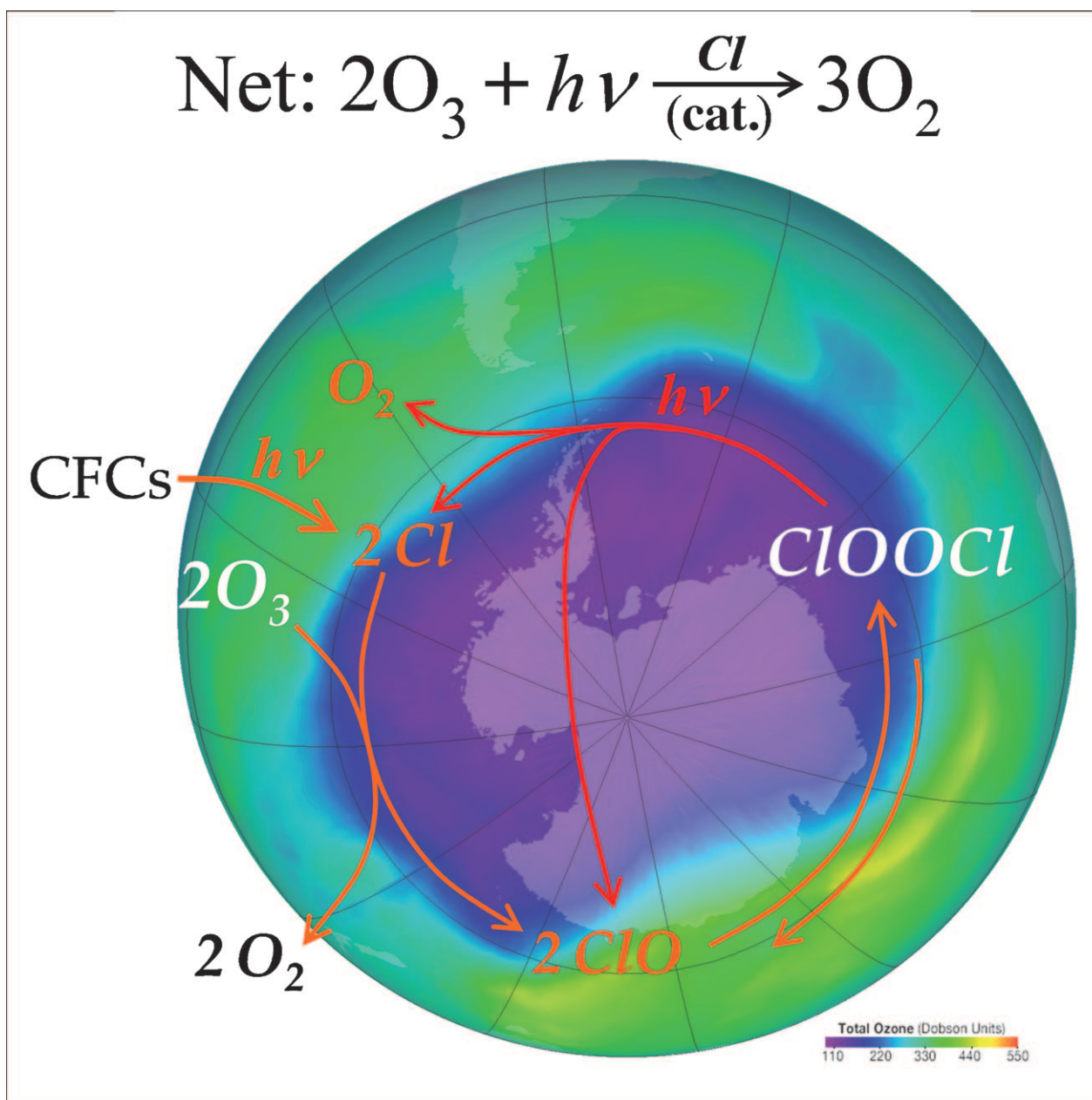# FOCUS REVIEWS

UV Photolysis of ClOOCl and the Ozone Hole

Jim J. Lin,[a, b, c] **Andrew F Chen,**[a] **and Yuan T. Lee**[a, b]

On the occasion of the 150th anniversary of the Department of Chemistry, The University of Tokyo

Abstract: The photochemistry of the ClO dimer (ClOOCl) plays a central role in the catalytic destruction of polar stratospheric ozone. In spite of decades of intense investigations, some of its laboratory photochemical data had not reached the desired accuracy to allow a reliable simulation of the stratospheric ozone loss until recently. Inevitable impurities in ClOOCl samples have obstructed conventional measurements. In particular, an absorption measurement of ClOOCl in 2007, which gave much lower cross sections than previous studies, implied that the formation of the ozone hole cannot be explained with current chemical models. Scientists have wondered whether the model is insufficient or the data is erroneous. Efforts aiming to resolve this controversy are reviewed in this paper, which emphasizes newly developed experiments to determine two critical photochemical properties of ClOOCl—its absorption cross section and product branching ratio—including the first reported product branching ratio at 351.8 nm photolysis.

Keywords: absorption cross section · atmospheric chemistry · ozone · photochemistry · photolysis

1. Introduction

Since the discovery of the ozone hole in 1985,[1] the scientific community has made great efforts to understand the underlying mechanism and to find possible ways to prevent it. Although the emission of related pollutants has decreased very significantly due to the heavy regulation of the Montreal Protocol and its amendments, there is still pronounced ozone depletion because the atmospheric lifetimes of the ozone-depleting substances such as CFCs (chlorofluorocarbons) and Halons (bromine-containing haloalkanes) are long, ranging from tens of years to a century. With satellite data,[2] we can find the variation of the ozone concentration on a daily basis. Figure 1 shows the largest ozone hole ever observed, in which the total ozone mass deficit was more than 40 million tons.[2] The thinning of the polar ozone layer is most apparent in the springtime, which is when the light begins to appear after the long polar night. It is clear that solar radiation is crucial for the chemistry of the ozone hole. Nowadays it is known that the chemical processes responsible for the polar ozone loss are primarily due to the following two catalytic cycles that involve chlorine and bromine oxides:[3]
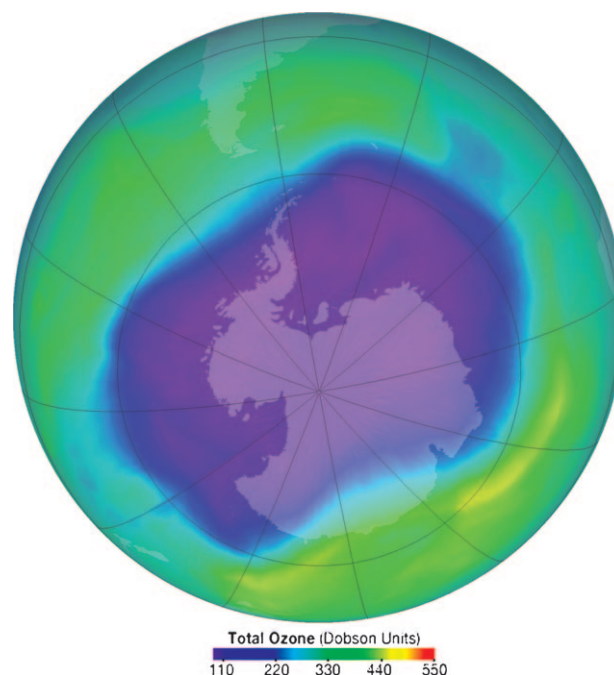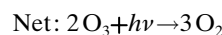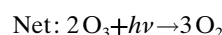
1) ClO dimer cycle [Eqs. (1)–(3)]:

$$ClO + ClO + M \rightarrow ClOOCl + M \tag{1}$$

$$ClOOCl + h\nu \rightarrow 2\,Cl + O_2 \tag{2}$$

Figure 1. The largest ozone hole ever observed occurred on 24 September 2006. Image from NASA Ozone Hole Watch.[2]

$$2\,[Cl + O_3 \rightarrow ClO + O_2] \tag{3}$$

Net: $2\,O_3 + h\nu \rightarrow 3\,O_2$

2) ClO–BrO cycle [Eqs. (4)–(6)]:

$$Br + O_3 \rightarrow BrO + O_2 \tag{4}$$

$$Cl + O_3 \rightarrow ClO + O_2 \tag{5}$$

$$BrO + ClO + h\nu \rightarrow Br + Cl + O_2 \tag{6}$$

Net: $2\,O_3 + h\nu \rightarrow 3\,O_2$

In the cold polar stratosphere, two ClO radicals tend to form a dimer (ClOOCl); after absorbing sunlight, the ClO dimer decomposes and releases Cl atoms that quickly react

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with O_3 to generate ClO radicals again, resulting in a catalytic cycle that may destroy thousands times more O_3 molecules during the Antarctic springtime. In current models,[4] the ClO dimer cycle accounts for the major chemical loss of the polar stratospheric ozone. The bottleneck of this cycle is the Cl-atom production rate J_{Cl} in the photolysis of ClOOCl, which depends on the following three wavelength (λ)-dependent factors: 1) the incoming solar flux $I(\lambda)$, 2) the absorption cross section of ClOOCl $\sigma(\lambda)$, and 3) the quantum yield of Cl-atom production $\phi_{Cl}(\lambda)$ as shown in Equation (7):

$$J_{Cl} = \int I(\lambda)\,\sigma(\lambda)\,\phi_{Cl}(\lambda)\,d\lambda \tag{7}$$

The efficiency of the ClO dimer cycle also affects the ClO–BrO cycle through Equation (6). A very recent model calculation[4b] indicates that the dominant source of model uncertainty in polar ozone loss is uncertainty in the ClOOCl photolysis reaction.

The ClO dimer cycle was proposed by Molina and Molina[5] in 1987 to play a role in the Antarctic stratosphere in which the total ozone content in the spring had fallen remarkably. However, their reported UV absorption spectrum of ClOOCl is significantly different in shape from other studies[6] and possibly affected by the presence of Cl_2O_3 and other impurities. In 1988, Cox and Hayman[6a] reported an absorption spectrum of ClOOCl of higher quality. The UV absorption spectrum of ClOOCl shows a strong and broad feature with a maximum at approximately 245 nm and a tail extending to beyond 300 nm (Figure 2). The absorption of ozone strongly modifies the spectrum of solar radiation reaching the stratosphere. Figure 2 shows the absorption cross section of ozone[7] and the spectra of solar flux[8] at conditions that may be relevant to the Antarctic stratosphere. Because the incoming sunlight at $\lambda < 300$ nm is extremely weak, it is the weak tail of the ClOOCl absorption spectrum at $\lambda > 300$ nm that is responsible for its photodecomposition in the atmosphere. Due to the limited signal-to-noise ratio in the tail region, the Cox and Hayman 1988 spectrum[6a] (see Figure 2) is, however, not good enough to precisely estimate the photolysis rate of ClOOCl, especially at $\lambda > 320$ nm.

Figure 2. Absorption cross sections of O_3 at 218 K, Cl_2O and Cl_2 at 298 K,[7] and ClOOCl at 265 K[6a] and examples of actinic solar flux calculated using the online NCAR TUV calculator[8] for a solar zenith angle of 86° at an altitude of 20 km. (The solar zenith angle is the angle between the local zenith (vertical line) and the line of sight to the sun. D.U. is the Dobson Unit.)

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Abstract in Chinese:

過氧化氯(ClOOCl)之光化學，在極區臭氧層的催化性破壞中扮演主角。數十年來，雖已有許多研究，此分子之光化學數據的準確度，直到一兩年前，仍不足以進行可靠的臭氧大氣化學模擬。樣品中無法避免的雜質，嚴重干擾著傳統的測量。尤其在 2007 年，一項吸收光譜的實驗數據，指出臭氧洞的形成無法用現有化學模型來解釋，引發重大爭論。科學家亟需進一步的證據，來揭露真相。在此文中，我們回顧想要解開此爭論的研究，著重於此分子兩項關鍵的光化學性質 — 吸收截面積與產物量子產率；同時首次發表，在 351.8 奈米激發波長，過氧化氯光分解的產物量子產率。
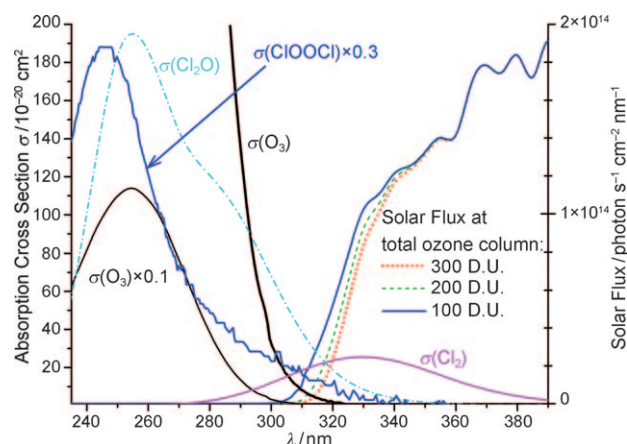
2. Issue of the Absorption Cross Section of ClOOCl

There are a few UV absorption spectra of ClOOCl that were reported in the 1990s.[6c–e] These and earlier[6a,b] spectra are consistent in the peak region around 245 nm, but different from each other in the long-wavelength tail by a factor of approximately 2 at 350 nm (Figure 3). In 1990, Burkhold-
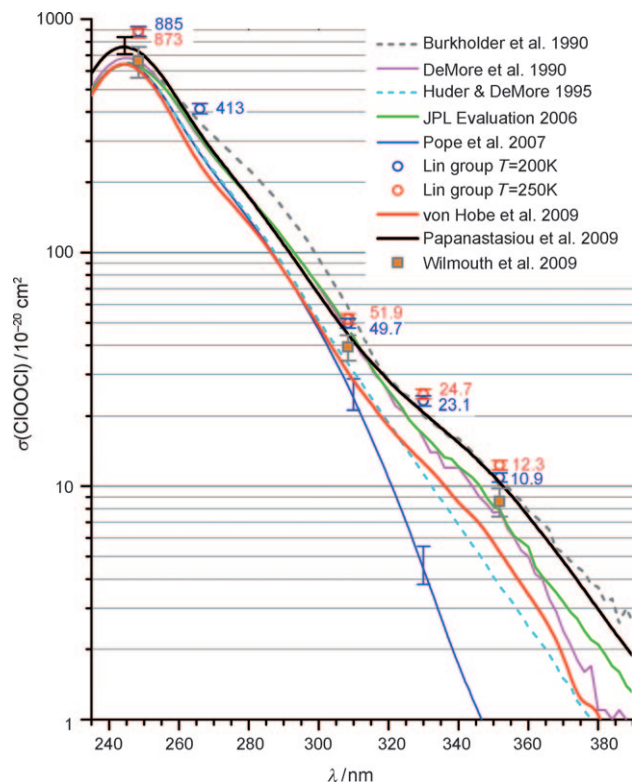

Figure 3. Comparison of a few cross-section measurements of ClOOCl, including the JPL 2006 evaluation.[7] The sample temperatures are 205–250 K for Burkholder et al. (1990),[6c] 195–217 K for DeMore and Tschuikow-Roux (1990),[6d] 195 K for Huder and DeMore (1995),[6e] 193 K for Pope et al. (2007),[11] 4–6 K (neon matrix) for von Hobe et al. (2009),[14] 200 K for Papanastasiou et al. (2009),[16] 240 K for Wilmouth et al. (2009).[15] Due to a more precise determination of the laser wavelengths, some of our cross sections (Lin group)[17–19] are slightly revised and the values are noted along with the data points. The reported error bars are shown only selectively to avoid crowding the figure.

er et al.[6c] used three independent ClO source reactions, $Cl+O_3 \rightarrow ClO+O_2$, $Cl+Cl_2O \rightarrow ClO+Cl_2$, and $Cl+OClO \rightarrow ClO+ClO$, to generate ClOOCl in a flow tube and measured its absorption spectrum. Also in 1990, DeMore and Tschuikow-Roux[6d] used a static photolysis cell containing Cl_2/Cl_2O or Cl_2/O_3 mixtures or pure Cl_2O to generate ClOOCl and recorded its spectrum. In 1995, Huder and DeMore[6e] revisited the ClOOCl absorption spectrum with a similar static photolysis cell. Due to the small absorbance in the long wavelength tail, the authors[6e] considered a logarithmic extrapolation is a better estimate of the cross sections than

the actual data for $\lambda > 310$ nm. This single set of data was chosen by the IUPAC Subcommittee for Gas Kinetic Data Evaluation[9] to represent the ClOOCl absorption cross section. On the other hand, the Jet Propulsion Laboratory (JPL) 2006 evaluation[7] is mainly based on an average of a few selected ClOOCl spectra.[6a–d]

There is a common concern in these earlier works:[6] a precursor (mostly Cl_2O) was used to synthesize ClOOCl and the spectrum of ClOOCl was measured in the presence of the precursor along with byproducts, which are inevitable in ClOOCl samples. The reported ClOOCl spectrum was obtained by subtracting the precursor contribution. As Huder and DeMore[6e] mentioned, "The basic problem is to determine how much of the Cl_2O spectrum to subtract." The subtraction process relies on the concentrations of ClOOCl, the precursor, and byproducts, which were estimated by using the observed spectral evolution. Unfortunately, the spectra of the involved species like ClOOCl, Cl_2O, O_3, and Cl_2 (see Figure 2) are all very broad and nearly featureless such that the spectral change is not a sensitive tool to determine the concentrations. Different approaches have been used, but none of them can be proven to be free from error. Basically, the situation is that a measurement of the ClOOCl spectrum depends on the concentrations of the involved species, but the concentration estimation also depends on the ClOOCl spectrum. The relative accuracy of the ClOOCl cross section becomes worse at $\lambda > 300$ nm where the ClOOCl absorbance is diminishingly small.

More difficulties arise from the fact that the chemistry of ClOOCl synthesis is not simple and side reactions introduce further complications. For example, one of the side reactions is shown in Equation (8):

$$Cl+ClOOCl \rightarrow Cl_2+ClOO \rightarrow Cl_2+O_2+Cl \tag{8}$$
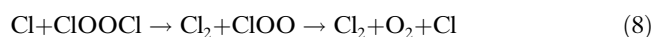
This process is very fast[6a] and catalytic (the Cl atom is regenerated). Moreover, little is known about the involved surface reactions.[6f]

Based on in situ observations of ClO and ClOOCl[10] and model calculations, a 2006 report[3] of the World Meteorological Organization (WMO), United Nations, noted, "There are indications that the chlorine monoxide (ClO) dimer cycle may be a more efficient process for polar ozone loss than previously thought. Uncertainties in the laboratory absorption cross section of the chlorine monoxide dimer (ClOOCl) are large."

Obviously, ClOOCl is a difficult molecule to handle in a laboratory. It is difficult to prepare ClOOCl in a pure form; it is also difficult to quantify side reactions and to know the concentrations of all absorbing species. As a result, the confidence in the ClOOCl absorption cross section is not enough, especially in the weak tail region above 300 nm.

In 2007, Pope et al.[11] utilized a new method of sample preparation and measured the spectrum of ClOOCl. Different from previous works,[6] Pope et al.[11] condensed gaseous ClOOCl to a solid form at about 150 K, then pumped out the precursor gases, let solid ClOOCl sublimate, and mea-

sured its spectrum. This synthesis method offers a ClOOCl sample of a high absorbance (high concentration) and low impurities. However, there was still significant absorption due to Cl_2, either from the co-condensed reactant or from decomposition of ClOOCl. To remove the contribution of Cl_2, which varied in concentration during the sublimation process, Pope et al.[11] used a least-squares fitting procedure that assumed two Gaussian-like expressions representing the ClOOCl spectrum. To everyone's surprise, the reported cross section of ClOOCl (see Figure 3) is much smaller in the tail region of $\lambda > 300$ nm, more than 10 times smaller than the JPL 2006 evaluated value[7] at 350 nm. This result[11] suggests a much slower ClOOCl photolysis rate than previously thought. If so, the occurrence of the ozone hole cannot be explained with current models, which indicates that either there are unknown mechanisms for the ozone hole,[12] or the new data of Pope et al.[11] are erroneous. Scientists started to wonder and investigate whether this was the case.[13]

A few groups[14–19] revisited the absorption spectrum of ClOOCl as the new results of Pope et al.[11] cast doubt on the current understanding of the ozone hole formation. Von Hobe et al.[14] followed the synthesis method of Pope et al. (Method 1 of Ref. [11]) but managed to prepare a pure ClOOCl sample isolated in a neon matrix, the impurity of which was checked with IR and Raman spectroscopy. More importantly, the authors confirmed that ClOOCl is the only isomer formed from the dimerization of ClO. However, light scattering of the solid sample limited the accuracy of their ClOOCl spectrum in the important tail region. In addition, the temperature of the neon matrix was about 4–6 K, much lower than those in the stratosphere. At that time, the temperature effect of the cross section was not yet known. The results of von Hobe et al.[14] suggest that the ClOOCl cross sections at $\lambda > 300$ nm are unlikely to be as small as those reported by Pope et al.[11] Von Hobe et al.[14] also performed an analysis to fit previously reported ClOOCl spectra[6a,c,d,f] with contributions of their matrix spectrum and possible impurities like Cl_2, Cl_2O, and Cl_2O_3. Because the matrix spectrum is not a perfect one and the temperature is very different, this fitting may not provide quantitative information. Nonetheless, it does show that impurities and "the amount to subtract" play a role in previous measurements.[6,11] To make precise measurements of the ClOOCl absorption cross section, free from the complication caused by impurities, a new method needs to be developed.

To avoid the impurity problem of ClOOCl, our group[17–19] has developed a method to circumvent this problem. Figure 4 illustrates two concepts of measuring an absorption cross section. In conventional spectroscopic measurements, the number of molecules is usually much larger than the number of photons. Thus, the density of the molecules is almost unaffected by the photon beam. In addition to the photon beam intensities I_0 and I (before and after the absorption cell, respectively), the knowledge of the number density n and path length l are required to obtain the absorption cross section σ [Eq. (9)]:
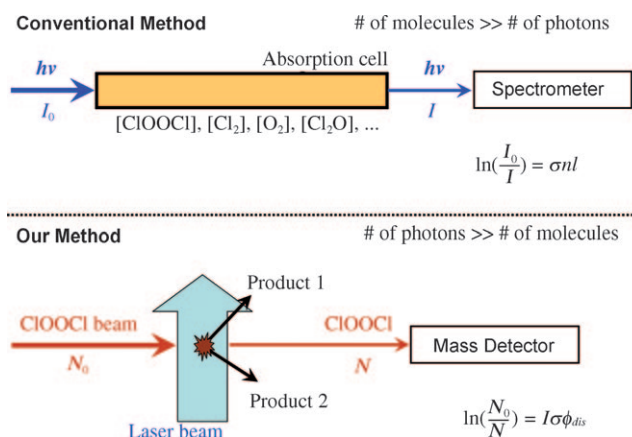

Figure 4. Schematic of two different concepts to measure an absorption cross section.

$$\ln\left(\frac{I_0}{I}\right) = n\sigma l \qquad (9)$$

As a mature technology, the conventional method has a few advantages. For example, measurements over a broad range of wavelength can be done at once with a diode array detector. But it does not provide any direct information about the identities of the molecules contained in the sample, which becomes an issue when measuring an unstable or impure sample.

As illustrated in Figure 4, we made a molecular beam containing ClOOCl and only measured the number of ClOOCl molecules with a mass spectrometric detector before and after laser irradiation. After absorbing a photon, ClOOCl will dissociate in a time scale much shorter than the transient time to the detector (≈ 1 ms); thus, the number of ClOOCl molecules reaching the detector is reduced. The probability of the photodissociation is proportional to the absorption cross section and the laser fluence. Under conditions in which the number of photons greatly exceeds the number of molecules, we may write down the related kinetic equations as follows [Eqs. (10a) and (10b)]:

$$dN = -N\sigma\phi_{dis}dI \qquad (10a)$$

$$\ln\left(\frac{N_0}{N}\right) = I\sigma\phi_{dis} \qquad (10b)$$

in which σ is the absorption cross section, ϕ_{dis} is the dissociation quantum yield, I is the laser fluence in number of photons per unit area, N_0 is the number of molecules before laser irradiation, and N is the number of molecules after laser irradiation. For a group of molecules that dissociate very fast (≤ 1 ps) after absorbing a photon, other slower stabilization processes like emitting another photon (which requires more than 1 ns) cannot compete with dissociation at all, leading to 100% dissociation ($\phi_{dis}=1$). This group of fast dissociating molecules includes ClOOCl and our reference molecules like O_3, Cl_2, and Cl_2O. As the upper limit of ϕ_{dis} is 1, the error bar of ϕ_{dis} is negligible in our studied cases.

To have a precise measurement, we compared the laser depletion signal of ClOOCl with that of a reference molecule of which the absorption cross section and dissociation quantum yield are well known. In this way, we can quantify the photolysis cross section $\sigma\phi_{dis}$ of ClOOCl with the following equation [Eq. (10c)]:[17–19]

$$\frac{[\sigma\phi_{dis}]_{ClOOCl}}{[\sigma\phi_{dis}]_{ref}} = \frac{I_{ref}}{I_{ClOOCl}} \frac{\ln(N_0/N)_{ClOOCl}}{\ln(N_0/N)_{ref}} \qquad (10c)$$

In Equation (10c), we only need relative values, which can be measured with high precision. This approach has the following advantages: 1) the knowledge of absolute concentration is not needed; 2) as far as the impurities are at different detection masses, the interference from impurities can be eliminated; 3) with a powerful laser that causes appreciable depletion ($\approx 20\%$) of ClOOCl, the sensitivity of the measurement does not depend on the magnitude of the cross section. That is, the precision of measuring a cross section on the order of 10^{-19} cm$^{2[17]}$ is not worse than that on the order of 10^{-17} cm^2.[18]

When there are more than one reference molecule available, it offers an opportunity to examine not only the precision but also the accuracy of this method. As shown in the cross section measurements of ClOOCl at 266[18] and 308.4 nm,[17] essentially the same results have been obtained with two reference molecules, of which the cross sections are quite different, which indicates that this method is reliable. A limitation of this method is the need of an intense laser beam. This hindrance has been partly overcome by utilizing a multipass laser beam to enhance the effective laser fluence.[19]

In the "atmospheric window" above 300 nm where most incoming solar radiation occurs, our results at 308.4, 330, and 351.8 nm[17,19] indicate that the ClOOCl absorption cross sections are in fact slightly larger than the JPL 2006 recommended values.[7] The resulting higher estimate of the photolysis rate of ClOOCl also agrees better with the field measurements of the [ClOOCl]/[ClO]^2 ratio[10] and the amounts of ozone loss.[3,4] Furthermore, it seems that Pope et al.[11] overcorrected the absorbance of the Cl$_2$ impurity in their measurements of the ClOOCl cross sections at wavelengths where Cl$_2$ absorbs, which resulted in too small cross section values for ClOOCl at $\lambda > 300$ nm.

The precision of our method allows us to observe the temperature effect of the ClOOCl absorption cross section. There is a limit of the temperature range in which ClOOCl can be investigated in a laboratory: at $T < 160$ K, the vapor pressure of ClOOCl is not high enough for most experiments; on the other hand, the thermal decomposition of ClOOCl becomes significant at $T > 260$ K. Figure 5 shows the relative absorption cross section of ClOOCl as a function of temperature at four wavelengths. It is intriguing that the temperature effect has a strong dependence on wavelength. It is slightly negative at 248.4 nm[18] and becomes slightly positive at 308.4 nm,[17] then it turns much more pro-
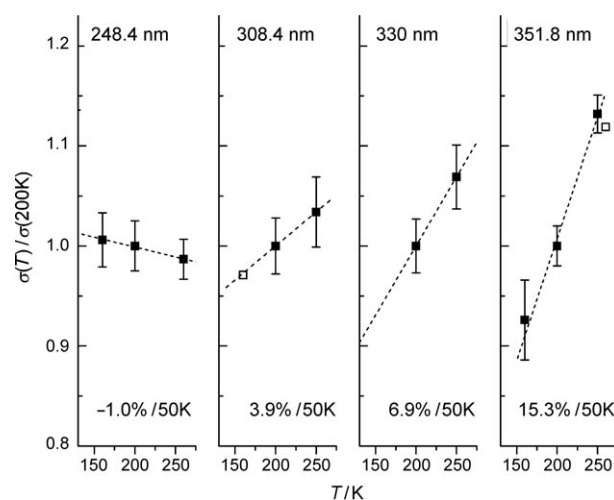

Figure 5. Relative absorption cross section of ClOOCl as a function of temperature.

nounced at longer wavelengths of 330[19] and 351.8 nm[17] where the atmospheric photolysis rate of ClOOCl is much more significant. These results would provide a rigorous test for theories. If a theory can reproduce the temperature effect of the cross section at these four wavelengths from 248 to 352 nm, it may be used to predict the temperature effect at longer wavelengths.

Although previous measurements[6] are consistent with each other near the absorption peak at about 245 nm, our data at 248.4 and 266 nm[18] indicate the peak cross section of ClOOCl had been underestimated by about 25% (also see Figure 3). This underestimation of cross section might be due to overestimation of the ClOOCl concentration in those bulk experiments. Because it is difficult to quantify the extent of side reactions or wall loss (i.e. loss of ClOOCl on reactor walls), overestimation of the ClOOCl concentration is quite likely. Some studies[6e,f,11,14] only measured the shape of the ClOOCl spectrum (not on an absolute scale). If we renormalize those relative data to our cross section value at 248.4 nm, the overall consistency will become better.[18]

Papanastasiou et al.[16] measured a series of absorption spectra of a static cell containing Cl$_2$O or Cl$_2$O/Cl$_2$ precursors along the course of stepwise pulsed laser photolysis. The authors utilized spectral isosbestic points combined with reaction stoichiometry and chlorine mass balance in the analysis and reported a spectrum of ClOOCl. However, upon close examination, the isosbestic point observed near 313 nm is not strictly constant but shifts gradually toward longer wavelengths during the course of an experiment. The authors mentioned "the shift toward longer wavelength is consistent with the breakdown of the reaction stoichiometry due to the loss of Cl$_2$O$_2$ via secondary chemistry, photolysis, and reaction with Cl atoms. The breakdown in stoichiometry is systematic and predictable …". Ideally, one can obtain a "cleaner" ClOOCl spectrum from the data at very early photolysis times before significant secondary reactions take place; practically, the absorbance change due to ClOOCl is

quite small at early photolysis times. Although the loss of ClOOCl through secondary processes is predictable, the precise amount of the loss still depends on a few parameters. Overall, with respect to our high precision data,[17–19] the ClOOCl spectrum of Papanastasiou et al.[16] is more consistent than previous ones[6] (see Figure 3).

In addition to experimental investigations, there are a number of theoretical studies[20] on the ground and excited states of ClOOCl and its absorption spectrum. Quite a few excited states, including singlet and triplet ones,[20e] are involved in the absorption from 200 to 400 nm. Due to the complexity of this molecule, however, it is difficult to quantitatively reproduce the experimental absorption spectrum, especially in the long wavelength region. A very recent work by Ončák et al.[20f] indicates: 1) the excitation characteristics of ClOOCl are sensitive to molecular geometries; 2) single-reference methods tend to overestimate the absorption cross section and lead to a blueshift in the absorption maximum. However, the long wavelength tail region is still difficult for theory. The first conclusion of Ončák et al.[20f] indicates that the absorption is sensitive to molecular vibrations, thereby providing a hint to the above-mentioned temperature effect of the ClOOCl absorption cross section.

With a closer examination of the available data of the ClOOCl absorption cross section, the following features can be observed: 1) The disagreements among different measurements[6] are already large even before the work of Pope et al.[11] 2) The Burkholder 1990 spectrum[6c] has an extra bump at about 290 nm, which is probably caused by impurities such as Cl_2O and Cl_2O_3.[14] 3) The shapes of the ClOOCl spectra of Pope et al.,[11] von Hobe et al.,[14] and Papanastasiou et al.[16] are very similar for $\lambda < 300$ nm. Because Pope et al.[11] only have Cl_2 as a contaminant and the cross section of Cl_2 is relatively minor at $\lambda < 290$ nm ($\sigma(Cl_2)^{290nm} \cong 6 \times 10^{-20}$ cm^2),[7] the shape of their spectrum[11] should be fine at $\lambda < 290$ nm. The data of Pope et al.[11] and von Hobe et al.[14] are relative measurements (only the shape, not the absolute magnitude); if we renormalize their relative data to our new cross section at 248.4 nm,[18] the overall consistency would be improved significantly. The renormalized spectrum of von Hobe et al.[14] has a small dip at about 267 nm and is lower than that of Papanastasiou et al.[16] at $\lambda > 300$ nm; these differences may be explained by the temperature effect. 4) The spectrum of Papanastasiou et al.[16] covers a broad wavelength range and is consistent with our high precision measurements[17–19] within the experimental error bars.

Combining our precise measurements[17–19] at a few selected wavelengths and recent continuous spectra,[14,16] one may better estimate the photolysis rate of ClOOCl. But the $2Cl+O_2$ channel [Eq. (2)] is not necessarily the only product channel in the UV photolysis of ClOOCl. The yield of another possible ClO+ClO channel will affect the photochemistry. We will discuss this issue in Section 4.

3. Isomers of Cl_2O_2

There are three stable low-energy isomers of Cl_2O_2: ClOOCl, ClOClO, and ClClO$_2$.[21–23] For quite a long time, ClOOCl had been considered to be the most stable isomer, until recently Matus et al.[23] performed high-level coupled cluster computations [CCSD(T) extrapolated to the complete basis set limit (CBS)]. The results of Matus et al.[23] indicate that ClClO$_2$ is the most stable isomer and ClOOCl is less stable by 3.1 kcal mol^{-1}. However, experimental studies[6d,14,24] have shown that ClOOCl is the only product formed through dimerization of ClO. Why is the most stable isomer not formed? We believe the answer lies in the chemical kinetics, which is discussed below. Zhu and Lin[25] have studied this system theoretically at the G2M (modified Gaussian-2) level. A few transition states (TS) connecting various isomers have been located with the B3LYP hybrid density functional method. Hong et al.[26] revisited this system but using a more sophisticated hybrid density functional method, BMK (Boese–Martin for kinetics),[27] for the geometry optimization. Although the widely used B3LYP functional is excellent for geometry optimization of stable structures, the BMK functional is believed to perform better for transition states. The best available energetics of singlet Cl_2O_2 isomers is shown in Figure 6.
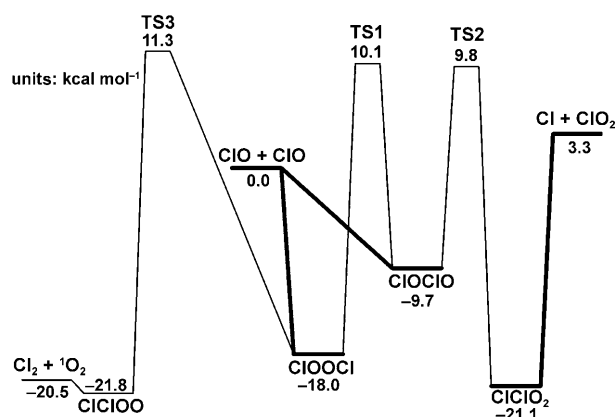

Figure 6. Schematic energy diagram showing the relative energies and transition states for relevant isomers of the singlet Cl_2O_2 system. The relative energies of ClO+ClO, ClOOCl, ClOClO, ClClO$_2$, and Cl+ClO$_2$ (thick lines) are from Matus et al. (theory level: CCSD(T)/CBS// CCSD(T)/aug-cc-pV(T+d)Z).[23] The other energetics are from Hong et al.[26] (theory level: CCSD(T)/aug-cc-pV(Q+d)Z//BMK/aug-cc-pV-(T+d)Z) and referenced to the energy of ClO+ClO. Unit: kcal mol^{-1}.

The dimerization of ClO may form both the symmetric and asymmetric structures (ClOOCl and ClOClO, respectively). Because ClOOCl is more stable than ClOClO by 8.3 kcal mol^{-1},[23] the equilibrium at a moderate temperature strongly favors ClOOCl by several orders of magnitude. However, the theoretical calculation by Zhu and Lin suggests that the formation rates of both dimer structures are comparable and the asymmetric dimer accounts for about

23% of the total dimer yield at 200 K and 22% at 298 K at 100 torr N_2,[25] if the yields are governed by the formation rates. Comparable formation rates of ClOOCl and ClOClO are also in accordance with the experimental observations[21] that both forms have been detected in cryogenic matrices with IR spectroscopy, in which the low temperature environment indicates no barrier to form both ClOOCl and ClOClO.

The equilibrium constant between ClO and either one of its dimers is simply the ratio of the formation rate constant and the dissociation rate constant. Therefore, if the formation rate constants are similar for ClOOCl and ClOClO, the dissociation rate constants will be very different to account for the equilibrium concentrations among ClO, ClOOCl, and ClOClO. The thermal dissociation rates calculated by Zhu and Lin[25] indicate that ClOClO is only stable for approximately 10^{-3} s at about 200 K, whereas ClOOCl is quite stable with a lifetime longer than 10^3 s. The thermal dissociation rates are very sensitive to temperature, but the dissociation rate constant of ClOClO is always much larger than that of ClOOCl. As a result, ClOClO may be formed in the stratosphere but will not last for any significant time, which results in a negligible concentration.

ClClO$_2$ can be formed either through Cl+ClO$_2$ or through isomerization of ClOClO. The barrier (TS2 in Figure 6) of the isomerization reaction is about 9.8 kcal mol^{-1} higher than the bond dissociation energy of ClOClO.[26] At a moderate temperature, the isomerization cannot compete with the dissociation at all, thereby resulting in an extremely smaller yield for the isomerization. The G2M calculation by Zhu and Lin[25] predicted a slightly lower TS2 energy, but it is still about 6.9 kcal mol^{-1} higher than the energy of ClO+ClO. Even with the lower barrier height, ClClO$_2$ is still not easily accessible from ClOClO at the low temperatures of the stratosphere.[25] As a result, one may expect that ClClO$_2$ is formed mostly through Cl+ClO$_2$. However, ozone is much more abundant than all chlorine oxides in the stratosphere, thus, the vast majority of the Cl atoms will become ClO after reacting with O$_3$; the chance of forming ClClO$_2$ is much lower. Based on the above arguments, we conclude that ClOOCl is still the most important form among the Cl$_2$O$_2$ isomers in the stratosphere.

4. Quantum Yield of Chlorine-Atom Production

Figure 7 shows an energy diagram[28] for UV photolysis of ClOOCl. The weakest bond in the ClOOCl molecule is the ClO−OCl bond, which will dissociate first upon thermal excitation.[29] After absorbing a UV photon, Cl−O bond fission may happen to form ClOO+Cl or Cl+O$_2$+Cl. The ClOO is very weakly bound;[28c] with internal excitation it may decompose spontaneously to release the Cl atom. More importantly, if ClO−OCl bond fission occurs in the photodissociation, this process forms two ClO radicals and becomes a null cycle without destroying O$_3$ (ClOOCl+hv→2 ClO, 2 ClO+M→ClOOCl+M, net: hv→heat). The efficiency of
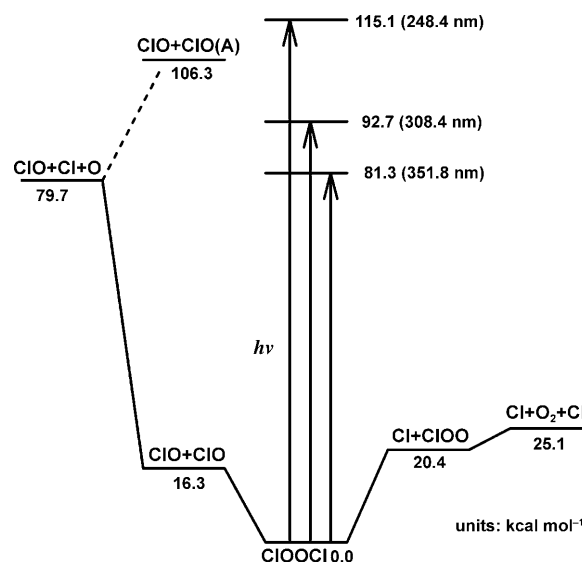

Figure 7. Energy diagram for relevant product channels of UV photolysis of ClOOCl. The numbers are relative energies[28] in kcal mol^{-1} for each channel at 0 K.

the ClO dimer cycle [Eqs. (1)–(3)] will be reduced if the ClO+ClO channel has a substantial yield.

To measure the product quantum yields of ClOOCl photolysis is a difficult problem. The primary experimental concern is still on the sample purity. Because a pure sample of ClOOCl is not available, most experiments have been performed in the presence of a precursor together with inevitable byproducts. The common precursor includes Cl$_2$O, O$_3$, and OClO, which react with Cl to form ClO; then dimerization of ClO produces ClOOCl. The OClO precursor also makes ClClO$_2$ via Cl+OClO→ClClO$_2$ (see Section 3). In addition, Cl$_2$ is an inevitable byproduct because of the very fast reaction of Cl+ClOOCl→Cl$_2$+ClOO→Cl$_2$+O$_2$+Cl.[15] The UV absorption bands of the precursors and likely byproducts heavily overlap with that of ClOOCl. The photolysis of them may produce ClO, Cl, or O$_2$, which overlap with the major photoproducts of ClOOCl. Furthermore, to have a better control of the synthesis chemistry, the precursor concentration is often in excess. Under this circumstance, there are two major difficulties in determining the product quantum yields of ClOOCl photolysis: 1) it is hard to quantify the small amount of signal due to ClOOCl in the presence of a large background originating from the precursor; 2) even if a product of ClOOCl photolysis has been quantified, to determine its quantum yield requires the concentration of ClOOCl, which is hard to know exactly (see Section 2).

Before discussing the product quantum yields, it is important to clarify that some of the literature used $\phi_{Cl}=1$ if the 2 Cl+O$_2$ channel is the only product channel. But this may cause confusion. The situation is that 2 Cl atoms are produced per absorbing photon. Therefore, $\phi_{Cl}=2$ is chosen for this situation to be consistent with Equation (7).

Early bulk studies around 1990[6a,30] indicate a high yield of Cl-atom production in ClOOCl UV photolysis. But the

uncertainty is substantial. Cox and Hayman[6a] examined this process indirectly by steady-state photolysis of Cl_2O at 254 nm in a static cell. They deduced $\phi_{Cl} = 3.7 \pm 1.5$ for ClOOCl photolysis from a kinetic model. Molina et al.[30] used atomic resonance fluorescence to measure the Cl-atom yield directly from ClOOCl photolysis at 308 nm in a flow tube and found $\phi_{Cl} = 2.06 \pm 0.24$. However, the ClOOCl concentration determination is not certain in their work. In addition, Molina et al.[30] detected no ClO product with an NO titration method ($ClO + NO \rightarrow Cl + NO_2$), but they also mentioned that adding NO complicated the experiment because NO absorbed the detection vacuum UV radiation and introduced additional chemical reactions. As a result, the authors[30] claimed that the quantum yield for primary ClO production is not larger than 0.5.

A couple of years later, Minton et al.[31] investigated the photolysis of a similar compound, $ClONO_2$, in a molecular beam experiment that provided a direct measurement of the ClO product channel. Based on the observation that the $ClO-NO_2$ bond fission and the $Cl-ONO_2$ bond fission have comparable yields, the authors[31] raised the possibility that the analogous bond-breaking processes ($ClO-OCl$ versus $Cl-OOCl$) in ClOOCl photolysis may also have comparable yields. If there is a substantial yield of ClO production in ClOOCl photolysis, it would reduce the efficiency of the ClO dimer cycle. In 1994, Jacobs et al.[21] studied the photochemistry and vibrational spectroscopy of Cl_2O_2 isomers isolated in cryogenic matrices. Three isomers, ClOClO, ClClO$_2$, and ClOOCl, have been identified with infrared spectroscopy. For the ClOOCl photolysis under matrix-isolation conditions, they reported two product channels: 1) ClOO+Cl, resulting in Cl_2+O_2 and 2) 2ClO, giving rise to ClOClO. In 1999, Moore et al.[32] studied the photodissociation of ClOOCl in a molecular beam at two excimer laser wavelengths, 248.4 and 308.4 nm. The precursor used in their experiment is Cl_2O, which produces ClO and Cl upon photolysis and interferes with the measurements. The branching ratio of Cl versus ClO was measured to be $(0.88 \pm 0.07):(0.12 \pm 0.07)$ at 248.4 nm and $(0.9 \pm 0.1):(0.1 \pm 0.1)$ at 308.4 nm. In 2004, Plenge et al.[33] reported detection of the photoproducts of ClOOCl with vacuum UV photoionization mass spectrometry. Their synthesis scheme is: $Cl + OClO \rightarrow 2ClO$; $2ClO + M \rightarrow ClOOCl + M$; some $ClClO_2$ ($\approx 17\%$) was also formed in their sample.[33] Notably Plenge et al.[33] found no evidence of ClO production (yield ≤ 0.02 at 250 nm, ≤ 0.10 at 308 nm) and assigned the photoproducts completely as Cl and O_2, a different observation from Jacobs et al.[21] and Moore et al.[32]

On the other hand, theoretical calculations[34] indicate that the ClO channel only becomes significant at high photon energies (>4.4 eV, <280 nm); the ClO yield is predicted to be zero at lower photon energies. Kaledin and Morokuma[34a] studied the photodissociation of ClOOCl with classical trajectories where the energy and gradient were computed on the fly by the state-averaged complete active space self-consistent field (CASSCF) calculations. Their results indicate that in the energy regime corresponding to

308 nm excitation, the major dissociation fragments are Cl and O_2, both in the ground state; the higher energy (248 nm) excitation yields additional fragments like ClO, O, and ClOO. Toniolo et al.[34b] performed a more thorough theoretical study. Simulations of the nonadiabatic photodissociation dynamics have been run with a direct semiclassical method. They found that dissociation to $2Cl + O_2$ is the main photoreaction, and a small amount of ClO+ClO ($\approx 5\%$) is produced only at higher excitation energies (>4.4 eV, <280 nm).

At this point, there is a controversy around the existence of the ClO product channel, which was observed in the matrix study[21] but not observed in the molecular beam study by Plenge et al.[33] Moore et al.[32] might have observed some minor yields of ClO at 308.4 nm photolysis but with a large uncertainty. Theoretical studies[34] indicate that the ClO channel only becomes significant at shorter excitation wavelengths (<280 nm) at which the atmospheric photolysis is not important. As a result, most modelers choose not to include the ClO yield in modeling the ozone chemistry.[3]

In 2009, Wilmouth et al.[15] directly measured the production of Cl atoms as well as Cl_2 impurity from ClOOCl photolysis in a flow tube. In their experiments, a ClOOCl sample was synthesized with the scheme: $Cl + O_3 \rightarrow ClO + O_2$, $2ClO + M \rightarrow ClOOCl + M$. The sample was photolyzed by an excimer laser operating at 248.4, 308.4, or 351.8 nm, and the produced Cl atoms were detected with time-resolved atomic resonance fluorescence; Cl_2, the primary contaminant, was measured directly with vacuum UV fluorescence. Their precursors (Cl_2, O_3, O_2, CF_2Cl_2) either produce no signal or have been quantified. Other impurities like ClO, OClO, and Cl_2O_3 were quite minor in relative amounts in their photochemical simulation. The time-resolved detection eliminates the effect of secondary reactions after the photolysis by extrapolating the signals to $t = 0$.

It is important to note that the data of Wilmouth et al.[15] are not only the absorption cross section but also include the Cl-atom quantum yield. Their reported cross section is in fact as follows [Eq. (11)]:

$$\sigma_{Cl} = \sigma \frac{\phi_{Cl}}{2} \tag{11}$$

The factor of $1/2$ is due to the stoichiometry that 2Cl atoms are produced per absorbed photon in Equation (2). In principle, this type of data should give the quantum yield ϕ_{Cl} of Cl-atom production if the absorption cross section (σ) is known. With precisely determined σ at 248.4, 308.4, and 351.8 nm (see Section 2), a new assessment of ϕ_{Cl} can be made.

The Cl-atom product-specific cross section (σ_{Cl}) of ClOOCl photolysis reported by Wilmouth et al.[15] was obtained by comparing the ClOOCl signal with a reference signal. The resulted value depends on the reference cross section and quantum yield; if the reference values are changed, the reported σ_{Cl} of ClOOCl should be revised. Two types of references were used by the authors:[15] one is the

absorption cross section of ClOOCl at 248.4 nm from the JPL 2006 evaluation,[7] the other is the absorption cross sections of Cl_2 at 308.4 and 351.8 nm.[7] The latter type of reference is well established as the absorption cross sections of Cl_2 have been well measured and it is of no doubt that $\phi_{Cl}(Cl_2)=2$. But, the former type of reference, $\sigma(ClOOCl)$ and ϕ_{Cl} at 248.4 nm, needs to be reconsidered.

In Table 1, we compare some relevant data of σ_{Cl} and σ from the results of Wilmouth et al. (Method B)[15] and ours (Method A)[17,18] at three excimer laser wavelengths. Both of the measurements are direct in nature, but are relative to reference molecules. The choice of the reference values may be revised as shown in Table 1 due to newer data being available or by treating the wavelengths more precisely. At all three wavelengths, the σ_{Cl} reported by Wilmouth et al.,[15]

Table 1. Comparison of selected data of the absorption cross section (σ) and Cl-atom quantum yield (ϕ_{Cl}) of ClOOCl photolysis at three wavelengths (248.4, 308.4, 351.8 nm). Cross section unit: 10^{-20} cm^2.

Method[a] (Temperature)	Measured quantity	Reference values[b]	Deduced value for ClOOCl	Inferred $\phi_{Cl}/2$
$\lambda = 248.4$ nm[c]				
A ($T=260$ K)	$\frac{(\sigma\phi_{dis})_{ClOOCl}}{(\sigma\phi_{dis})_{ref}} = 0.822$	$\sigma(O_3)=1062$ (248.4 nm) $\phi_{dis}(O_3)=1$	$\sigma = 873$	–
B1 ($T=240$ K)	$\frac{(\sigma\phi_{Cl})_{ClOOCl}}{(\sigma\phi_{Cl})_{ref}} = \frac{1}{0.0257}$	$\sigma(Cl_2)=17.60$ (308.4 nm) $\phi_{Cl}(Cl_2)=2$	$\frac{\sigma\phi_{Cl}}{2}=685$	0.78[d]
B1 ($T=240$ K)	$\frac{(\sigma\phi_{Cl})_{ClOOCl}}{(\sigma\phi_{Cl})_{ref}} = \frac{1}{0.0276}$	$\sigma(Cl_2)=17.90$ (351.8 nm) $\phi_{Cl}(Cl_2)=2$	$\frac{\sigma\phi_{Cl}}{2}=649$	0.74[d]
C ($T\leq200$ K)	$\frac{[ClO]}{[Cl]}=\frac{0.15}{1}$, $\frac{[O]}{[O_2]}=\frac{0.12}{1}$	–	–	0.87
$\lambda = 308.4$ nm				
A ($T=250$ K)	$\frac{(\sigma\phi_{dis})_{ClOOCl}}{(\sigma\phi_{dis})_{ref}} = 2.953$	$\sigma(Cl_2)=17.58$ (308.4 nm) $\phi_{Cl}(Cl_2)=2$	$\sigma = 51.9$	–
B1 ($T=240$ K)	$\frac{(\sigma\phi_{Cl})_{ClOOCl}}{(\sigma\phi_{Cl})_{ref}} = \frac{1}{0.431}$	$\sigma(Cl_2)=17.60$ (308.4 nm) $\phi_{Cl}(Cl_2)=2$	$\frac{\sigma\phi_{Cl}}{2}=40.8$	0.79[d]
B1/B2[e] ($T=240$ K)	$\frac{(\sigma\phi_{Cl})_{ClOOCl}}{(\sigma\phi_{Cl})_{ref}} = \frac{1}{17.0}$	$\sigma(ClOOCl)=873$[d] (248.4 nm)	$\frac{\sigma\phi_{Cl}^{308.4nm}}{\phi_{Cl}^{248.4nm}}=51.4$	$\phi_{Cl}^{308.4nm}=0.99\,\phi_{Cl}^{248.4nm}$
C ($T\leq200$ K)	$\left(\frac{[ClO]}{[O_2]}\right)^{308.4nm} = 1.5\left(\frac{[ClO]}{[O_2]}\right)^{248.4nm}$	–	–	0.81
$\lambda = 351.8$ nm				
A ($T=250$ K)	$\frac{(\sigma\phi_{dis})_{ClOOCl}}{(\sigma\phi_{dis})_{ref}} = 0.687$	$\sigma(Cl_2)=17.88$ (351.8 nm) $\phi_{Cl}(Cl_2)=2$	$\sigma = 12.3$	–
B1 ($T=240$ K)	$\frac{(\sigma\phi_{Cl})_{ClOOCl}}{(\sigma\phi_{Cl})_{ref}} = \frac{1}{2.08}$	$\sigma(Cl_2)=17.90$ (351.8 nm) $\phi_{Cl}(Cl_2)=2$	$\frac{\sigma\phi_{Cl}}{2}=8.61$	0.70[d]
B1/B2[e] ($T=240$ K)	$\frac{(\sigma\phi_{Cl})_{ClOOCl}}{(\sigma\phi_{Cl})_{ref}} = \frac{1}{72.2}$	$\sigma(ClOOCl)=873$[d] (248.4 nm)	$\frac{\sigma\phi_{Cl}^{351.8nm}}{\phi_{Cl}^{248.4nm}}=12.1$	$\phi_{Cl}^{351.8nm}=0.99\,\phi_{Cl}^{248.4nm}$
C[f] ($T\leq200$ K)	$\left(\frac{[ClO]}{[O_2]}\right)^{351.8nm} = 0.80\left(\frac{[ClO]}{[O_2]}\right)^{308.4nm}$	–	–	0.84[f]

[a] Method A: Mass-resolved laser depletion method developed by our group.[17,18] The dissociation yield $\phi_{dis}(ClOOCl)$ is unity. Method B: Detection of Cl atoms with time-resolved atomic resonance fluorescence by Wilmouth et al.[15] The source chemistry is $Cl+O_3\rightarrow ClO+O_2$, $2\,ClO\rightarrow ClOOCl$. Two Cl-atom sources were used. B1: microwave discharge of Cl_2; B2: photolysis of CF_2Cl_2. Method C: Velocity-resolved mass spectrometry (molecular beam translational spectroscopy).[35] [b] Maybe slightly different from values on previously works[15,17] due to a more precise treatment of the excimer laser wavelengths. The absorption cross sections of Cl_2 and O_3 are from the JPL 2006 evaluation.[7] If 2 Cl atoms are produced per absorbed photon, $\phi_{Cl}=2$. [c] Three excimer (KrF, XeCl, XeF) laser wavelengths were used in both types of investigations. More precision values of the wavelengths are from Ref. [15]. [d] Use the σ value of Method A. [e] Average value of the results of Methods B1 and B2. [f] This work.

which is referenced to the Cl_2 absorption cross section, is smaller than our photolysis cross section σ,[17,18] thereby suggesting that the $2Cl+O_2$ channel is not the only product channel. Remarkably, if we use $\sigma(ClOOCl)^{248.4nm}=873\times 10^{-20}$ cm^2[18] as a new reference value for the relative measurements of σ_{Cl} at 308.4 and 351.8 nm of Wilmouth et al., the results (see Table 1, Method B1/B2) indicate that ϕ_{Cl} does not vary with wavelength.

Direct observation of ClO product from ClOOCl photolysis has been reported very recently by our group[35] (Method C in Table 1). We prepared a molecular beam containing only ClOOCl, Cl_2, and O_2 (and He as the buffer gas), and dissociated the molecular beam with an excimer laser operating at 248.4 or 308.4 nm. The photoproducts were measured at an angle away from the molecular beam with a time-resolved mass spectrometer equipped with a 70 eV electron-impact ionizer.[36] Basically, the measurements are mass-, velocity-, and angle-resolved. Detailed dynamics of the photodissociation has been studied with these data.[35] To obtain the product branching ratio, we need to integrate the signal of each product over the 3D velocity space[37] and calibrate the relative detection sensitivity between different chemical species. For Cl versus ClO, the sensitivity calibration has been performed[35] with the photodissociation of Cl_2O[38] in which the momentum-matched ClO and Cl products have a fixed 1:1 ratio.

Our synthesis scheme follows Method 1 of Pope et al.:[11] $Cl+O_3 \rightarrow ClO+O_2$, $2ClO+M \rightarrow ClOOCl+M$, $ClOOCl_{(g)} \rightarrow ClOOCl_{(s)} \rightarrow ClOOCl_{(g)}$. The condensation–sublimation process enhances both the concentration and purity of ClOOCl. As mentioned in Section 2, the only significant impurities are O_2 and Cl_2. Figure 8 shows a mass spectrum of our ClOOCl molecular beam, which is ionized by electron impact at 70 eV. The purity of our sample is further evidenced by the following observations: 1) the photodissociation cross secti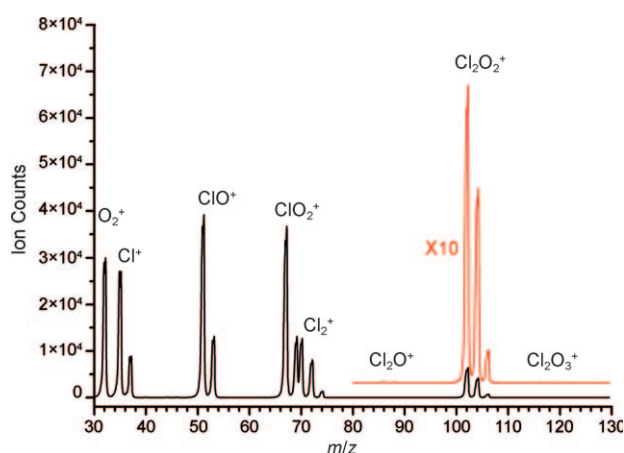ons measured at the parent ion ($Cl_2O_2^+$) and at daughter ions (ClO^+, ClO_2^+) are the same;[18,19] 2) when we varied the partial pressure of ClOOCl by slightly changing the evaporation temperature (by ≈ 1 K), all daughter ions showed the same intensity variation as the parent ion.

At 248.4 nm photoexcitation, we do not have any contribution from the impurities because O_2 and Cl_2 do not absorb light at this wavelength. Four photoproducts Cl, ClO, O_2, and O have been observed.[35] Based on the measured relative product yields, $[ClO]/[Cl]=(0.15\pm0.04):1$ and $[O]/[O_2]=0.12:1$, we estimated the branching ratios among the $(Cl+O_2+Cl)/(ClO+ClO)/(ClO+Cl+O)$ product channels to be $0.82:0.08:0.10$,[35] which give $\phi_{Cl}=2\times0.82+0.1=1.74$. Remarkably, we have successfully measured the time-of-flight (TOF) spectra of O_2 and ClO photoproducts at 308.4 nm photolysis.[35]

If the ClO+Cl+O product channel needs to be considered, we cannot determine the branching ratios without knowing the relative amount of the Cl-atom product. Fortunately, based on the observed translation energy of the ClO product,[35] it is certain that the ClO+Cl+O product channel is energetically not possible at 308.4 nm excitation and thus only the ClO+ClO and Cl+O_2+Cl channels need to be considered. By comparing the experimental $[ClO]/[O_2]$ ratios at 248.4 and 308.4 nm, we have estimated the branching ratio between the $(Cl+O_2+Cl)/(ClO+ClO)$ product channels to be $0.81:0.19$ at 308.4 nm.[35]

More importantly, in this work we have further extended the investigation to 351.8 nm, which is more relevant to atmospheric chemistry because the incoming solar flux (see Figure 2) is much higher at this wavelength than at 308.4 nm. Figure 9 shows a comparison of TOF (time of flight of the neutral product) spectra of O_2 and ClO photo-
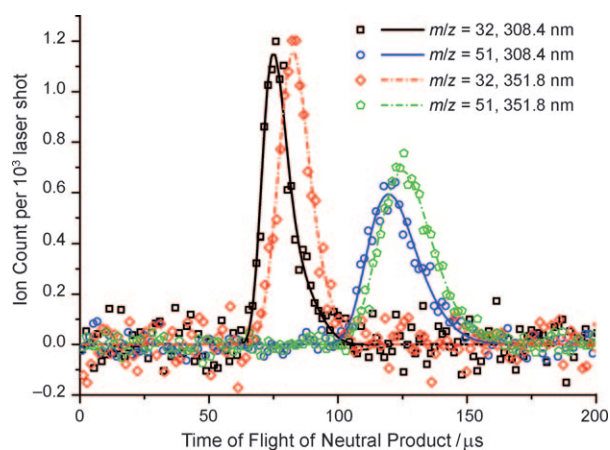
Figure 8. Electron-impact mass spectrum of our molecular beam. In addition to the parent ion of ClOOCl, its daughter ions (Cl^+, ClO^+, ClO_2^+) are also observed. The only significant impurities are O_2 and Cl_2. Other chlorine oxides like Cl_2O and Cl_2O_3 are extremely minor or absent.

Figure 9. Time of flight (TOF) spectra of O_2 (detected at m/z 32) and ClO (detected at m/z 51) photoproducts of a ClOOCl molecular beam photolyzed at 308.4 nm (laser pulse energy = 50 mJ) and 351.8 nm (laser pulse energy = 250 mJ). The detector angle and laser polarization angle were designed to probe the products at the magic angle to eliminate the anisotropy effect. The data acquisition was done in a way that the detection masses (m/z 32 and 51) were flipped back and forth many times to average out the intensity fluctuation of the molecular beam. The experimental condition is similar to that of Ref. [35].

products at 308.4 and 351.8 nm photolysis wavelengths. In Figure 9, we can see that the O_2 and ClO photoproducts at 351.8 nm photolysis wavelength are slightly slower (longer TOF) than the corresponding ones at 308.4 nm. Slower photoproducts are less translationally excited, which may be expected if one considers the photon energy at 351.8 nm is lower (see Figure 7).

To better determine the relative product yields, we should check whether the ClO photoproduct absorbs another laser photon and dissociates to Cl+O. The absorption band of ClO at room temperature covers from 220 to 310 nm, but the nascent ClO photoproduct is excited in vibrational and rotational degrees of freedom and may absorb at longer wavelengths. To check the extent of the ClO second-photon dissociation, we used the following approach. First, based on the energies of O_2 excited states, we are sure that the O_2 photoproduct does not absorb light at all three photolysis wavelengths. Second, we measured the relative signal ratio of ClO to O_2 at a series of laser power. As expected, at 248.4 and 308.4 nm this ratio decreases with laser power, which indicates that some of the ClO product is photolyzed by the laser beam. We analyzed this situation with a simple kinetic model [Eqs. (12a) and (12b)]:

$$ClOOCl + h\nu \xrightarrow{k_1} 2ClO \tag{12a}$$

$$ClO + h\nu \xrightarrow{k_2} Cl + O \tag{12b}$$
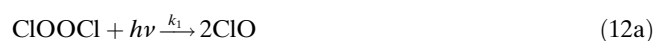
which considers absorption of the first photon ($k_1 = \sigma_1 F$, in which F is the laser flux) and the second photon ($k_2 = \sigma_2 F$). As expected, the relative contribution of the second photon vanishes at zero laser power. Figure 10 shows the ratio of the integral signals[37] of ClO and O_2 photoproducts as a function of laser power. By extrapolating the data to zero laser power, we obtained the ClO/O_2 integral signal ratio at

the single photon limit. The data allow us to estimate the branching ratio between the (Cl+O_2+Cl)/(ClO+ClO) product channels to be 0.84:0.16 at 351.8 nm photolysis wavelength. The results including the corresponding ϕ_{Cl} at 248.4, 308.4, and 351.8 nm are summarized in Table 1, noted as results of Method C.

In Table 1, we find that there is some small variation in ϕ_{Cl}, depending on the data sources and how to deduce it. However, its wavelength dependence is not obvious at all in the present data. Moreover, as mentioned above, combination of selected data of Methods A and B indicates that ϕ_{Cl} does not depend on the excitation wavelength. At present, we can only conclude that the value of ϕ_{Cl} is about 1.6 at excitation wavelengths from 248 to 352 nm.

Because the atmospherically relevant region of ClOOCl absorption overlaps with the absorption bands of other chlorine oxides (Cl_2O, OClO) that may be used as a precursor to synthesize ClOOCl, it is difficult to quantify the ClO product from ClOOCl photolysis when a large background from precursor photolysis is present. Pope et al.[11] reported a very useful synthesis method that allows researchers to prepare a ClOOCl sample without interference from other chlorine oxides. Although the Cl_2 contaminant is inevitable[15] and still produces Cl atoms in the photolysis experiments at 308.4 and 351.8 nm, we have utilized detection of the O_2 photoproduct to circumvent this problem. The success of our experiments relies on time- and velocity-resolved detection, which distinguishes the O_2 photoproduct from the large O_2 background in the sample. Alternatively, Wilmouth et al.[15] chose to measure the Cl_2 contaminant directly and obtained the net signals of the Cl-atom product from ClOOCl photolysis after background subtraction.

Similar to many photochemical measurements of multi-channel products, it is more difficult to obtain precise results of the product quantum yields. The major reason is that it is harder to compare the amounts of different chemical species, unless there is a suitable system for calibration. The advantage of Method C is that the nascent products are measured directly under the collision-free conditions in a molecular beam, thus eliminating any interference from secondary reactions. But significant amounts of internal energy in the nascent products may cause some variation in detection sensitivity, which is hard to quantify. Based on the possible variation of the detection sensitivities, we made an educated guess that the error bar is about 25% for the relative yields of [ClO]/[O_2].[35] Notably, if one channel prevails ($\approx$80%), the error bar of the corresponding absolute branching ratios will become smaller ($\approx$10%).

As mentioned above, present theoretical calculations[34] suggest that the ClO+ClO channel only takes place at a high photon energy of about 5 eV (248 nm) and the 2 Cl+O_2 channel is the only product channel at excitation wavelengths longer than 300 nm. Direct experimental observations of the ClO product with noticeable yields at 308.4 and 351.8 nm indicate the need for further theoretical calculations at a higher level. Present theoretical results[34] show that the excited-state potential energy surfaces are repulsive
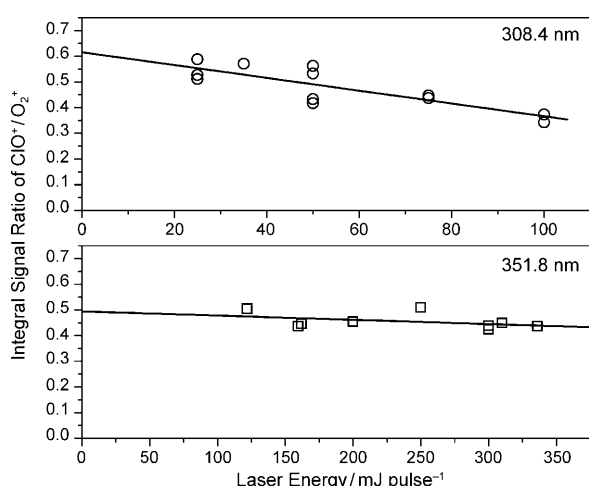

Figure 10. Ratio of the integral (over the 3D velocity space) signals of ClO and O_2 as a function of laser power. The ClO product was probed at m/z 51 (ClO$^+$) and O_2 was probed at m/z 32 (O_2^+). The calibration of detection sensitivity is not included in these data.

along the Cl−OOCl bond length, but they are also repulsive along the ClO−OCl bond length. The competition between breaking the Cl−OOCl bond and breaking the ClO−OCl bond would depend on the exact shapes of the potential energy surfaces and the nonadiabatic couplings among them, which require extensive calculations of higher sophistication.

5. Perspectives

To better understand the ozone hole chemistry, field measurements, model calculations, and laboratory data are all crucial. The molecule under recent debate, ClOOCl, plays a central role in ozone hole formation. Understanding its photochemistry is a key to understanding the mechanism of stratospheric ozone loss. While the field measurements provide more and more data and model calculations become more and more sophisticated, the quality of the laboratory data should not be left behind. Laboratory scientists have encountered a few technical challenges in determining the basic photochemical data of ClOOCl. Newly developed methods and improved experiments have provided data of higher accuracy and at atmospherically more relevant conditions.

Although impurities in a ClOOCl sample are inevitable, various experimental strategies have been used to overcome or, in a better sense, to circumvent this problem. Among them, the method of molecular beam translational spectroscopy (Method C) is unique in the following aspects: 1) the low number density of a molecular beam ensures a collision-free condition such that secondary reactions will not take place; 2) the mass-resolved detection allows one to separate the target species from others; 3) the velocity- and time-resolved detection allows one to distinguish the photodissociation events from backgrounds.

Even for a stable species, caution may be required in its photochemical measurements. An example is the photodissociation of OClO, of which the product branching ratio was under debate for years.[7,9,39] The UV photolysis of OClO may yield two product channels: the predominant one is O+ClO and the minor one is Cl+O$_2$. The latter will destroy ozone but the O atom in the former channel will produce ozone through O+O$_2$→O$_3$. A few photodissociation studies of OClO[40] reported a substantial yield of the Cl+O$_2$ channel, but some other studies[41] showed that the yield of the O+ClO channel is almost unity. Finally, Davis and Lee[42] performed unambiguous measurements, in which all product species, ClO, O, Cl, and O$_2$, have been measured in a velocity-resolved manner. If two fragments originate from a dissociation event, the sum of their linear momentum should be zero in the center-of-mass frame. This momentum-match offers an additional check such that the assignment of the product channels can be much more certain. Davis and Lee[42] have observed the O+ClO and Cl+O$_2$ products as momentum-matched pairs; the measured quantum yield of the Cl+O$_2$ channel, however, reaches a maximum of (3.9 ±

0.8)% near 404 nm and decreases to <0.2% under the absorption peaks in the wavelength range 350–370 nm.[42] The earlier experiments[40] showing much larger Cl-atom yields employed multiphoton ionization detection of Cl atoms; their signals are likely due to a secondary process ClO(v≥4)+$h\nu$→Cl+O.[43]

Regarding the absorption cross section (σ) and product quantum yields (ϕ) of ClOOCl, we suggest the following based on the best available data. The absorption cross section[17–19] of ClOOCl is larger than the widely used JPL 2006 evaluated value,[7] especially at λ≥330 nm (see Figure 3). But the Cl-atom production yield ϕ_{Cl} (see Table 1) is smaller than what most people thought previously.[3,9] Remarkably, there is no significant wavelength dependence of ϕ_{Cl} and ϕ_{ClO} at 248, 308, and 352 nm, contrary to present theoretical predictions.

Most atmospheric modeling assumes that the Cl+ClOO channel is the only product channel.[3] But the ClO+ClO channel has been observed directly at atmospherically relevant wavelengths such as 308 and 352 nm; the yield is not large but noticeable. The impact to the atmospheric chemistry is yet to be modeled. As for the Cl-atom production rate (J_{Cl}), which affects directly the ozone destruction rate, some errors may be cancelled if models use the underestimated absorption cross section (σ) from the JPL 2006 evaluation[7] and the overestimated Cl-atom quantum yield (ϕ_{Cl}=2). The refined (more accurate) values of σ and ϕ_{Cl} should affect certain kinetic data. For example, the field measurements of [ClOOCl]/[ClO]^2 ratios[10] are more sensitive to the total J-value of ClOOCl than to J_{Cl}.[4c,10] Moreover, although ClOO in current models eventually dissociates to Cl+O$_2$ after collisions, the production of stable ClOO from ClOOCl UV photolysis has never been observed and is not likely to form based on the photodissociation dynamics.[35]

Advanced measurements of ClOOCl by our group and other groups have offered significantly better data for modelers, as shown in the "Scientific Assessment of Ozone Depletion: 2010" by WMO/UNEP:[44] "Recent laboratory measurements of the ClO dimer (ClOOCl) dissociation cross section and analyses of observations from aircraft and satellites have reaffirmed the fundamental understanding that polar springtime ozone depletion is caused primarily by the ClO+ClO catalytic ozone destruction cycle, with significant contributions from the BrO+ClO cycle."

After all the works performed by various groups worldwide over the last two decades, Molina's mechanism of the chemistry of the ozone hole has been vindicated. For ClOOCl, the quality of its laboratory data has been significantly improved, especially during the past two years, which allows more reliable modeling of ozone loss. The data are not perfect yet and there are more molecules that deserve similar scientific efforts, although they are mostly found high in the air.

Acknowledgements

[1] J. C. Farman, B. G. Gardiner, J. D. Shanklin, *Nature* **1985**, *315*, 207–210.

[2] NASA Ozone Hole Watch. Available at http://ozonewatch.gsfc.nasa.gov/.

[3] World Meteorological Organization (WMO), *Scientific Assessment of Ozone Depletion: 2006, Global research and monitoring project—Report No. 50*, (WMO, Geneva, Switzerland, **2007**); http://ozone.unep.org/Assessment_Panels/SAP/Scientific_Assessment_2006.

[4] a) K. Frieler, M. Rex, R. J. Salawitch, T. Canty, M. Streibel, R. M. Stimpfle, K. Pfeilsticker, M. Dorf, D. K. Weisenstein, S. Godin-Beekmann, *Geophys. Res. Lett.* **2006**, *33*, L10812; b) S. R. Kawa, R. S. Stolarski, P. A. Newman, A. R. Douglass, M. Rex, D. J. Hofmann, M. L. Santee and K. Frieler, *Atmos. Chem. Phys.* **2009**, *9*, 8651; c) M. von Hobe, R. J. Salawitch, T. Canty, H. Keller-Rudek, G. K. Moortgat, J.-U. Groos, R. Müller, F. Stroh, *Atmos. Chem. Phys.* **2007**, *7*, 3055.

[5] L. T. Molina, M. J. Molina, *J. Phys. Chem.* **1987**, *91*, 433–436.

[6] a) R. A. Cox, G. D. Hayman, *Nature* **1988**, *332*, 796–800; b) T. Permien, R. Vogt, R. N. Schindler, "Absorption spectra of HOCl and Cl₂O₂," in Mechanics of gas phase and liquid phase chemical transformations. Air Pollution Report, No. 17, Environmental Research Program of the CEC, EUr 12035 EN, (Ed.: R. A. Cox) Brussels, Belgium, **1988**, pp. 149–153; c) J. B. Burkholder, J. J. Orlando, C. J. Howard, *J. Phys. Chem.* **1990**, *94*, 687–695; d) W. B. DeMore, E. Tschuikow-Roux, *J. Phys. Chem.* **1990**, *94*, 5856–5860; e) K. J. Huder, W. B. DeMore, *J. Phys. Chem.* **1995**, *99*, 3905–3908; f) J. R. McKeachie, M. F. Appel, U. Kirchner, R. N. Schindler, T. Benter, *J. Phys. Chem. B* **2004**, *108*, 16786–16797.

[7] S. P. Sander, B. J. Finlayson-Pitts, R. R. Friedl, D. M. Golden, R. E. Huie, H. Keller-Rudek, C. E. Kolb, M. J. Kurylo, M. J. Molina, G. K. Moortgat, V. L. Orkin, A. R. Ravishankara, P. H. Wine, *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies 06–2*, Jet Propulsion Laboratory, Pasadena, **2006**.

[8] S. Madronich, *Tropospheric Ultraviolet and Visible (TUV) Radiation Model* **2009**: http://cprm.acd.ucar.edu/Models/TUV/.

[9] R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, J. Troe, *Atmos. Chem. Phys.* **2007**, *7*, 981–1191; Also available at IUPAC Subcommittee for Gas Kinetic Data Evaluation: http://www.iupac-kinetic.ch.cam.ac.uk/index.html.

[10] R. M. Stimpfle, D. M. Wilmouth, R. J. Salawitch, J. G. Anderson, *J. Geophys. Res.* **2004**, *109*, D03301.

[11] F. D. Pope, J. C. Hansen, K. D. Bayes, R. R. Friedl, S. P. Sander, *J. Phys. Chem. A* **2007**, *111*, 4322–4332.

[12] M. von Hobe, *Science* **2007**, *318*, 1878–1879.

[13] Stratospheric Processes and Their Role in Climate (SPARC), The Role of Halogen Chemistry in Polar Stratospheric Ozone Depletion: Report from the June 2008 Cambridge, UK Workshop for an Initiative under the Stratospheric Processes and Their Role in Climate (SPARC) Project of the World Climate Research Programme, **2009**. Available at: http://www.atmosp.physics.utoronto.ca/SPARC/HalogenChem_Final_20090213.pdf

[14] M. von Hobe, F. Stroh, H. Beckers, T. Benter, H. Willner, *Phys. Chem. Chem. Phys.* **2009**, *11*, 1571–1580.

[15] D. M. Wilmouth, T. F. Franco, R. M. Stimpfle, J. G. Anderson, *J. Phys. Chem. A* **2009**, *113*, 14099–14108.

[16] D. K. Papanastasiou, V. C. Papadimitriou, D. W. Fahey, J. B. Burkholder, *J. Phys. Chem. A* **2009**, *113*, 13711–13726.

[17] H.-Y. Chen, C.-Y. Lien, W.-Y. Lin, , Y. T. Lee, J. J. Lin, *Science* **2009**, *324*, 781–784.

[18] C.-Y. Lien, W.-Y. Lin, H.-Y. Chen, W.-T. Huang, B. Jin, I-C. Chen, J. J. Lin, *J. Chem. Phys.* **2009**, *131*, 174301.

[19] B. Jin, I-C. Chen, W.-T. Huang, C.-Y. Lien, N. Guchhait, J. J. Lin, *J. Phys. Chem. A* **2010**, *114*, 4791–4797.

[20] a) F. Jensen, J. Oddershede, *J. Phys. Chem.* **1990**, *94*, 2235–2237; b) J. F. Stanton, R. J. Bartlett, *J. Chem. Phys.* **1993**, *98*, 9335–9339; c) A. Toniolo, M. Persico, D. Pitea, *J. Phys. Chem. A* **2000**, *104*, 7278–7283; d) P. Tomasello, M. Ehara, H. Nakatsuji, *J. Chem. Phys.* **2002**, *116*, 2425–2432; e) K. A. Peterson, J. S. Francisco, *J. Chem. Phys.* **2004**, *121*, 2611–2616; f) M. Ončák, L. Šištík, P. Slavíček, *J. Chem. Phys.* **2010**, *133*, 174303.

[21] J. Jacobs, M. Kronberg, H. S. P. Müller, H. Willner, *J. Am. Chem. Soc.* **1994**, *116*, 1106–1114.

[22] a) M. P. McGrath, K. C. Clemitshaw, F. S. Rowland, W. J. Hehre, *J. Phys. Chem.* **1990**, *94*, 6126–6132; b) W.-K. Li, C.-Y. Ng, *J. Phys. Chem. A* **1997**, *101*, 113–115.

[23] M. H. Matus, M. T. Nguyen, D. A. Dixon, K. A. Peterson, J. S. Francisco, *J. Phys. Chem. A* **2008**, *112*, 9623–9627.

[24] a) B.-M. Cheng, Y.-P. Lee, *J. Chem. Phys.* **1989**, *90*, 5930–5935; b) M. Birk, R. R. Friedl, E. A. Cohen, H. M. Pickett, S. P. Sander, *J. Chem. Phys.* **1989**, *91*, 6588–6597.

[25] R. S. Zhu, M. C. Lin, *J. Chem. Phys.* **2003**, *118*, 4094–4106.

[26] J.-T. Hong, Y.-L. Sun, W.-P. Hu, "*Relative Stability and Isomerization Dynamics of Cl₂O₂*", unpublished results.

[27] A. D. Boese, J. M. L. Martin, *J. Chem. Phys.* **2004**, *121*, 3405–3416.

[28] a) J. D. Cox, D. D. Wagman, V. A. Medvedev, *CODATA Key Values for Thermodynamics*, Hemisphere, New York, **1989**; b) M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, *JANAF Thermochemical Tables (Third Edition)*, *J. Phys. Chem. Ref. Data, Suppl. 1* **1985**, *14*, 1; c) K. Suma, Y. Sumiyoshi, Y. Endo, S. Enami, S. Aloisio, M. Hashimoto, M. Kawasaki, S. Nishida, Y. Matsumi, *J. Phys. Chem. A* **2004**, *108*, 8096–8099.

[29] V. Ferracci, D. M. Rowley, *Phys. Chem. Chem. Phys.* **2010**, *12*, 11596–11608.

[30] a) M. J. Molina, A. J. Colussi, L. T. Molina, R. N. Schindler, T.-L. Tso, *Chem. Phys. Lett.* **1990**, *173*, 310–315; b) Their synthesis method was as follows: chlorine atoms were produced through F+HCl→Cl+HF, using F atoms from microwave discharge of a F₂/He mixture. ClOOCl was produced by reacting Cl with O₃ downflow in a passivated fast-flow reactor maintained at low temperature.

[31] T. K. Minton, C. M. Nelson, T. A. Moore, M. Okumura, *Science* **1992**, *258*, 1342–1345.

[32] T. A. Moore, M. Okumura, J. W. Seale, T. K. Minton, *J. Phys. Chem.* **1999**, *103*, 1691–1695.

[33] J. Plenge, R. Flesch, S. Kuhl, B. Vogel, R. Muller, F. Stroh, E. Ruhl, *J. Phys. Chem. A* **2004**, *108*, 4859–4863.

[34] a) A. L. Kaledin, K. Morokuma, *J. Chem. Phys.* **2000**, *113*, 5750–5762; b) A. Toniolo, G. Granucci, S. Ingleseb, M. Persico, *Phys. Chem. Chem. Phys.* **2001**, *3*, 4266–4279.

[35] W.-T. Huang, A. F Chen, I.-C. Chen, C.-H. Tsai, J. J.-M. Lin, *Phys. Chem. Chem. Phys.* **2011**, *13*, 8195–8203.

[36] J. J. Lin, D. W. Hwang, S. Harich, Y. T. Lee, X. Yang, *Rev. Sci. Instrum.* **1998**, *69*, 1642–1646.

[37] a) In the experiment, we performed a coordinate transformation from the laboratory frame to the center-of-mass frame to obtain the velocity and angular distributions and the integral intensity of a photoproduct. For information about the coordinate transformation, see: b) R. K. Sparks, K. Shobatake, L. R. Carlson, Y. T. Lee, *J. Chem. Phys.* **1981**, *75*, 3838–3846.

[38] a) The structure of Cl₂O is similar to H₂O with a slightly larger ClOCl angle; b) C. M. Nelson, T. A. Moore, M. Okumura, T. K. Minton, *J. Chem. Phys.* **1994**, *100*, 8055–8064; c) T. A. Moore, M. Okumura, T. K. Minton, *J. Chem. Phys.* **1997**, *107*, 3337–3338.

[39] V. Vaida, J. D. Simon, *Science* **1995**, *268*, 1443–1448.

[40] a) V. Vaida, S. Solomon, E. C. Richard, E. Ruehl, A. Jefferson, *Nature* **1989**, *342*, 405–408; b) E. Ruehl, A. Jefferson, V. Vaida, *J. Phys. Chem.* **1990**, *94*, 2990–2994; c) E. Bishenden, J. Haddock, D. J. Donaldson, *J. Phys. Chem.* **1991**, *95*, 2113–2115; d) E. Bishenden, J. Haddock, D. J. Donaldson, *J. Phys. Chem.* **1992**, *96*, 6513.

[41] a) A. J. Colussi, *J. Phys. Chem.* **1990**, *94*, 8922–8926; b) W. G. Lawrence, K. C. Clemitshaw, V. A. Apkarian, *J. Geophys. Res.* **1990**, *95*, 18591–18595.

[42] a) F. H. Davis, Y. T. Lee, *J. Phys. Chem.* **1992**, *96*, 5681–5684; b) F. H. Davis, Y. T. Lee, *J. Chem. Phys.* **1996**, *105*, 8142–8163.

[43] R. F. Delmdahl, S. Ulrich, K.-H. Gericke, *J. Phys. Chem. A* **1998**, *102*, 7680–7685.

[44] WMO/UNEP (United Nations Environment Programme), *Executive Summary of WMO/UNEP "Scientific Assessment of Ozone Depletion: 2010"*, **2010**. http://ozone.unep.org/Assessment_Panels/SAP/Scientific_Assessment_2010/02-Executive_Summary.pdf.