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Ion imaging studies of ClONO₂ photodissociation: Primary branching ratios and secondary dissociation

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ABSTRACT

The photodissociation dynamics of ClONO₂ at 235 nm has been reinvestigated using velocity map ion imaging. We report branching ratios for the Cl + NO₃ and ClO + NO₂ channels to be 0.49:0.51 with anisot-ropy parameters of $\beta = 0.5 \pm 0.1$ and $\beta = -0.1 \pm 0.3$ for the Cl and ClO production channels, respectively. Photodissociation at 248 nm and 262 nm results in similar branching ratios and dynamics as observed at 235 nm. Measured O(³P₂) images arising from ClONO₂ dissociation at 226 nm suggest that oxygen atoms result from the spontaneous dissociation of metastable NO₃. The quantum yield of O atoms arising from the spontaneous dissociation of NO₃ varies from 0.09 at 262 to 0.38 at 235 nm based on the derived internal energy distributions of the NO₃ fragments. We also describe a Monte-Carlo forward-convolution fitting of imaging data which permits detailed analysis of both spontaneous secondary dissociation and secondary photodissociation.

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Chemical Physics

1. Introduction

Chlorine compounds are known to play a key role in stratospheric ozone loss in the Polar Regions. Chlorine nitrate (ClONO₂) is an important temporary reservoir for reactive chlorine in the atmosphere [1,2]. As a consequence there have been numerous experimental and theoretical investigations to assess the thermochemistry, kinetics, and photochemistry of this species. Photolysis is the primary stratospheric loss channel of ClONO₂ during the day [3–5]. Thus, quantification of the wavelength-dependent photolysis product yields is critical to understanding stratospheric chlorine chemistry and modeling atmospheric ozone.

The ClONO₂ absorption spectrum exhibits broad structure, including peaks at 190 nm, 215 nm and a small feature near 370 nm which is thought to involve low lying triplet states [1,6]. Grana et al. have assigned 190 nm peak to $n \rightarrow \pi^*$ transition and 215 nm peak to $\pi \rightarrow \pi^*$ transition on the NO₂ group based on a comparison with *ab initio* vertical excitation energies [7]. The authors concluded that two of the lowest excited states are correlated to the Cl + NO₃ and ClO + NO₂ channels. The result suggests that the quantum yields associated with specific product channels may exhibit strong wavelength dependence. There are three dissociation pathways that are energetically accessible following ultraviolet excitation,

$$CIONO_2 + h\nu \to Cl(^2P_J) + NO_3 \tag{1}$$

$$\rightarrow \text{CIO}(X^2\Pi_{\Omega}) + \text{NO}_2 \tag{2}$$

 $\rightarrow ClONO + O(^{3}P_{J}) \tag{3}$

While channel 1 provides a catalytic route to ozone depletion, channel 2 is simply the reverse of the ClONO₂ formation reaction. Early studies on the photochemistry of ClONO₂ using static-cells or flow-tubes and atomic resonance fluorescence reported that channel 1 was the major dissociation pathway [8-11] based on the observation of O(³P) following photolysis, but could not establish whether these products originated from a primary channel or a secondary process. Marinelli and Johnston detected NO₃ by absorption following ClONO₂ photolysis at 248 nm and reported a yield of 0.5 ± 0.3 for channel 1 [12]. More recently, Nelson et al. investigated the photodissociation of ClONO₂ at 193 nm, 248 nm, and 308 nm using photofragment translational energy spectroscopy in a molecular beam [13-15]. The relative yields of channels 1 and 2 were calibrated using the photodissociation of Cl₂O at 308 nm [16]. The authors reported that $ClO + NO_2$ and $Cl + NO_3$ were the primary photoproducts at these wavelengths and determined relative branching ratios of ClO:Cl to be 0.66:0.34 at 193 nm, 0.54:0.46 at 248 nm, and 0.33:0.67 at 308 nm. No conclusive evidence for channel 3 was observed and the detection of O atom fragments was attributed to the spontaneous secondary dissociation of NO₃. Photofragment anisotropy indicated that dissociation was rapid compared to parent rotational motion at all wavelengths.

Ravishankara and co-workers measured quantum yields for the photoproducts of ClONO₂ for wavelengths ranging from 193 nm to



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352.5 nm using both Cl and O atomic resonance fluorescence [17] and direct absorption of NO₃ [18]. The authors reported relative branching ratios for the Cl + NO₃:ClO + NO₂ channels along with NO₃ quantum yields at these wavelengths and the results were consistent with the molecular beam experiments.

A previous study employing one-color ion time-of-flight (TOF) translational spectroscopy at 235 nm demonstrated the ability to distinguish between Cl fragments from channel 1 and those arising from the combination of channel 2 and the photodissociation of the nascent ClO products [19],

$$\operatorname{ClO}(X^2 \Pi_{\Omega}) + h\nu \to \operatorname{Cl}({}^2P_J) + \operatorname{O}({}^3P_J, {}^1D_2)$$
(4)

Since the focussed laser beam, necessary for 2 + 1 REMPI detection of Cl at 235 nm, ensured complete dissociation of ClO, quantitative relative branching ratio information for channels 1 and 2 could be derived from only Cl detection. Based on simulations to the TOF data relative Cl atom and ClO quantum yields of 0.42 ± 0.1 and 0.58 ± 0.1 , respectively, were determined. In addition, the fraction of nascent NO₃ fragments that undergo secondary dissociation was calculated based on the derived internal energy distribution yielding a quantum yield of 0.20 for the NO₃ \rightarrow NO₂ + O channel.

In the present experiments, we employ the ion imaging technique to reinvestigate the photodissociation at 235 nm. We find that the advantage of ion imaging over ion TOF is the determination of quantitative speed-dependent anisotropy which is critical in constraining forward-convolution modeling of the data. Our new analysis confirms the previous conclusions albeit with minor differences. We have also extended these studies to the photodissociation at 248 nm and 262 nm. Finally, we have measured the $O({}^{3}P_{2})$ fragment images arising from ClONO₂ photolysis at 225 nm and, based on the forward-convolution modeling, demonstrate that the oxygen atoms derive from the secondary dissociation of vibrationally excited NO₃ fragments.

2. Experimental

A detailed description of the velocity map ion imaging apparatus can be found elsewhere [20,21]. Briefly, a pulsed molecular beam of 2% ClONO₂ in He was collimated by a conical skimmer and intersected at 90° by either one or two linearly polarized laser beams. In all cases, the probe beam was the frequency doubled output of a Nd:YAG (Spectra Physics LAB-150-10) pumped dye laser (LAS LDL). A photoelastic modulator (PEM-80, HINDS) was used to rotate the polarization of the probe beam. The photolysis beam was the frequency doubled output of a Nd:YAG (Spectra Physics LAB-150-10) pumped dye laser (Spectra Physics PDL-1). An assembly consisting of four Pellin-Broca prisms was used to maintain overlap of the photolysis and probe laser beams during the REMPI scans. Typical photolysis and probe pulse energies were 800 µJ and 200 µJ, respectively. The fundamental wavelengths of both lasers were accurately calibrated using a Ne-filled hollow cathode lamp. The $Cl(^{2}P_{3/2})$ and $Cl(^{2}P_{1/2})$ atoms were probed using 2 + 1 REMPI transitions at 235.336 nm (4p $^2D_{3/2} \leftarrow$ 3p $^2P_{3/2})$ and 235.205 nm $(4p \ ^2P_{1/2} \leftarrow 3p \ ^2P_{1/2})$, respectively [22]. The O(3P_2) atoms were probed using 2+1 REMPI transitions at 225.572 nm [23]. The resulting ions were accelerated by velocity mapping ion optics [24] through a 50 cm long field-free flight tube. The ions were projected on a position-sensitive detector consisting of a dual microchannel plate-phosphor assembly. Images were acquired using a CCD camera and a frame grabber controlled by commercial software (Coda32) which included nearest neighbor centroiding and event counting [25]. Due to the magnitudes of the fragment velocities, images were obtained by scanning over the Doppler profiles. Fragment speed and angular distributions were reconstructed from the images using the basis set expansion (BASEX) algorithm developed by Reisler and co-workers [26].

ClONO₂ was prepared by the method of Schmeisser through the reaction of N_2O_5 and Cl_2O [27]. Cl_2O was synthesized by the method of Cady [28]. Impurities in the ClONO₂ sample (mainly Cl_2) were removed by vacuum distillation. The purity of samples was confirmed by UV–Vis absorption spectroscopy. Although we found that minor Cl_2 contamination (<5%) was present the absorption cross section of Cl_2 is nearly two orders of magnitude smaller than that of ClONO₂ and the contribution of Cl_2 photolysis to the images is small and easily distinguished from the ClONO₂ signal [29].

3. Results and discussion

Fig. 1 shows raw $Cl(^{2}P_{3/2})$ and $Cl(^{2}P_{1/2})$ images arising from the 235 nm photodissociation of $ClONO_{2}$. No signal was observed when the laser was detuned from the $Cl(^{2}P_{J})$ REMPI transitions. By inspection there are clear differences between the two images; (1) the $Cl(^{2}P_{3/2})$ image shows evidence for a significant contribution from low speed fragments and (2) the anisotropy of the $Cl(^{2}P_{3/2})$ is more sharply peaked than expected. Based on the image intensity and correcting for the relative detection efficiency we determine a $Cl(^{2}P_{1/2})/Cl(^{2}P_{3/2})$ branching ratio of 0.09 ± 0.01 . This reflects a slightly greater contribution of $Cl(^{2}P_{1/2})$ than has been previously reported. Fig. 2 shows the corresponding speed distributions derived from the images in Fig. 1 [19]. The $Cl(^{2}P_{J})$ atoms can be formed from either channel 1 or the photodissociation of ClO produced via channel 2. However, we have shown previously that the photodissociation of CIO at 235 nm results in predomi-



CI (2P1/2)



Fig. 1. Raw Cl($^2P_{3/2})$ and Cl($^2P_{1/2})$ images arising from ClONO_2 photodissociation at 235 nm.



Fig. 2. Speed distributions derived from the $Cl(^2P_{1/2})$ (upper panel) and $Cl(^2P_{3/2})$ (lower panel) images in Fig. 1.

nately $Cl({}^{2}P_{3/2}) + O({}^{1}D_{2})$ with an anisotropy parameter of 1.8 ± 0.1 [30]. We assume, therefore, that the $Cl({}^{2}P_{1/2})$ image is dominated by chlorine atoms originating from channel 1. Converting the $Cl({}^{2}P_{1/2})$ atom speed distribution to a center-of-mass translational energy distribution yields an average translational energy for this channel of 163 kJ/mol with a FWHM of 62 kJ/mol and is consistent, albeit exhibiting a slightly different shape, with previous lower resolution measurements [19]. The asymmetric shape of the distribution is very similar to the distribution reported by Nelson et al. at 248 nm. In addition, the $Cl({}^{2}P_{1/2})$ fragments are well described by a single *speed-independent* anisotropy parameter of 0.5 ± 0.1, providing further evidence that these products arise exclusively from channel 1. The measured anisotropy parameter for this channel is identical to the values reported by Nelson et al. at 193 nm, 248 nm, and 308 nm [13,15].

Unlike the $Cl(^{2}P_{1/2})$ signal, the $Cl(^{2}P_{3/2})$ signal consists of contributions from both channel 1 and the combination of channels 2 and 3. In order to analyze the speed distribution and spatial anisotropy of the ground state $Cl(^{2}P_{3/2})$ atoms produced via secondary photodissociation in the tightly focused laser beam, we employ a forward-convolution fitting scheme. We assume that only a single asymptotic channel, $Cl(^{2}P_{3/2}) + O(^{1}D_{2})$, contributes in the photodissociation of ClO. In previous work, employing a hot source of ClO which populates v > 1 states, identical branching ratios and anisotropy parameters for CIO photodissociation were observed [31]. Since the spin orbit energy of $Cl(^{2}P_{J})$ is small (~10.6 kJ/mol), the energy distributions of $Cl(^{2}P_{3/2})$ and $Cl(^{2}P_{1/2})$ are expected to be similar. We therefore assume that the measured $Cl(^{2}P_{1/2})$ speed distribution describes the contribution from channel 1 to the $Cl(^{2}P_{3/2})$ image. A fit to the $Cl(^{2}P_{3/2})$ then involves an iteratively adjusted speed and angular distributions associated with the primary photodissociation channel 2 of chlorine nitrate to form ClO and NO₂, and a relative branching ratio between channels 1 and 2. The forward-convolution modeling of the data implements a Monte-Carlo sampling over the speed and angular distributions

of these channels and a more complete description can be found in the Appendix A. Fig. 3 displays a best-fit (solid line) to the measured $Cl({}^{2}P_{3/2})$ speed distribution which is the sum of the contributions from the $CIO + NO_2$ and $CI + NO_3$ channels (dashed lines). Based on the best forward-convolution fit, we determine a ClO + - $NO_2:Cl(^2P_{3/2}) + NO_3$ branching ratio of $0.52 \pm 0.05:0.48 \pm 0.05$ contributing to the $Cl(^{2}P_{3/2})$ image. However, the *total* branching of channels 1 and 2 requires the overall Cl(²P_{1/2})/Cl(²P_{3/2}) ratio. Combining the forward-convolution fitting results with the $Cl(^{2}P_{1/2})/$ $Cl(^{2}P_{3/2})$ ratio, we find an overall $ClO + NO_{2}:Cl + NO_{3}$ branching of 0.51 ± 0.05 : 0.49 ± 0.05 in good agreement with previous results [19]. The center-of-mass translational energy distribution for the ClO + NO₂ channel, derived from the forward-convolution fitting procedure is shown in Fig. 4. The distribution is peaked away from zero with an average energy of 124 kJ/mol. Nelson et al. have reported slightly lower values for this channel which, interestingly, decrease with decreasing wavelength although the variation is not large. The general shape our derived $P(E_T)$ distribution is in good agreement with the $P(E_T)$ reported by Nelson et al. at 248 nm and 193 nm [13].

There are two important observations regarding the spatial anisotropy of the $Cl(^{2}P_{3/2})$ fragments. The spatial anisotropy was fitted using the following form,

$$P(\theta) \propto (1 + \beta_2(\nu)P_2(\cos\theta) + \beta_4(\nu)P_4(\cos\theta))$$
(5)

since the signal is a composite of both 1- and 2-photon processes (see Appendix A). Fig. 5 shows speed-dependent $\beta_2(v)$ and $\beta_4(v)$ terms derived from the Cl(²P_{3/2}) image analysis averaged over 120 m/s intervals. The data exhibit a clear speed-dependence as do the best-fit Monte-Carlo forward-convolution fits. For comparison, forward-convolution fits using three different speed-*independent* anisotropy parameters for the ClO + NO₂ channel of -1, 0, and 2 are shown. The simulations result in distinctive speed-dependent anisotropy for each case. Based on the best-fit to the data we determine a best-fit speed-independent anisotropy parameters for the ClO + NO₂ channel based on a comparison to the data. Although inspection shows that relaxing the constraint of a speed-independent anisotropy for the ClO + NO₂ channel provides an improved fit we did not pursue additional parameterization.

In order to extend the study to additional wavelengths we performed photodissociation experiments at 248 nm and 262 nm. The 235 nm probe laser power was decreased so that only a small sig-



Fig. 3. Forward-convolution fit to the $Cl(^{2}P_{3/2})$ speed distribution. The contributions due to $ClO + NO_2$ (followed by ClO photodissociation) and $Cl + NO_3$ channels are shown as dashed lines and the weighted sum as a solid line (see text for details).



Fig. 4. Derived center-of-mass translational energy distribution for the ${\rm CIO}$ + ${\rm NO}_2$ channel at 235 nm.



Fig. 5. Speed-dependent anisotropy parameters ($\beta_2(v)$ and $\beta_4(v)$) for the Cl(²P_{3/2}) fragments arising from ClONO₂ photodissociation at 235 nm along with the forward-convolution fit using three different anisotropy parameters to describe the ClO + NO₂ channel.

nal was observed in the absence of the dissociation laser. This minor contribution from the probe laser was subtracted from the final images prior to analysis. Although the signal-to-noise of the corrected two-color images was not as good as the one-color experiments at 235 nm it was sufficient for forward-convolution analysis. Images arising from the photodissociation of ClONO₂ at

248 nm and 262 nm were qualitatively similar. As observed at 235 nm, analysis of the $Cl({}^{2}P_{3/2})$ images revealed speed-dependent anisotropy while the $Cl({}^{2}P_{1/2})$ data could be described by a single speed-independent anisotropy of $\beta = 0.5 \pm 0.1$ at both 248 nm and 262 nm. Based on the $Cl(^{2}P_{1/2})$ speed distributions we derive average $E_{\rm T}$ values of 146 kJ/mol and 153 kJ/mol for the Cl + NO₃ channel at 248 nm and 262 nm, respectively. The values are consistent with a value of 170 kJ/mol reported by Nelson et al. at 248 nm [13]. The relative insensitivity of the average energy to wavelength is not surprising given the rather modest change in available energy. The $Cl({}^{2}P_{1/2})/Cl({}^{2}P_{3/2})$ branching ratio was determined to be 0.10 ± 0.03 and 0.11 ± 0.03 for 248 nm and 262 nm, respectively. Fig. 6 shows the derived $Cl(^{2}P_{3/2})$ speed distribution and the associated forward-convolution fits for photolysis at 248 nm (lower panel). The upper panel of Fig. 6 shows the speed-dependent anisotropy $(\beta_2(v))$ and the forward-convolution fit. Forward-convolution fits yield anisotropy parameters of $\beta = 0.0 \pm 0.3$ and β = -0.1 ± 0.4 for the ClO + NO₂ channel for photodissociation at 248 nm and 262 nm, respectively. As with the 235 nm analysis the $Cl(^{2}P_{1/2})$ speed distribution serves the basis function for the primary Cl + NO₃ channel in fitting the Cl(${}^{2}P_{3/2}$) data. The speed distribution derived from the $Cl(^{2}P_{3/2})$ images is similar in shape to the 235 nm distribution but shows a decrease in average speed with increasing wavelength. The results of the analysis for the primary dissociation channels at all three wavelengths are summarized in Table 1.

3.1. Spontaneous dissociation of nascent NO₃

The nascent internal energy distribution of NO_3 can be deduced from the energy conservation of the Cl + NO_3 channel. A plot of the nascent NO_3 internal energy distribution at 235 nm derived from the $Cl(^2P_{3/2})$ speed distribution is shown in Fig. 7. There are two possible dissociation pathways for energized NO_3 (see Table 2),

$$NO_3 \rightarrow NO + O_2,$$
 (6)

$$NO_3 \to NO_2 + O(^3P) \tag{7}$$

and the relative branching of these two channels with respect to atmospheric photolysis is important for estimating ozone deletion



Fig. 6. Speed-dependent anisotropy parameters, $\beta_2(v)$, (upper panel) and speed distribution (lower panel) arising from ClONO₂ photodissociation at 248 nm. The solid and dashed lines are the results of simulations as described in the text.

Table 1				
Summary of primary channels in the photodissociation of $CIONO_2$ at the wavelengths investigated in the study.				
235 nm	248 nm			

	235 nm		248 nm		262 nm	262 nm	
	Cl + NO ₃	ClO + NO ₂	Cl + NO ₃	ClO + NO ₂	Cl + NO ₃	$ClO + NO_2$	
Φ	0.49 ± 0.04	0.51 ± 0.04	0.44 ± 0.08	0.56 ± 0.08	0.51 ± 0.1	0.49 ± 0.1	
$\langle E_{\rm T} \rangle^{\rm a}$	163	124	146	96	153	104	
β	0.5 ± 0.1	-0.1 ± 0.3	0.5 ± 0.1	0.0 ± 0.4	0.5 ± 0.2	-0.1 ± 0.4	





Fig. 7. Internal energy distribution of the nascent NO₃ radicals arising from 235 nm photodissociation of ClONO₂ based on the $Cl(^2P_{1/2})$ speed distribution. The vertical line denotes the energetic threshold associated with the secondary dissociation of NO₃ to give NO₂ + O products.

Table :	2
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Fraction of spontaneous NO₃ decomposition in the photodissociation of ClONO₂.

Wavelength (nm)	Oxygen atom yield	Reference
193	0.4	[17]
193	0.54	[13]
235	0.38 ± 0.04	This work
248	0.18 ± 0.03	This work
262	0.09 ± 0.03	This work
308	0.0	[15]

since NO participates in catalytic cycle whereas the production NO₂ participates in a null cycle. Davis et al. studied these two channels using molecular beam photofragment translational spectroscopy and determined thresholds for channels 6 and 7 to be $47.3 \pm$ 0.8 kcal/mol and 48.69 ± 0.25 kcal/mol, respectively [32]. Since channel 7 involves a loose transition state this pathway will dominate for energies above this threshold although recent reports of 'roaming' dynamics in formaldehyde dissociation [33] suggest that the situation may be more complex. The quantum yield of secondary O(³P) can be therefore, obtained by integrating the normalized NO3 internal energy distribution above the threshold corresponding to channel 7. It should be noted that collisional stabilization of energetic NO₃ radicals which exceed the energy of dissociation should not be significant under stratospheric conditions since the rates of spontaneous dissociation exceed the collision frequency even for energies a few kcal/mol above the threshold [19]. Given the fraction of NO₃ which dissociates to NO₂ + O(³P), the final O(³P) quantum yield can be calculated by weighting this fraction by the Cl + NO₃ branching ratio value. Based on such analysis we derive O(³P) yields of 0.38 ± 0.04, 0.18 ± 0.03, and 0.09 ± 0.03 at 235 nm, 248 nm, and 262 nm respectively. The value of 0.54 reported by Nelson et al. is consistent with the increasing trend with decreasing wavelength, a consequence of increasing available energy and only a modest increase in the average translation energy of the Cl + NO₃ channel.



Fig. 8. Raw O(³P₂) image arising from ClONO₂ photodissociation at 226 nm.



Fig. 9. Derived speed-dependent anisotropy parameters (upper panel) and speed distribution (lower panel) for $O(^{3}P_{2})$ fragments arising from ClONO₂ photodissociation at 226 nm (symbols) along with forward-convolution fit (solid lines).

We have observed a direct evidence of the spontaneous dissociation of primary NO₃ generated in coincidence with $Cl(^{2}P_{1})$. Fig. 8 shows a representative $O({}^{3}P_{2})$ ion image arising from the photodissociation of ClONO₂ at 226 nm. In these one-color experiments no signal was observed when the laser was detuned from the oxygen REMPI transition. If the oxygen atoms originated from the primary ClONO + O channel one would expect the $O({}^{3}P_{2})$ image to exhibit a broad annular feature similar to $Cl(^{2}P_{1})$ image arising from $Cl + NO_{3}$ channel, a result of large recoil velocities. By inspection, the $O({}^{3}P_{2})$ image is more consistent with secondary dissociation. In order to confirm this assignment we have modeled this process using Monte-Carlo forward-convolution (see Appendix A for details) [32] the fitting procedure employed the $P(E_T)$ derived from the $Cl(^{2}P_{1/2})$ images at 235 nm to model the translational energy distribution of the primary Cl + NO₃ channel. As shown in Fig. 9, the forward-convolution fits (solid lines) assuming spontaneous secondary dissociation of NO₃ are in excellent agreement with the speed-dependent anisotropy parameters, $\beta_2(\nu)$, and speed distribution of the $O({}^{3}P_{2})$ fragments derived from the image in Fig. 8.

4. Conclusions

We have reinvestigated the photodissociation dynamics of ClONO₂ at 235 nm using velocity map ion imaging. Based on the forward-convolution fit we have determined relative branching ratio for the $Cl + NO_3$ and $ClO + NO_2$ to be 0.49:0.51 along with anisotropy parameters of $\beta = 0.5 \pm 0.1$ and $\beta = -0.1 \pm 0.3$ for the Cl and CIO production channels, respectively. The reported branching ratios and average translational energy distributions are consistent with previous measurements. We have also extended our measurements to examine the photodissociation of ClONO₂ at 248 nm and 262 nm. Photolysis at these wavelengths results in similar branching and dynamics as observed at 235 nm. Measured $O({}^{3}P_{2})$ images arising from ClONO₂ dissociation at 226 nm suggest that the O atom fragments observed in laboratory studies result from the spontaneous dissociation of metastable NO₃. We have determined that the quantum yield of O atom arising from the spontaneous dissociation of NO3 varies from 0.09 at 262 nm to 0.38 at 235 nm based on the derived internal energy distribution of the NO₃ products. The trend is consistent with increasing available energy and little change in the average translation energy release for the Cl + NO₃ channel.

We present a Monte-Carlo forward-convolution approach to the analysis of imaging data. The method permits detailed analysis of both spontaneous secondary dissociation and secondary photodissociation. Specifically, we find that analysis of the velocity-dependent anisotropy can provide additional constraints in model such processes.

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Appendix A

The advantage of imaging techniques is their multiplexing ability, through reconstruction of the full center-of-mass velocity distribution. As a result the correlation between the angular and speed distributions can be extracted to provide considerable insight into the photodissociation dynamics. Often the laser powers or absorption cross sections ensure that some secondary photodissociation of the primary photofragments is unavoidable. In other cases, the quantitative photodissociation of primary products can provide beneficial results given proper analysis. In this Appendix A, we demonstrate that there are clear signatures of secondary photodissociation in the speed-dependent angular distribution. Thus, if either photodissociation step is well-characterized then considerable information regarding the speed and angular distribution of the other photodissociation step, obtained at higher laser powers, can be extracted. In order to illustrate the sensitivity we have performed forward-convolution simulations for a simple test case although the procedure is general. We then provide details on the Monte-Carlo forward-convolution simulation specific to the case of ClONO₂ photodissociation.

A.1. Modeling secondary photodissociation

Fig. A1 shows a schematic representation of the vector addition involved in calculating the resultant secondary fragment atom speed and angular distributions from the combination of two separate photodissociation steps. The forward-convolution procedure uses Monte-Carlo sampling over a model velocity distribution for the primary fragment and sampling over a model second step velocity distribution, constrained by conservation of energy. As a test case to demonstrate the forward-convolution fitting procedure we first consider two identical Gaussian speed distributions, v = 1000 m/s and FWHM = 200 m/s, characteristic of direct dissociation on a repulsive potential to describe the two photodissociation steps. The anisotropy parameter for the second step was fixed at 2 and the anisotropy parameter for the first step was chosen to be -1, 0, and 2. We assume that the spatial anisotropy for each step is independent of speed.

In order to facilitate comparison with experiment we have fit the resultant speed-dependent anisotropy from the Monte-Carlo simulation using the following equation [34],

$$I(\theta; \nu) = \frac{1}{4\pi} [1 + \beta_2(\nu) P_2(\cos \theta) + \beta_4(\nu) P_4(\cos \theta)], \tag{A.1}$$

where $P_2(\cos \theta)$ and $P_4(\cos \theta)$ are the second and fourth Legendre polynomial, and θ is the angle between the fragment recoil direction and laser polarization direction. Such analysis mimics the analysis of experimental ion images.



Fig. A1. Coordinate system for the forward-convolution fitting of secondary photodissociation. The values v_1 and θ_1 correspond to the primary process (ClO + NO₂ in the case of ClONO₂) and the values v_2 and θ_2 correspond to the second photodissociation process (ClO photodissociation in the case of ClONO₂). $P(v,\theta)$ describes the resultant laboratory speed and angular distributions for the secondary fragment (Cl(²P_{3/2}) atoms in the case of ClONO₂).

The upper panel of Fig. A2 shows the resultant product speed distributions for first step anisotropy parameters of -1, 0, and 2 (dashed, dotted, and solid lines, respectively). All the distributions are broadened about 1000 m/s and have significant population near 2000 m/s. The lower panels show the resultant $\beta_2(v)$ and $\beta_4(v)$ from the simulations. Although both steps are described by speed-independent anisotropy the resultant fragments exhibit strongly speed-dependent anisotropy. In addition, the $\beta_4(v)$ terms are significant and the sign of these terms can be used as a robust measure for the signs of the anisotropy parameters for the two individual steps. If the photodissociation steps both have positive anisotropy then the resultant products anisotropy is more sharply peaked than $\cos^2\theta$, (*i.e.* positive $\beta_4(v)$) whereas if the two photodissociation steps have opposite signs the product angular distribution will exhibit clear fourfold symmetry (*i.e.* negative $\beta_4(v)$). Finally, if either step is isotropic, then the angular distribution of the final products will be described by $\cos^2\theta$. These conclusions are most easily observed when the velocity distributions for both steps are comparable.

It should be noted that this contrasts with a process in which the parent molecule absorbs two photons sequentially prior to dissociation. Although such a process can give rise to non-zero $\beta_4(v)$, it is unlikely to produce the identical strong speed-dependence observed in the present case. Often only $\beta_2(v)$ values are reported for features which are attributed to secondary photodissociation. We suggest that including the $\beta_4(v)$ term in fits to the fragment angular distributions could provide important constraints on such analysis.

A.2. Secondary photodissociation in ClONO₂

In order to fit the $Cl(^{2}P_{3/2})$ fragment speed and angular distribution arising from the combination of channels 2 and 4, each photo-

Fig. A2. The top shows the resultant product speed distributions for first step anisotropy parameters of -1, 0, and 2 (dashed, dotted, and solid lines, respectively) given the initial speed distribution described in the text. The lower panels show the resultant $\beta_2(v)$ and $\beta_4(v)$ values from the simulations.

dissociation steps, we first perform Monte-Carlo sampling over the initial center-of-mass speed (v_1) of the ClO fragment using the following probability distribution [35],

$$P(v_1) = \left(\frac{v_1}{v_{\max}}\right)^a \left(1 - \frac{v_1}{v_{\max}}\right)^b,\tag{A.2}$$

where v_{max} is the maximum speed for the ClO fragment and *a* and *b* are adjustable parameters. Monte-Carlo sampling then selects the polar angle (θ_1) with respect to the polarization axis of the dissociation laser using a *speed-independent* probability distribution,

$$P(\theta_1) = 1 + \beta \times \left(\frac{3\cos^2\theta_1 - 1}{2}\right). \tag{A.3}$$

Since the primary photodissociation is the result of one-photon absorption using linearly polarized light, there is azimuthal symmetry about the polarization axis. The joint probability distribution associated with the velocity of the ClO fragment is then given by,

$$P(\overline{\nu_1}) = P(\nu_1) \times P(\theta_1). \tag{A.4}$$

The energy partitioned to the ClO fragment and available following the secondary photodissociation step is determined by energy conservation,

$$E_{avail} = hv - D_o^o(ClO - NO_2) = \frac{1}{2}\mu g^2 + E_{int}(ClO) + E_{int}(NO_2), \quad (A.5)$$

where hv is the photon energy, $D_o^0(\text{CIO}-\text{NO}_2)$ is the bond dissociation energy of CIONO_2 (Refs. [36,37]) and $E_{\text{int}}(\text{CIO})$ and $E_{\text{int}}(\text{NO}_2)$ are the internal energies of the CIO and NO₂ fragments, respectively. The fitting requires an additional parameter to reflect the fraction of the internal energy partitioned to the CIO fragment, $E_{\text{int}}(\text{CIO})$ as this ultimately defines the available energy for the second step. Such an approximate treatment is severe but certainly not unreasonable. The translational energy of the resultant $\text{Cl}(^2P_{3/2})$ atom upon photodissociation of the CIO will include this internal energy,

$$E_T = hv + E_{\text{int}}(\text{ClO}) - D_o^o(\text{Cl-O}) - E_{\text{SO}}(\text{O}), \qquad (A.6)$$

where $D_o^o(\text{Cl}-\text{O})$ is the bond dissociation energy of ClO (38,050 cm⁻¹) [38], and E_{SO} (*O*) is electronic energy of the O(¹D₂) (18,650 cm⁻¹). The secondary angular distribution is given by the same functional form as (A.3), using an anisotropy parameter of β = 1.8 determined previously. The probability of the Cl(²P_{3/2}) fragments having particular speed (v_2) is evaluated according to (A.5) and (A.6).

The vector sum of the two photodissociation steps provides a resultant vector representing the $Cl(^{2}P_{3/2})$ atom velocity with respect to the axis of linear polarization of the dissociation laser with a probability equal to the product of the individual probabilities. Integration over the azimuthal angle allows one to derive the speed-dependent angular distribution, $P(\theta)$, while integration over both angular coordinates results in the final center-of-mass speed distribution, P(v). The resulting final spatial anisotropy can be described by Eq. (A.4). There is no a priori reason to believe that the speed-dependent anisotropy resulting from a secondary photodissociation process should be described by a second Legendre polynomial (such as given by (A.3)). In fact, for secondary photodissociation the final angular distribution requires inclusion of a $\cos^4\theta$ term, where the sign of the coefficient is a strong function of the β values for the two individual steps. Fitting of the simulated speed-dependent angular distributions provides values for $\beta_2(v)$ and $\beta_4(v)$ that can be directly compared to experimental values.

The forward-convolution fitting scheme for ClONO₂ ultimately involves five adjustable parameters in the total fit of the ground state $Cl(^{2}P_{3/2})$ experimental data. Our initial estimates for the parameters *a*, *b*, and β were based on the earlier PTS experiments



of Nelson and co-workers at 248 nm. [13] As a first approximation of the fraction of internal energy partitioned into the ClO fragment for channel 2 we consider two limiting models; a prior, or statistical, model and an impulsive model. The prior model [39] yielded a value of 0.21 while the soft-fragment impulsive model yielded 0.41. [40] We found that the best-fit to the data was obtained using a value between these two cases.

To determine the best-fit to the data, the program was run with a minimum sampling of 1×10^6 points. A χ^2 minimization of the weighting of the secondary and primary $Cl(^2P_{3/2})$ speed distributions provided the branching ratio between channels 1 and 2. Once an adequate fit of the speed distribution was achieved the derived speed-dependent anisotropy was compared to the experimental measurement and the optimization repeated.

A.3. Spontaneous secondary dissociation in ClONO₂

Fig. A3 shows the vector addition involved in evaluating determining the resultant $O({}^{3}P_{2})$ atom speed and angular distributions. Arising from a two-step dissociation. The relevant quantities have been defined above. In the case of ClONO₂, measurement of the $Cl({}^{2}P_{1/2})$ speed distribution yields both the speed distribution for the momentum matched NO₃ fragment, and by energy conservation the internal energy of the NO₃ fragment,

$$E_{avail} = hv - D_o^0(\text{Cl-ONO}_2) = \frac{1}{2}\mu g^2 + E_{\text{int}}(\text{Cl}) + E_{\text{int}}(\text{NO}_3), \qquad (A.7)$$

where hv is the photon energy, $D_o^o(\text{CI-ONO}_2)$ is the bond dissociation energy of CIONO₂, and $E_{int}(\text{CI})$ and $E_{int}(\text{NO}_3)$ are the internal energies of the Cl and NO₃ fragments, respectively. Those NO₃ fragments with energy in excess of the NO₂ + O threshold will undergo a secondary dissociation. The energy available to the oxygen atoms fragments is given by conservation of energy,

$$E_{avail} = E_{int}(NO_3) - D_o^o(NO_2 - O) = \frac{1}{2}\mu g^2 + E_{int}(O) + E_{int}(NO_2),$$
(A.8)

where $D_o^0(NO_2-O)$ is the bond dissociation energy of NO₃ (Ref. [41]) and $E_{int}(j)$ is the internal energy of the *j*th species. Monte-Carlo sampling is used to select the secondary speed of the oxygen atoms, weighted according to the SSE model, appropriate for statistical dissociation [42]. The polar angle (θ_2) is sampled using the probability

Fig. A3. Coordinate system for the forward-convolution fitting of spontaneous dissociation. Parameters for Cl + NO₃ dissociation (v_{1,θ_1}) are based on the previous measurement. $P(v,\theta)$ describes the laboratory speed and angular distributions for O(³P₂) arising from spontaneous dissociation of NO₃.

distribution given in (A.4). The β parameter in this case is an adjustable parameter in the fit to the resultant oxygen atom data. It is important to note that the angular distribution is defined relative to primary step relative velocity vector. In the case of a long-lived intermediate, relative to its rotational period, there is forward– backward symmetry and β = 2.0 would represent the oblate top limit and β = -1 the prolate top limit. The secondary dissociation has azimuthal symmetry about the primary velocity vector.

A vector sum of the two dissociation steps provides a resultant vector representing the $O({}^{3}P_{2})$ atom velocity with respect to the axis of linear polarization of the dissociation laser with a probability equal to the joint probabilities of the individual vectors. Vector addition of the two vectors ($\overline{v_{1}}$ and $\overline{v_{2}}$) was achieved by a coordinate frame transformation via rotation using Euler angles. Once the speed and angular distributions are obtained for the resultant oxygen atom, a translational energy distribution, $P(E_{T})$, can be determined.

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