) = \frac{1}{4\pi}[1 + \beta P_2(\cos \theta)],
\]

where \(\beta\) is the spatial anisotropy parameter, \(P_2(\cos \theta)\) is the
second Legendre polynomial, and \(\theta\) is the angle between the
fragment recoil direction and laser polarization direction. We
find best-fit anisotropy parameters of 1.9\(\pm\)0.1 for the
Cl(\(^{2}\text{P}_{{3/2}}\)) +O(\(^{1}\text{D}_{{2}}\)) channel, −1.0\(\pm\)0.1 for the Cl(\(^{2}\text{P}_{{1/2}}\))
+O(\(^{1}\text{D}_{{2}}\)) channel, and 1.4\(\pm\)0.1 for the Cl(\(^{2}\text{P}_{{1/2}}\)) +O(\(^{3}\text{P}_{{2}}\))
channel. The anisotropy parameters for the four dissociation
channels above O(\(^{1}\text{D}_{{2}}\)) threshold are provided in Table I. We
did not observe any evidence for orbital alignment of the
Cl(\(^{2}\text{P}_{{j}}\)) fragments. There was no appreciable difference in
the measured anisotropies when the polarization of the probe
laser was aligned parallel or perpendicular to the photodis-
sociation laser. We found, however, that the ClO rotational
temperature was a sensitive function of nozzle temperature.

![Figure 2](image1)

**FIG. 2.** The upper panel shows raw ion images of Cl(\(^{2}\text{P}_{{3/2}}\)) (left) and Cl(\(^{2}\text{P}_{{1/2}}\)) (right) acquired at 235 nm. The lower panels show the corresponding angular
distributions. The solid lines are the best-fit simulations obtained using Eq. (7) in the text.

![Figure 3](image2)

**FIG. 3.** Speed distributions derived from Cl(\(^{2}\text{P}_{{3/2}}\)) (bottom panel) and Cl(\(^{2}\text{P}_{{1/2}}\)) (top panel) ion images for ClO photodissociation at 255 nm. The
arrows indicate the speeds associated with the formation of specific product
channels. The dashed lines indicate the speeds associated with the 235 nm
probe laser photodissociation.
and the pulsed valve conditions and that photodissociation channels involving the O(1D₂) result in recoil velocities low enough that rotational depolarization is expected and observed. This effect is especially pronounced near the O(1D) threshold (vide infra). In order to extract intrinsic anisotropy parameters for these channels we fit only the leading edge of the peaks corresponding to the lowest CIO rotational states. This resulted in anisotropy parameters closer to the limiting values than anisotropy parameters averaged over the entire speed distribution. The photodissociation channels corresponding to the O(3P) product result in larger recoil velocities and the measured anisotropy parameters are not as sensitive to parent rotational state. Thus, for these channels the analysis involved an average over the entire velocity distribution.

Davis and Lee measured a nonlimiting anisotropy parameter of 1.2±0.2 for the dominant Cl(2P₃/2)+O(1D₂) channel at 248 nm which is lower than the present result. The authors attributed this low anisotropy parameter to the 2Σ⁺ state which would be required to carry ~30% of the oscillator strength at this wavelength. Such a large contribution of the 2Σ⁺ state is inconsistent with theoretical calculations which suggest that this state makes a minor contribution (<1%) at this wavelength. We have also previously reported a nonlimiting anisotropy parameter of 1.2±0.2 for this channel at 235 nm. We believe that the low value reported in our previous work arose, in part, from the large entrained atomic signal which made analysis of the core-sampled TOF spectra difficult.

Although both the 2Σ⁺ and A²Π states diabatically correlate to O(1D₂) products, we find strong evidence for the role of the 2Σ⁺ state in the dissociation. The minor Cl(2P₃/2)+O(1D₂) channel has an anisotropy parameter of −1.0±0.1 which is consistent with excitation to the 2Σ⁺ state via a perpendicular transition (ΔΩ=±1). An alternative source of these fragments could be curve crossing from another state reached via a perpendicular transition. The wavelength-dependent yield of the Cl(2P₁/2)+O(1D₂) channel, assuming that these products arise from direct dissociation of the 2Σ⁺ state, is in good agreement with the previous theoretical study and is therefore a more likely explanation. Toniole et al. conclude that absorption to this state occurs from 210 to 242 nm, contributing approximately 2.5% of the oscillator strength in this wavelength range. Figure 4 summarizes the wavelength-dependent branching between channels (1)–(4) above the O(1D₂) threshold.

Since the A²Π state is the only state with appreciable oscillator strength that is reached via parallel transition (ΔΩ=0) and this state diabatically correlates to O(1D₂) products, any curve crossing (adiabatic behavior) will result in O(3P) products with an anisotropy parameter of 2.0. Thus, the cumulative crossing probability from the A²Π state to the 3Π, 12Δ, and 2Σ⁻ states can be determined by measuring the parallel component to the channels resulting in O(3P) production relative to the total parallel contribution at each wavelength. Based on this analysis and the data provided in Table I, the curve crossing probability decreases from a maximum value of 2% at 262 nm to <0.2% at 244 nm, as shown in Fig. 5. This decrease derives primarily from the overall decrease in the O(3P) fragments. We note that both the magnitudes and wavelength dependence are consistent with the theoretical work of Persico. It is not possible, however, to obtain curve crossing probabilities between specific states and A²Π state to compare with theory. The perpendicular contribution to the O(1D₂) channels could, in principle, permit a determination of the curve crossing probability to the A²Π from other states. Although less than limiting values for the anisotropy parameter are observed for the dominant Cl(2P₃/2)+O(1D₂) channel, this variation most likely reflects uncertainties in the anisotropy measurements rather than very large curve crossing probabilities from states reached via a perpendicular transition.

B. Photodissociation of CIO near the O(1D₂) threshold

We have investigated the photodissociation dynamics of CIO at wavelengths near the O(1D₂) threshold. The formation of Cl atoms in coincidence with O(1D₂) in this region results in little translational energy. As a result, the measured speed distributions are extremely sensitive to the available energy, i.e., the precise value of the Cl–O bond dissociation energy and the initial energy content of the CIO radicals. The lower panel of Fig. 6 shows the Cl(2P₃/2) speed distribution derived from the measured image at 262 nm. This wavelength corresponds to excitation just above the O(1D₂) threshold. At higher speeds, not shown in the figure, we observed a small feature consistent with the formation of coin-
cident \(O(3P_J)\). The finite width of the measured speed distribution is a reflection of the initial internal state distribution of the ClO radical. The speeds associated with individual ClO rotational levels in both spin-orbit states are indicated by the vertical lines in the figure. The rotational distribution is characterized by a temperature of 100 K and the spin-orbit branching ratio by an electronic temperature of 200 K. We have assumed that the vibrational temperature is 200 K based on a lack of clear signal corresponding to \(v=1\) ClO. The line spectrum has been convoluted with a Gaussian to reflect instrumental resolution. The resulting solid line provides a reasonable fit to measured speed distribution. We have assumed a threshold energy of 38 050±20 cm\(^{-1}\) for fitting the speed distributions. The fits are extremely sensitive to this value near threshold, both in terms of the absolute speeds and the spacing between peaks which correspond to each spin-orbit state fixed at 318 cm\(^{-1}\).

The threshold energy was derived from the fits to speed distributions acquired at multiple wavelengths, some below the threshold where the fragments produced arise from ClO radicals with nonzero internal energy.

The speed-dependent anisotropy parameters for the Cl\(^2P_{3/2}\) fragments are shown in the upper panel of Fig. 6. Excitation in this wavelength region involves a parallel transition to the \(\bar{A}^2\Pi\) state above the O\(^1D_2\) threshold followed by direct dissociation. In the axial recoil approximation, where the recoil axis and molecular axis are nearly equivalent, the anisotropy parameter would be near its limiting value of 2. The measured anisotropy parameters, however, are substantially lower than this limiting value. The decrease in anisotropy parameter is due to a breakdown in the axial recoil approximation, i.e., a reorientation of the recoil velocity resulting from initial angular momentum of the parent. Evidence for this effect was reported recently in the near threshold photodissociation of IBr. The breakdown of the axial recoil approximation is expected when the radial and tangential velocities are comparable and the larger the parent rotational state the larger the magnitude of the effect. A comparison of the measured anisotropy parameters with parent rotational states demonstrates that the measurements are consistent with such a trend. In particular, the sudden increase in the anisotropy parameter corresponding to the lowest rotational states of the ClO spin-orbit excited state provides compelling evidence. A more quantitative treatment of the speed-dependent anisotropy parameters can be obtained using a simple classical model. Following the discussion of Wrede \textit{et al}. the classical motion of a rotating diatomic molecule is described by the effective Hamiltonian, ignoring internal angular momentum.
\[ H = V(R) + \frac{p^2}{2\mu} + \frac{J^2}{2\mu R^2} \]  
(8)

and the relation between the angle of rotation (\( \gamma \)) and internuclear separation can be expressed by solving Hamiltonian's equation of motion

\[ \frac{\partial \gamma}{\partial R} = \frac{J}{p(R)R^2}, \]  
(9)

where the conjugate momentum \( p(R) \) is given by

\[ p(R) = [2\mu(E - V(R)) - J^2/R^2]^{1/2}. \]  
(10)

In Eq. (10), \( J \) is the rotational angular momentum, \( V(R) \) is a Morse potential describing the \( A^2\Sigma^+ \) state, and \( E \) is the photon energy. The molecular constants of the \( X^2\Pi \) state and \( A^2\Sigma^+ \) state potential curves were obtained from previous spectroscopic results.41

The final angle of rotation is given by

\[ \gamma = \int_{r_0}^{\infty} \frac{JdR}{p(R)R^2}, \]  
(11)

where \( R_0 \) is the turning point of the Morse potential at the corresponding excitation energy. Although the choice of the inner turning point as the initial condition for the classical trajectory is an oversimplification, the repulsive wall of the \( A^2\Sigma^+ \) state lies nearly directly above the ground-state minimum at excitation energies near the \( O(1D_2) \) threshold.

The azimuthally averaged addition theorem42 permits the anisotropy parameter to be written as a product of two terms

\[ \beta = 2P_2(\cos \chi)P_2(\cos \gamma), \]  
(12)

where \( \chi \) is the recoil angle relative to the molecular axis, the second term reflects the reorientation of the recoil axial from the molecular axis by angle \( \gamma \). The predictions using Eqs. (9)–(12) are shown as the solid lines in the upper panel of Fig. 6. Although there is qualitative agreement with the data the model consistently underestimates the magnitude of the effect. The classical treatment includes the rotational angular momentum of the ClO but ignores orbital angular momentum of both ClO and the angular moment of the atomic fragments. A second source of systematic error involves the treatment of low velocities that result in small ion images. Since all the ions are projected on a limited number of pixels, the derived anisotropy parameters will be more isotropic than the intrinsic angular distribution although our simulations indicate that the effect is small in agreement with the conclusions reached by Wrede et al.

Based on the analysis of the images discussed previously we have established both the energy of the threshold (38.050 ± 20 cm⁻¹) and the internal energy distribution of the ClO radicals. As additional confirmation we have measured the relative \( O(1D_2) \) and \( O(3P_J) \) yields near the threshold. The insets of Fig. 7 show Cl\( (2P_{3/2}) \) images acquired at two wavelengths near threshold. The outer ring in the 265 nm image corresponds to \( O(3P_J) \) formation arising from the predissociation below threshold. The inner ring in the image is due to \( O(1D_2) \) formation and the intermediate ring is from the 235 nm probe laser. In the lower 262 nm image the outer ring is very weak and the innermost ring has increased noticeably in radius. In order to extract relative branching ratios for \( O(1D_2) \) and \( O(3P_J) \) formed in coincidence with Cl\( (2P_{3/2}) \) the wavelength-dependent images were converted to speed distributions and the integrated areas of the peaks associated with each channel were compared. Previous work by Wrede et al. has shown that ClO excitation in this wavelength region results in the formation of ion-pair states. We find that photodissociation through these states results in intense Cl\(^+\) and O\(^+\) images. A full description of this process is the subject of future publication. We have selected wavelengths near threshold which avoid these ion-pair states to facilitate analysis. Figure 7 shows a plot of the wavelength-dependent Cl\( (1D_2) \) quantum yield near the threshold using

\[ \Phi^{Cl}(O(1D_2)) = \frac{I(O(1D_2))}{I(O(1D_2)) + I(O(3P_J))}, \]  
(13)

where \( I(O(1D_2)) \) and \( I(O(3P_J)) \) represent areas of the peaks in the derived speed distributions corresponding to the Cl\( (2P_{3/2})+O(1D_2) \) and Cl\( (2P_{3/2})+O(3P_J) \) channels, respectively. The data show a dramatic change in the \( O(1D_2) \) yield between 262.5 and 264.5 nm consistent with the energetic threshold for \( O(1D_2) \) formation. The finite width of this onset is the result of nonzero ClO internal energy which allows for \( O(1D_2) \) formation at wavelengths corresponding to energies below the threshold. The solid and dashed lines in the figure represent simulations of the \( O(1D_2) \) fixing the quantum yield for total energies exceeding the threshold at 0.97. It should be noted that the reported \( O(1D_2) \) yields are based only on the Cl\( (2P_{3/2}) \) images. Although above the threshold the Cl\( (2P_{1/2}) \) yield is minor, below threshold we find that the Cl\( (2P_{3/2})/Cl(2P_{1/2}) \) ratio is approximately 1.5 and the overall
O(\(^1D_2\)) yields should, therefore, include this correction. As evidence of the Cl(\(^2P_{3/2}\))/Cl(\(^2P_{1/2}\)) branching ratio Fig. 8 shows an O(\(^3P_2\)) image acquired at 291.71 nm along with an expanded region of the speed distribution (bottom panel). The O(\(^3P_2\)) image exhibits two distinctive rings indicating the evidence of O(\(^3P_2\)) in coincidence with Cl(\(^2P_{3/2}\)) and Cl(\(^2P_{1/2}\)). Integration of the peaks in the speed distribution results in a branching ratio of Cl(\(^2P_{3/2}\))/Cl(\(^2P_{1/2}\)) of 1.5±0.1 at 291.71 nm. A similar result was obtained from measurements at 266 nm.

The solid line in Fig. 7 corresponds to a threshold energy of 38 050 cm\(^{-1}\) and the dashed lines represent ±40 cm\(^{-1}\), as well as 10% of the maximum yield. The apparent redshift of the onset value to our threshold value can be attributed to the ClO thermal energy. In addition, the authors observed a steeper onset curve than anticipated, suggesting the presence of a rotational barrier. However, we fail to detect evidence for such an effect. Schmidt et al. made a similar measurement using 2+1 REMPI detection of the O(\(^1D_2\)) fragments and reported a value of 37 965±30 cm\(^{-1}\) corresponding to the cutoff of the O(\(^1D_2\)) signal. The value is consistent with a thermal redshift from the energetic threshold. Neither Flesch et al. nor Schmidt et al. addressed the nonzero yield of O(\(^3P_j\)) above the O(\(^1D_2\)) threshold or observed evidence for a separate onset due to spin-orbit excited (A \(^2\Pi_{1/2}\)) ClO. Our approach differs from the previous studies in that each measurement of the Cl(\(^2P_{3/2}\)) speed distribution provides the yield of both O(\(^3P_j\)) and O(\(^1D_2\)) and given the resolution of the technique avoids interference from other dissociation channels.

C. Photodissociation of ClO below the O(\(^1D_2\)) threshold

In this section we report on our initial investigation of ClO photodissociation below the O(\(^1D_2\)) threshold. We focus on the determination of state-selected predissociation lifetimes based on the analysis of photofragment angular distributions and discuss the Cl(\(^2P_{3/2}\))/Cl(\(^2P_{1/2}\)) branching ratio. At wavelengths below ~267 nm only channels (1) and (2), which involve O(\(^3P_j\)) fragments, are observed.

The top panel of Fig. 9 shows the wavelength dependence of the anisotropy parameter in the region of 9-0 band (left) and 8-0 band (right) for the Cl(\(^2P_{3/2}\))/Cl(\(^2P_{1/2}\)) channel. The bottom panel shows spectral simulations of 9-0 band and 8-0 band along with the measured photofragment excitation (PHOFEX) spectra (closed circles), corresponding to the Cl(\(^2P_{3/2}\))/Cl(\(^2P_{1/2}\)) image features as a function of wavelength. The spectral simulations based on the sum of P, Q, and R branches of the A \(^2\Pi_{1/2}\) → X \(^2\Pi_{1/2}\) transition using molecular constants are obtained from previous spectroscopic results. The simulations are restricted to the \(^{35}\)Cl\(^{16}\)O isotope, since we detect only m/z=35 and we have used a rotational temperature of 100 K. Although the PHOFEX data qualitatively matched the band envelopes we were unable to resolve the rotational structure since the individual images consisted of a limited number of laser shots, necessary to avoid drifts in the source and laser powers. It should be noted that it was necessary to analyze images, rather than the total ion signals, as a function of wavelength in order to distinguish between the true signal and signal due to entrained Cl(\(^2P_{3/2}\)) atoms or ion-pair signal. The effect of finite lifetime on the anisotropy parameter can be calculated using the following equation:

\[
\beta(\tau) = \beta(\tau = 0) \frac{1 + \omega^2 \tau^2}{1 + 4\omega^2 \tau^2},
\]

where \(\tau\) is the predissociation lifetime, \(\omega\) is the rotational angular velocity, \(\beta(\tau)\) is the observed anisotropy parameter, and \(\beta(\tau = 0)\) is the intrinsic anisotropy parameter which should be 2.0 for a parallel transition (A \(^2\Pi\) → X \(^2\Pi\)). Since the ob-
served anisotropy parameter is very sensitive to rotational state as well as the predissociation lifetime, we measured a series of image intensities across the bandhead to identify the rotational state of ClO.\textsuperscript{16} Lane \textit{et al.} reported that the lifetime broadening showed no dependence on the rotational states, i.e., the predissociation mechanism is dominated by spin-orbit interaction between the $A\ ^{2}\Pi$ and the dissociative state. Assuming a $J'$-independent predissociation lifetime, we can fit the wavelength-dependent anisotropy parameters for the 9-0 band and 8-0 band using Eq. (14). The peaks in the lower panels of Fig. 9 represent overlapping $P(J)$ and $R(J+5)$ branch lines and the anisotropy parameters calculated using Eq. (14) represent weighted averages of the excited-state $J$ values. Based on this analysis, and illustrated in the top panels of Fig. 9, we have determined predissociation lifetimes of $1.5\pm0.2$ and $1.0\pm0.4$ ps for the 9-0 (left) and the 8-0 (right) bands, respectively. Our results are in reasonable agreement with the lifetimes reported in previous high-resolution spectroscopic studies, as indicated in Table II.\textsuperscript{11-13} The differences between the lifetimes estimated using Eq. (14) and the lifetimes reported from line broadening measurements are not unexpected. The derivation of Eq. (14) relies on the coherent excitation of different upper $J$ states via $P'$-, $R'$-, and $Q'$-branch transitions which leads to a classical time evolution in orientation sampled by delayed dissociation. However, the present case is characterized by narrow-band excitation, essentially cw on the time scale of predissociation. The optical selection of individual parent $J$ states (albeit overlapping $J$ states due to $P'$- and $R'$-branch transitions) implies predissociation slow enough to permit partially resolved rotational lines, suggesting that the conditions necessary for the implementation of Eq. (14) are not realized. We are currently pursuing studies aimed at further investigation of the angular distributions arising from the photodissociation of these resolved bands using imaging of the $O(\ ^{3}\Pi \ P_{6})$ fragment to provide an unambiguous measure of the spatial anisotropy. A recent high-level \textit{ab initio} study employing Fermi golden rule calculations on the excited states of ClO by Lane \textit{et al.} identified the principal dissociative states that couple to $A\ ^{2}\Pi_{3/2}$ state. Candidate states for the predissociation of $A\ ^{2}\Pi$ state were se-

![Fig. 9](image)

**TABLE II.** $r$-dependent lifetimes for the $A\ ^{2}\Pi_{3/2}$ states of ClO.

<table>
<thead>
<tr>
<th>Band</th>
<th>$\tau^{a}$ (ps)</th>
<th>$\tau^{b}$ (ps)</th>
<th>$\tau^{c}$ (ps)</th>
<th>$\tau^{d}$ (ps)</th>
</tr>
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<tbody>
<tr>
<td>0-0</td>
<td>4.43</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-0</td>
<td>2.00</td>
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<td>2-0</td>
<td>1.97</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>3-0</td>
<td>0.97</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-0</td>
<td>1.28</td>
<td></td>
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<tr>
<td>5-0</td>
<td>1.06</td>
<td>0.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-0</td>
<td>1.15</td>
<td>0.53</td>
<td>1.0±0.3</td>
<td></td>
</tr>
<tr>
<td>7-0</td>
<td>1.08</td>
<td>1.06</td>
<td>1.02</td>
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</tr>
<tr>
<td>8-0</td>
<td>0.92</td>
<td>1.11</td>
<td>1.0±0.4</td>
<td></td>
</tr>
<tr>
<td>9-0</td>
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<td>1.03</td>
<td>1.5±0.2</td>
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<tr>
<td>10-0</td>
<td>1.45</td>
<td>0.94</td>
<td>1.0±0.3</td>
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<tr>
<td>11-0</td>
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<td>1.48</td>
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<tr>
<td>12-0</td>
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<td>1.42</td>
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<tr>
<td>13-0</td>
<td>2.56</td>
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<td>2.92</td>
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<tr>
<td>15-0</td>
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<td>16-0</td>
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<td>17-0</td>
<td>13.31</td>
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<tr>
<td>18-0</td>
<td>10.24</td>
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</table>

\textsuperscript{a}McLoughlin \textit{et al.} (Ref. 11).
\textsuperscript{b}Howie \textit{et al.} (Ref. 13).
\textsuperscript{c}Barton \textit{et al.} (Ref. 12).
\textsuperscript{d}Present work.
selected based on electronic configuration arguments. A comparison of the calculated predissociation lifetimes for each vibrational level and to experimental predissociation lifetimes derived from spectroscopic linewidths led the authors to assign the predissociation primarily to the $1\ ^{3}\Sigma^{+}$, $2\ ^{4}\Sigma^{-}$, and $3\ ^{4}\Pi$ states.

Figure 10 shows all the anisotropy parameters measured for the Cl($^{2}\Pi_{3/2}$)+O($^{3}\Pi$) channel below the O($^{1}\Delta_{2}$) threshold (upper panel) along with ClO absorption spectrum (bottom panel) taken from Trotier et al. The dashed line in the upper panel shows the classical long-time limit predicted by Eq. (14). The variation of anisotropy parameter with wavelength across specific vibronic bands is observed, consistent with Eq. (14) as previously discussed. At wavelengths approaching the O($^{1}\Delta_{2}$) threshold the anisotropy parameters for the Cl($^{2}\Pi_{3/2}$)+O($^{1}\Delta_{2}$) channel are far from their limiting value and several lie below the classical limit. The origin of these low anisotropy parameters below ~267 nm is due to several factors. There is spectroscopic evidence that these high vibrational states have long predissociation lifetimes (Table II). In addition, at wavelengths shorter than 267 nm the yield of O($^{3}\Pi$) decreases as the O($^{1}\Delta_{2}$) channels become energetically accessible and an increasing fraction of the O($^{3}\Pi$) fragments arises from direct dissociation rather than predissociation. Since O($^{3}\Pi$) formation above the threshold has contributions from direct dissociation of states reached via perpendicular transitions (Table I) anisotropy parameters below 0.5 are not unexpected.

IV. CONCLUSIONS

We have investigated the UV photodissociation dynamics of ClO above, near, and below the O($^{1}\Delta_{2}$) formation threshold using velocity map ion imaging. We find that Cl($^{2}\Pi_{3/2}$)+O($^{1}\Delta_{2}$) is the dominant dissociation pathway (>0.94) above O($^{1}\Delta_{2}$) threshold with minor contributions from the Cl($^{2}\Pi_{1/2}$)+O($^{3}\Pi$) and Cl($^{2}\Pi_{1/2}$)+O($^{1}\Delta_{2}$) channels. Based on the anisotropy parameter for the Cl($^{2}\Pi_{3/2}$)+O($^{1}\Delta_{2}$) channel we believe that this channel results from direct dissociation of the $2\ ^{2}\Sigma^{+}$ state. We observe O($^{3}\Pi$) fragments with positive anisotropy, strong evidence of curve crossing from the $A\ ^{2}\Pi$ to one of several dissociative states. Both the magnitude and wavelength dependence of the curve crossing probability are in good agreement with the theoretical calculations of Persico. A careful analysis of the speed distribution of Cl($^{2}\Pi_{3/2}$) fragments just above the O($^{1}\Delta_{2}$) threshold permits the accurate energetic determination of this threshold of 39.050 ± 0.020 cm$^{-1}$. Predissociation lifetimes ClO for selected vibronic bands have been obtained using the rotational depolarization of the photofragment angular distribution. We find values in the range of 1.0–1.5 ps depending on the upper-state vibrational level. We also find that the Cl($^{2}\Pi_{3/2}$)/Cl($^{2}\Pi_{1/2}$) branching ratio is approximately 1.5 ± 0.1 below the O($^{1}\Delta_{2}$) threshold based on careful measurements at 266 and 291 nm, respectively.

ACKNOWLEDGMENTS

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FIG. 10. Wavelength-dependent anisotropy parameters associated with the Cl($^{2}\Pi_{3/2}$)+O($^{3}\Pi$) channel (top panel). The dashed line is the classical long-time limit based on Eq. (14). The ClO absorption spectrum from Ref. 7 is shown for comparison in the bottom panel.
We predict a rate constant for the Cl$_2$O $\rightarrow$ ClO+Cl reaction at 700 K of 2.3 x $10^4$ s$^{-1}$ corresponding to a Cl$_2$O lifetime close to the transit time through the heated nozzle.