Ultraviolet Absorption Spectrum of Chlorine Peroxide, ClOOC1

Francis D. Pope,*† Jaron C. Hansen,‡ Kyle D. Bayes,* Randall R. Friedl, and Stanley P. Sander
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109
Received: November 17, 2006; In Final Form: March 6, 2007

The photolysis of chlorine peroxide (ClOOC1) is understood to be a key step in the destruction of polar stratospheric ozone. This study generated and purified ClOOC1 in a novel fashion, which resulted in spectra with low impurity levels and high peak absorbances. The ClOOC1 was generated by laser photolysis of Cl2 in the presence of ozone, or by photolysis of ozone in the presence of CF2Cl2. The product ClOOC1 was collected, along with small amounts of impurities, in a trap at about −125 °C. Gas-phase ultraviolet spectra were recorded using a long path cell and spectrograph/diode array detector as the trap was slowly warmed. The spectrum of ClOOC1 could be fit with two Gaussian-like expressions, corresponding to two different electronic transitions, having similar energies but different widths. The energies and band strengths of these two transitions compare favorably with previous ab initio calculations. The cross sections of ClOOC1 at wavelengths longer than 300 nm are significantly lower than all previous measurements or estimates. These low cross sections in the photolytically active region of the solar spectrum result in a rate of photolysis of ClOOC1 in the stratosphere that is much lower than currently recommended. For conditions representative of the polar vortex (solar zenith angle of 86°, 20 km altitude, and O3 and temperature profiles measured in March 2000) calculated photolysis rates are a factor of 6 lower than the current JPL/NASA recommendation. This large discrepancy calls into question the completeness of present atmospheric models of polar ozone depletion.

Introduction
The chlorine peroxide molecule, ClOOC1, is formed in the stratosphere when two ClO molecules combine in a three body collision, reaction 1a. This molecule, sometimes referred to as the “ClO dimer” or for this paper just “dimer”, participates in the chlorine catalyzed destruction of ozone in the stratosphere.1 When ClOOC1 is photolyzed in the near-ultraviolet, reaction 2,

\[ \text{ClO} + \text{ClO} + \text{M} \rightarrow \text{ClOOC1} + \text{M} \] (1a)
\[ \text{ClOOC1} + h\nu \rightarrow \text{ClO} + \text{Cl} \] (2)
\[ \text{ClO} + \text{M} \rightarrow \text{Cl} + \text{O}_2 + \text{M} \] (3)
\[ 2[\text{Cl} + \text{O}_3] \rightarrow \text{ClO} + \text{O}_2 \] (4)

it forms Cl + ClOO, rather than Cl + ClO.2−4 The ClOO radical is marginally stable and usually decomposes to Cl and O2, reaction 3. These two Cl atoms then can react with ozone, reaction 4, to re-form the two ClO molecules and, in so doing, destroy two O3 molecules.

Previous studies have identified a strong UV absorption band of ClOOC1 with a maximum at about 245 nm and a long tail extending to at least 350 nm.5−8 Cross sections longer than 300 nm are most important for calculating the photolysis rate of ClOOC1 in the atmosphere, because atmospheric ozone eliminates most solar radiation at shorter wavelengths.

Literature values for these long wavelength cross sections vary considerably, by as much as a factor of 5, because of the difficulties in subtracting out the contributions of spectrally featureless impurities such as Cl2, Cl2O, Cl2O3, and O3 that are usually present when ClOOC1 is generated in the laboratory. Analysis of field measurements of ClO and ClOOC1 indicates that the partitioning between these species is consistent with the present understanding of the rate constant for ClOOC1 formation only if the largest ClOOC1 cross sections are used.9−12

The present study reduces the problem of spectral contamination by freezing out the chlorine peroxide and then measuring its absorption spectrum in the gas phase as a function of time as the trap is slowly warmed. Fractionation of the gas stream exiting the trap occurs because of the differences in vapor pressures of different components.

Experimental Methods
A continuous flow of gases only slightly above atmospheric pressure passed through a photolysis cell, a cold trap, an absorption cell and then exited to the hood. The formation of ClOOC1 was initiated by laser photolysis in the first cell. The ClOOC1 was collected in the cold trap at −120 to −125 °C for 1−2 h. Then the laser and the reactive gases were turned off while the inert carrier gas continued to flow and the trap was rapidly cooled to −150 °C. After about another hour the trap was slowly warmed at a rate of 0.5−1 °C/min, and absorption spectra were recorded every 5.3 s. Significant absorption at 245 nm, due to ClOOC1, began to appear at about −120 °C, reached a maximum at about −115 °C, and approached zero again when the trap reached −90 °C.

* Author for correspondence. E-mail: kdbayes@jpl.nasa.gov. Fax: 818 393 5019. Tel: 818 393 3358.
† Currently at the Centre for Atmospheric Science, Department of Chemistry, University of Cambridge, Lensfield Rd., Cambridge CB2 1EW, United Kingdom.
‡ Currently at Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602.
The cell was cooled with circulating methanol at quartz cell from light, minimizing light-piping into the trap. The laser beam entered the photolysis cell at the end nearest surfaces seemed to be the least destructive of ClOOCl. 7,8

Figure 1. Diagram of the photolysis cell, trap and absorption cell. Quartz was used for all surfaces in contact with the gas stream. V indicates evacuated chambers to avoid water condensation on the windows. The UV analysis beam made two passes through the UV Absorption Spectrum of ClOOCl.  

Apparatus. A diagram of the quartz photolysis cell and trap is shown in Figure 1. As was observed previously, clean quartz surfaces seemed to be the least destructive of ClOOCl. 7,8 The laser beam entered the photolysis cell at the end nearest the gas exit. A metal ring with a circular opening of 16 mm diameter at the entrance window shielded the sides of the quartz cell from light, minimizing light-piping into the trap. The cell was cooled with circulating methanol at −80 °C. Evacuated spaces at both ends of the cell prevented condensation on the windows, except for humid days when a flow of dry N2 on the outside windows was also needed. The exit tube of the photolysis cell extended 2 cm into the cold trap to keep the gas stream cold as it passed through the spherical joint region.

The trap was a cylindrical quartz tube, approximately 15 cm in length and 12 mm in internal diameter. The trap temperature was controlled using dry nitrogen that had been cooled by flowing through a coil of copper tubing immersed in liquid nitrogen. The coolant entered through a hole in a metal shroud at the center of the trap and exited to the atmosphere at either end. Increasing the nitrogen flow rate decreased the temperature in the trap. A Pt-resistance thermometer rested against the outside of the trap opposite the cold nitrogen inlet. Thus the reported temperatures only approximately represent those inside the trap.

The absorption cell and optical setup have been described previously. 13 Briefly, a collimated beam from a deuterium lamp (Hamamatsu L1314) traversed the absorption cell twice, giving a total path length of 184 cm, and then was focused onto the entrance slit of a 0.25 m spectrometer. The dispersed spectrum was detected by a photodiode array (Princeton Instruments, Model PDA-1024H) and stored on a computer. The spectrometer had a 300 line/mm grating with a slit width giving a resolution of about 1 nm FWHM. The wavelength scale was calibrated using mercury lines emitted from a Penray lamp.

The noise level on the absorbance scale was about 0.001 for an integration time of 5 s. However, the baseline on the absorbance scale was not stable over long periods of time. Blank runs with no absorber in the cell showed that the signal was noticeably affected by the temperature cycling of the laboratory air conditioning system. Because the absorbances were determined by measurements of I1 during a run, and I0, which was usually taken at the end of a run, the baseline drift was as much as ±0.02 absorbance units over a period of 20 min. The baselines were almost independent of wavelength, although some blank runs show a slight nonlinearity at shorter wavelengths. The treatment of the baseline is discussed in the Spectral Analysis section below.

Before an experiment began, ozone was generated from pure oxygen using an ozonizer (Welsbach T816) and was trapped on silica gel at −80 °C. During ClOOCl generation, a fraction of the carrier gas was diverted through the ozone trap before entering the photolysis cell. The ozone concentrations were monitored by measuring the absorption of the 254 nm radiation from a mercury Penray lamp after passing through a 1 cm path length cell; the detector was a photomultiplier tube that was band-limited with a narrow interference filter. The partial pressure of O3 was constant to within 10% during a run.

Gas flows were controlled by calibrated flow controllers. The gases used were N2 (Airgas 99.9993%), He (Airgas 99.999%), O2 (Airgas 99.8%), 1% Cl2 in He (Matheson), CF2Cl2 (Liquid Carbonic), and CF4 (Matheson). The total flow rates were typically 1090 sccm during ClOOCl generation and 640 sccm during the desorption phase. The later flow rate, when converted to flows at −80 °C and 730 Torr gave a residence time for the gas in the absorption cell of approximately 90 s.

ClOOCl Generation and Experimental Spectra. Initially our experiments used a low-pressure fast flow system coupled to a quadrupole mass spectrometer14 to explore the conditions needed to generate, trap out, and transport chlorine peroxide with a minimum of impurities. Clean quartz surfaces were superior to Teflon, halocarbon wax, or Pyrex. Purification by trap-to-trap distillation was attempted, but this did not seem to improve the dimer purity. It was decided to use a minimum of connecting tubing between the generation, trapping and analysis cells, as shown in Figure 1. For measurements of absorption intensity, both a charge coupled device and a photodiode array were used, with the latter proving superior in signal-to-noise.

Spectra were collected on 26 different days. Because the temperature of the trap was controlled manually; no two runs were exactly the same. A major problem was stability of the deuterium lamp and detector, which affected the baseline drift. The analysis of spectra was focused on the five runs that combined strong dimer absorptions, good but not perfect baseline stability, and low impurities.

Two methods were used to generate ClOOCl, one that has been used in previous studies5,6,8 and a new scheme. These will be discussed separately.
Method 1: \( O_3 + Cl_2 + h\nu(351 \text{ nm}) \). A mixture of molecular chlorine and ozone, approximately 0.4 and 3 Torr, respectively, in nitrogen was irradiated with laser pulses of about 40 mJ at 351 nm and 10 Hz. The chlorine atoms that were formed by photolysis of \( Cl_2 \) reacted rapidly with ozone to form \( ClO \) radicals, reaction 4. For the pressure and temperature used (730 Torr and \(-80 \, ^{\circ}C\)) the \( ClO + ClO \) reaction formed primarily \( ClOOCl \) (1a); the competing bimolecular channels (reactions 1b, 1c, and 1d) are approximately a thousand times slower for these conditions.\(^{15–18}\) The gas mixture spent 3.5 s in the photolysis cell and was exposed to 35 laser pulses before exiting to the trap. Modeling showed that the dimer concentration was still increasing after 30 pulses, but at a slower rate because dimer formed by reaction 1a was being destroyed by reaction 5.

\[
Cl + ClOOCl \rightarrow Cl_2 + ClO \tag{5}
\]

Some dimer could be observed after collecting for only 10 or 15 min, but most runs trapped for periods of 1–2 h, resulting in maximum absorbances (\( \ln(I/I_0) \), base e) of 1–3. In addition to the known spectrum of \( ClOOCl \), there was also significant absorption by molecular chlorine. However, as the trap slowly warmed, the chlorine absorption usually peaked before the dimer absorption, indicating some fractionation was taking place.

Especially useful were the spectra taken near the end of the desorption phase. Figure 2 shows five of these spectra. While the \( ClOOCl \) absorption is decreasing with time, the \( Cl_2 \) peak decreases more rapidly. For the spectra shown in Figure 2 the molecular ratio \( Cl_2/ClOOCl \) is decreasing from 2.7 to 1.1 (see Spectral Analysis below). However, for the spectra from method 1, the ratio never went much below unity. Experiments designed to understand the source of this residual \( Cl_2 \) signal were inconclusive. Varying the residence time of the \( ClOOCl \) in the absorption cell from 2 min to 20 s did not change the final \( Cl_2/ClOOCl \) ratio significantly. By intermittently blocking the light coming from the deuterium lamp, we could observe an increase of \( Cl_2/ClOOCl \) by about 0.2 when the beam was reintroduced; this effect was largely eliminated by attenuating the intensity of the deuterium lamp. There was no evidence that ozone had been co-deposited with the dimer; this is expected because the vapor pressure of ozone at \(-125 \, ^{\circ}C\) is 340 Torr, well above the amount being used.

Method 2: \( CCl_2F_2 + O_3 + h\nu(248 \text{ nm}) \). A new scheme was devised to avoid the presence of large amounts of \( Cl_2 \). It is known that when ozone absorbs 248 nm radiation, an excited oxygen atom is formed;\(^{19–20}\)

\[
O_3 + h\nu(248 \text{ nm}) \rightarrow O(1D) + O_2 \tag{6}
\]

This \( O(1D) \) can then react either with ozone or with \( CCl_2F_2 \):

\[
O(1D) + O_3 \rightarrow 2O(3P) + O_2 \text{ (or } 2O_2) \tag{7}
\]

\[
O(1D) + CCl_2F_2 \rightarrow ClO + CClF_2 \tag{8a}
\]

\[
O(1D) + CCl_2F_2 \rightarrow O(3P) + CClF_2 \tag{8b}
\]

Previous studies have shown that approximately 80% of reaction 8 goes by channel 8a, with only 20% deactivation of \( O(1D) \) to the ground state, channel 8b.\(^ {21} \)

For our conditions (2 Torr \( CF_2Cl_2 \), 2–3 Torr \( O_3 \), balance \( He, 730 \) Torr and \(-80 \, ^{\circ}C\)), the chlorodifluoromethyl radicals formed in reaction 8a should react primarily with ozone to form chlorodifluoromethoxy radicals, reaction 9. Methoxy radicals

\[
CCIF_2 + O_3 \rightarrow CICF_2CO + O_2 \tag{9}
\]

in which there is at least one \( Cl \) or \( Br \) are known to decompose rapidly by ejecting a halogen atom.\(^ {22–25} \) Because the \( C-Cl \) bond is weaker than the \( C-F \) bond, one expects reaction 10 to dominate. The resulting \( Cl \) atom will then react with ozone to form another \( ClO \). Fortunately the UV absorption of the product \( CF_2O \) does not interfere with measurements of the \( ClOOCl \) spectrum.\(^ {26} \)

This new scheme has the potential to generate \( ClO \) dimer with very low amounts of \( Cl_2 \). Reaction 5 should be the only significant source of \( Cl_2 \). Modeling showed that for the conditions used, the molecular ratio of \( Cl_2 \) to \( ClOOCl \) would be about 0.06 after one pulse, 0.6 after the second pulse, and 1.4 after the third pulse of 248 nm in the same sample of gas. The very low production of \( Cl_2 \) in the first pulse results when \( Cl \) atoms formed by the laser are destroyed rapidly by reaction 4, mostly before the slower reaction 1a can form \( ClOOCl \). However, when the second pulse arrives, the new supply of \( Cl \) atoms can react with the \( ClOOCl \) formed in the first pulse, giving a larger ratio of \( Cl_2/ClOOCl \).
The early spectra (e.g., spectrum 23) show a peak absorbance at 245 nm indicating ClOOCl, but with significant OCIO evident at wavelengths longer than 300 nm. As the trap warmed, a shoulder builds on the long wavelength side of the 245 nm peak (spectrum 36), and eventually a new peak emerges at about 265 nm (spectrum 57) corresponding to the strong Cl2O3 band. The total time covered in Figure 3 is about 1 h.

Because it is known that reaction 8a forms vibrationally hot ClO,31 the possibility that this extra vibrational energy was responsible for OCIO formation was tested by replacing part of the He flow by CF4, which should be better than He at vibrationally relaxing hot ClO. The (OCIO + Cl2O3) signal was reduced by a factor of 10 for 21% CF4. Additional CF4 up to 71% did not reduce the OCIO further.

The reaction responsible for OCIO formation is not known. One possibility is that reaction 1d or reaction 12, normally slow, could be accelerated by the extra vibrational energy in the ClO. There was some indication that the OCIO formation was greater for the larger ozone concentrations, which would support reaction 12, but this possibility was not pursued further.

Spectral Analysis

Previous attempts to measure the spectrum of ClOOCl have also had to eliminate the contributions of impurities such as Cl2, Cl2O, OCIO, and Cl2O3. Because the spectra of the impurities are known, these were subtracted from the measured absorption in varying amounts until the resulting spectrum looked reasonable. For an impurity such as OCIO, which has a series of sharp peaks, this method works well. But for broad spectral features, such as those for Cl2 or Cl2O3, this method becomes quite subjective.

Figure 4 illustrates the uncertainties associated with the subtraction method. The black line in Figure 4 is a spectrum generated using method 1, chosen because it shows a distinct bump near 330 nm due to Cl2 and also because it extends to longer wavelengths than those in Figure 2. The colored curves in Figure 4 show the results of subtracting increasing amounts of the known Cl2 spectrum.28 Which one of the subtractions gives the best representation of the spectrum of pure ClOOCl? Clearly the lowest red curve results from subtracting too much. But beyond rejecting negative absorbances, what criteria can be used to decide on the “best” curve? There is no hint of a bump at 330 nm in any of the colored curves. Should the absorbance of ClOOCl at 360 nm really be zero, or some finite value? How can one decide?

Faced with this problem, Huder and DeMore,7 after subtracting the obvious Cl2 bump, decided to extrapolate their curve beyond 310 nm by using a straight line in a plot of log(α) vs wavelength. However, none of the colored lines in Figure 4 is a good straight line when plotted in this fashion. Also there is no real theoretical justification for a log-linear extrapolation. The decision of how much Cl2 spectrum to subtract comes down to a personal choice.

We have used a different approach to the problem of spectral subtraction by applying the method of least squares. This method requires an analytical expression for the unknown spectrum and either analytical expressions or recorded spectra for the impurities. For the spectra obtained using method 1, the only obvious impurity was Cl2. Maric et al. have found that an expression using two Gaussian-like terms is sufficient to describe the Cl2 spectrum.28,29 When adjusted to a temperature of −80 °C using their recommended temperature dependence, the cross sections

\[
\text{ClO}^* + O_3 \rightarrow \text{OCIO} + O_2 \quad (12)
\]
as a function of wavelength become

\[
\sigma(\text{Cl}_2) = 26.88 \exp(-96.0[\ln(329.5/\lambda)]^2) + 0.918 \exp(-88.7[\ln(406.5/\lambda)]^2) \quad (13)
\]

where the units of \(\lambda\) are nm and the units of \(\sigma\) are \(10^{-20}\) cm\(^2\) molecule\(^{-1}\); these units will be used throughout this report. Measurements on a dilute Cl\(_2\)/He mixture at \(-80^\circ\text{C}\) showed excellent agreement with eq 13.

Maric and co-workers have argued that Gaussian-like expressions similar to those used in eq 13 are the best representation for electronic transitions from bound lower states to repulsive excited states.\(^{28,29}\) In addition to Cl\(_2\), these expressions have been used to describe spectra of Br\(_2\),\(^{30}\) BrCl,\(^{29}\) HOBr,\(^{31}\) CF\(_3\)I,\(^{32}\) and peroxy radicals.\(^{33-36}\) Because the electronic transition in ClOOCl is also expected to be of the bound-to-repulsive type, we tried fitting spectra by using a combination of one Gaussian-like term and the above expression for \(\sigma(\text{Cl}_2)\). The resulting fit was very poor, obviously not the correct form for the ClOOCl spectrum. However, with two Gaussian-like terms, the fit to the measured absorbances, \(A(\lambda)\), was excellent. The analytical expression used was eq 14, where the least-squares method fits a total of eight parameters, three for each Gaussian (\(a\), \(w\), and \(L\)), one \((y)\) to match the amount of Cl\(_2\) present, and a constant term, \(B\), to allow for any nonzero baseline. All least-squares analyses of data were done using the program PSI Plot.

\[
A(\lambda) = a_1 \exp(-w_1[\ln(L_1/\lambda)]^2) + a_2 \exp(-w_2[\ln(L_2/\lambda)]^2) + y\sigma(\text{Cl}_2) + B \quad (14)
\]

Because we have made no measurements of absolute cross sections, it was necessary to scale our absorbances to previous absolute measurements to report cross sections as a function of wavelength. We have followed the current JPL-NASA recommendation\(^{18}\) that the peak cross section at 245 nm is \(640 \times 10^{-20}\) cm\(^2\) molecule\(^{-1}\). This conversion was done using eq 15,

\[
\sigma(\text{total}) = \frac{640(A(\lambda) - B)}{(A_{\text{max}} - B)} \quad (15)
\]

where \(A_{\text{max}}\) represents the maximum numerical value of absorbance in a spectrum, observed to be at 244.7 \pm 0.3 nm, and the fitted value for \(B\) has been subtracted to eliminate any nonzero baseline. As an example of this procedure, the five spectra in Figure 2 have been replotted as \(\sigma(\text{total})\) in Figure 5. It should be noted that the short wavelength portion of these spectra overlap very well when fitted to the same maximum cross section.

These cross sections, all in units of \(10^{-20}\) cm\(^2\), could be refitted by least squares using eq 16. The amplitude factors, \(C_1\) and \(C_2\), are in the same units as \(\sigma\), and \(x\) now represents the molecular ratio of Cl\(_2\) to ClOOCl. As expected, the values for \(w_1\), \(L_1\), \(w_2\), and \(L_2\) are identical whether fitting \(A(\lambda)\) to eq 14 or \(\sigma(\text{total})\) to eq 16. The ratios of \(C_1/\sigma_1\), \(C_2/\sigma_2\), and \(x/y\) are all equal to the scaling factor in eq 15, namely \(640/(A_{\text{max}} - B)\). The averages of the least-squares parameters for 57 spectra, including the five shown in Figure 5, are reported in Table 1. These 57 spectra, all taken during the same run, were the most consistent of the spectra taken using method 1. These spectra returned constant Gaussian parameters as the trap was warmed, indicating
TABLE 1: Average Gaussian Parameters and Their Standard Deviations Calculated by Least-Squares Fitting of Eq 16 to 57 Spectra Having $A_\text{max}$ Greater Than 1

<table>
<thead>
<tr>
<th>parameter</th>
<th>average</th>
<th>standard deviation</th>
<th>observed range</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1/10^{-20}$ cm$^2$</td>
<td>359.5</td>
<td>0.52</td>
<td>±20</td>
</tr>
<tr>
<td>$w_1$</td>
<td>294.0</td>
<td>0.85</td>
<td>±5</td>
</tr>
<tr>
<td>$L_1/\text{nm}$</td>
<td>244.1</td>
<td>0.01</td>
<td>±0.1</td>
</tr>
<tr>
<td>$C_2/10^{-20}$ cm$^2$</td>
<td>284.6</td>
<td>0.53</td>
<td>±20</td>
</tr>
<tr>
<td>$w_2$</td>
<td>51.1</td>
<td>0.39</td>
<td>±1.5</td>
</tr>
<tr>
<td>$L_2/\text{nm}$</td>
<td>248.5</td>
<td>0.027</td>
<td>±1.5</td>
</tr>
</tbody>
</table>

*These spectra were all taken during 1 day’s run using method 1 to generate dimer. As explained in the text, the last column indicates the approximate range of parameter values observed on four other runs.

Figure 6. Deviations between the measured and fitted cross sections for three of the spectra of Figure 5. The color coding is the same in both figures.

that no compounds other than ClOOCl and Cl$_2$ were present. For these 57 spectra, the baseline term, $B$, ranged from $\pm0.018$ to $\pm0.011$. Fits done with nonconstant baselines, either linear or quadratic in wavelength, gave slightly smaller $\chi^2$ values, but the resulting Gaussian parameters were less consistent than with a constant baseline. Because the largest covariance in the fits was between the baseline ($B$) and the amount of Cl$_2$ present ($x$ or $y$), and because blank runs showed very constant baselines for wavelengths longer than 290 nm, these multiparameter baselines were not used. Confidence in the use of a constant $B$ was achieved by its ability to mimic the increased cycling of the room temperature.

The three dotted lines in Figure 5 show the three terms in eq 16 for the least-squares fit to the lowest (green) spectrum. The deviations between the sum of the three dotted lines and the experimental spectrum are shown in Figure 6 as green circles. Most of these deviations are small, less than $1 \times 10^{-20}$ cm$^2$, but the pattern of deviations is reproducible as can be seen in Figure 6 for three different spectra. The source of these deviations is not known, but they might be due to the fact that only about 50% of the ClOOCl molecules at 193 K are in their lowest vibrational state. The vibrationally excited molecules will have Franck–Condon factors that differ from those of the ground state and this can influence the absorption spectrum; eq 16 does not address different Franck–Condon factors in the transition.

Using the fitted parameter $x$ in eq 16, it is possible to subtract out the contribution of $\sigma$(Cl$_2$) from each spectrum. This has been done in Figure 7 for the same five spectra shown in Figure 5; the lowest curve results from plotting individual points. The overlap of all five curves is excellent, diverging only when the cross sections approach $1 \times 10^{-20}$ cm$^2$. This lower curve is the best current measurement of the spectrum of pure ClOOCl. Equation 17, with parameters taken from Table 1, is the algebraic form of this ClOOCl spectrum, where “2Gauss”

$$\sigma(\text{2Gauss}) = (359.5) \exp(-294[\ln(244.1/\lambda)]^2) + \exp(-51.1[\ln(248.5/\lambda)]^2)$$  

indicates the use of two Gaussian functions.

For some runs there were drifts of the parameters as the dimer signal grew and then decreased. The limits given in the “observed range” column in Table 1 reflect these variations. These variations were not independent; they covaried so that the overall shape of the absorption changed only slightly. For example, if $C_1$ drifted, $C_2$ also changed in such a way that the sum $C_1 + C_2$ remained almost constant. Similarly, if $C_1/C_2$ increased (or decreased), both $L_2$ and $w_2$ increased (or decreased). The order of the ± or $\pm$ signs in Table 1 is important, and the variations need to be applied simultaneously. These variations in parameters affect the short wavelength cross sections more than those at longer wavelengths.

The cross sections for ClOOCl from this study are given in Table 2. These values have been calculated using eq 17, with small corrections for the average deviations from that equation, as shown in Figure 6. The precision of the cross sections in Table 2, as judged by the reproducibility of the 57 spectra that were used to derive the “average” parameters in Table 1, varies with wavelength. For the short wavelength region, 226–290 nm, a variation of $\pm0.2\%$ was observed, while for wavelengths longer than 290 nm the standard deviations were approximately $\pm0.2 \times 10^{-20}$ cm$^2$.

For the four runs made on other days, which resulted in the “observed range” of parameters listed in Table 1, the uncertain-
ties were larger, especially at shorter wavelengths. The observed deviations from eq 17 were up to ±9% at 226 nm, ±6% at 230 nm, decreasing to about ±1% at 240, and zero at 244.7 nm, because each spectrum was normalized there. Deviations increased to longer wavelengths, up to ±3% in the 270–310 nm range, and ±1 × 10⁻²⁰ cm² at longer wavelengths. The reasons for these variations in cross sections are not known, but certainly a drifting baseline is responsible for some of the deviations at long wavelengths where the absorbances were small. The deviations at the shorter wavelengths are probably due to impurities being present at low enough concentrations so that they are not recognized; evidence for this was the observation that in these runs the fitted parameters drifted as the absorbance changed.

Analysis of the spectra recorded using method 2 to generate the dimer were complicated by the presence of OCIO and Cl₂O₃ as well as Cl₂. To apply the method of least squares, it is necessary to have spectra of all of these contaminants. The OCIO was synthesized by the standard method, passing a 1% mixture of Cl₂ in He through a column containing glass beads and fresh Na(ClO₂). Smaller amounts of OCIO diluted in He flowed through the absorption cell cooled to dry ice temperature. The measured absorbance values were scaled to the absolute cross sections of Wahner et al. (1 nm resolution, 204 K) for use in the least-squares calculations. The absolute magnitude of these cross sections is not critical for our procedure because the values used to fit the spectra are also used to subtract out the contributions of OCIO.

Finding a reference spectrum for Cl₂O₃ was more difficult. There is general agreement on the approximate shape of the UV spectrum, with a strong maximum at about 265 nm, but there are serious disagreements about the cross sections, especially at the longer wavelengths. Some of our spectra using method 2 appeared to be mostly Cl₂O₃ (e.g., spectrum 59 in Figure 3), but they still contained unknown contributions of ClOCl and Cl₂. For the least-squares fitting, we have used the spectra of Burkholder et al. because this seemed to be most consistent with our observations in Figure 3.

Using the reference spectra for Cl₂, OCIO and Cl₂O₃, least-squares fits to the experimental spectra were attempted using an equation similar to eq 16, but with two additional fitted variables for the contributions due to OCIO and Cl₂O₃. There were now ten variables to be determined, three for each Gaussian, one each for contributions of Cl₂, OCIO, and Cl₂O₃, and one baseline term. For the spectra with only small amounts of Cl₂O₃, which were most useful for determining the long wavelength part of the dimer spectrum, the fits converged slowly or not at all, and the fitted constants were inconsistent from spectrum to spectrum. The main trouble appeared to be the large covariance between the coefficient for the amount of Cl₂O₃ and the parameters of the second (longer wavelength) Gaussian for ClOCl. A small bulge on the long wavelength side of the dimer spectrum (e.g., spectrum 36 in Figure 3) can be fit by a small contribution of Cl₂O₃, or by increasing the amplitude and width of the second Gaussian, or by a combination of both. Because of the convergence difficulties and the inconsistencies, this approach was abandoned.

The main purpose of using method 2 is to establish if the dimer spectrum consists of just the two Gaussians determined using method 1, or whether there is an additional electronic transition that looks so similar to the chlorine spectrum that it can be mistaken for a Cl₂ impurity. Instead of attempting to redetermine the six parameters of the two Gaussians, we have applied eq 18 to fit the absorbances in method 2 spectra. Here

\[
A(\lambda) = d_1\sigma(2\text{Gauss}) + d_2\sigma(\text{Cl}_2\text{O}_3) + d_4\sigma(\text{OCIO}) + d_5\sigma(\text{Cl}_2) + B \tag{18}
\]

\(\sigma(2\text{Gauss})\) is given by eq 17, the cross sections for Cl₂ are from eq 13, and the cross sections for OCIO and Cl₂O₃ are represented by columns of numbers in the least-squares fitting routine. Least-squares fitting of method 2 spectra to eq 18 converged rapidly.

There are two complications in applying eq 18 to the spectra of method 2. Because the amount of ClOCl collected using method 2 was considerably smaller than that from method 1, the maximum absorbances were less, typically 0.5 instead of 1.5–2.5. The region of critical interest is for \(\lambda > 300\) nm, which then involved absorbances of 0.05–0.01. Also, the amounts of Cl₂ were smaller in method 2 and, consequently, the covariance

<table>
<thead>
<tr>
<th>(\lambda)</th>
<th>(\sigma(\text{Cl}_2\text{O}_3))</th>
<th>(\lambda)</th>
<th>(\sigma(\text{Cl}_2\text{O}_3))</th>
<th>(\lambda)</th>
<th>(\sigma(\text{Cl}_2\text{O}_3))</th>
<th>(\lambda)</th>
<th>(\sigma(\text{Cl}_2\text{O}_3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>355</td>
<td>0.63</td>
<td>354</td>
<td>0.65</td>
<td>353</td>
<td>0.67</td>
<td>352</td>
<td>0.70</td>
</tr>
<tr>
<td>351</td>
<td>0.74</td>
<td>350</td>
<td>0.79</td>
<td>349</td>
<td>0.84</td>
<td>348</td>
<td>0.91</td>
</tr>
<tr>
<td>347</td>
<td>0.98</td>
<td>346</td>
<td>1.05</td>
<td>345</td>
<td>1.14</td>
<td>344</td>
<td>1.23</td>
</tr>
<tr>
<td>343</td>
<td>1.35</td>
<td>342</td>
<td>1.45</td>
<td>341</td>
<td>1.58</td>
<td>340</td>
<td>1.72</td>
</tr>
<tr>
<td>339</td>
<td>1.88</td>
<td>338</td>
<td>2.06</td>
<td>337</td>
<td>2.26</td>
<td>336</td>
<td>2.49</td>
</tr>
<tr>
<td>335</td>
<td>2.75</td>
<td>334</td>
<td>3.02</td>
<td>333</td>
<td>3.33</td>
<td>332</td>
<td>3.66</td>
</tr>
<tr>
<td>331</td>
<td>4.02</td>
<td>330</td>
<td>4.41</td>
<td>329</td>
<td>4.85</td>
<td>328</td>
<td>5.34</td>
</tr>
<tr>
<td>327</td>
<td>5.86</td>
<td>326</td>
<td>6.43</td>
<td>325</td>
<td>7.05</td>
<td>324</td>
<td>7.70</td>
</tr>
<tr>
<td>323</td>
<td>8.40</td>
<td>322</td>
<td>9.15</td>
<td>321</td>
<td>10.0</td>
<td>320</td>
<td>10.8</td>
</tr>
<tr>
<td>319</td>
<td>11.8</td>
<td>318</td>
<td>12.8</td>
<td>317</td>
<td>13.8</td>
<td>316</td>
<td>15.0</td>
</tr>
<tr>
<td>315</td>
<td>16.2</td>
<td>314</td>
<td>17.5</td>
<td>313</td>
<td>18.9</td>
<td>312</td>
<td>20.4</td>
</tr>
</tbody>
</table>

*The units are nm for \(\lambda\) and \((10^{-20} \text{ cm}^2 \text{ molecule}^{-1})\) for \(\sigma\). The last digit for each cross section is of marginal significance. The precision of the cross section measurements is observed to be ±0.2% from 230 to 290 nm and ±0.2 × 10⁻²⁰ cm² at longer wavelengths. Because these cross sections have been scaled to the average of maximum absorbances of the cross section measurements are observed to be ±0.2% from 230 to 290 nm and ±0.2 × 10⁻²⁰ cm² at longer wavelengths, because each spectrum was normalized there.
between parameters \(d_1\) and \(B\) in eq 18 became quite large. This problem was minimized by a two-step procedure. First, eq 18 was fit to the full data set (1024 points) and the resulting coefficient \(d_2\) was used to subtract out the contribution of \(\text{Cl}_2\text{O}_3\). The resulting data set was then truncated to 511 points (\(\lambda > 290\) nm) and refit to eq 19, which is similar to eq 18 but without the term \(d_2\sigma(\text{Cl}_2\text{O}_3)\). The parameters \(d_1\) and \(d_3\) were similar in fitting eq 18 or 19, but the parameters \(d_4\) and \(B\) changed significantly.

\[
A(\lambda) = d_1\sigma(\text{2Gauss}) + d_3\sigma(\text{OCIO}) + d_4\sigma(\text{Cl}_2) + B
\]

(19)

As a test of the reasonableness of the fit, the terms \(d_1\sigma(\text{2Gauss})\), \(d_3\sigma(\text{OCIO})\), and \(B\) were subtracted from the truncated data set and the remainder was plotted as a function of wavelength. Using the results from fitting eq 19 to the truncated data set gave a weak spectrum with a maximum at 330 nm, consistent with the presence of \(\text{Cl}_2\) and the results of method 1. Applying the same stripping procedure to the results of fitting eq 18 to the full data set gave residuals that did not always look like \(\text{Cl}_2\), and in several cases resulted in negative absorbances. Use of the truncated data set and eq 19 appears to result in a baseline correction, \(B\), that is more realistic for the weak signals at long wavelengths.

Absorbances from method 2 were converted to cross sections using a procedure similar to that used for method 1. Although neither OCIO nor \(\text{Cl}_2\) absorb appreciably at 245 nm, \(\text{Cl}_2\text{O}_3\) does.\(^{40}\) Consequently, it was necessary to consider the contribution of \(\text{Cl}_2\text{O}_3\) to the maximum so that when its contribution is subtracted, the remaining spectrum has a maximum cross section of 640. Instead of eq 15, eq 20 was used to convert method 2 absorbances to cross sections, where \(d_2/\sigma_1\) represents the fitted molecular ratio of \(\text{Cl}_2\text{O}_3/\text{ClOOCl}\) using the full data set, 989 is the cross section of \(\text{Cl}_2\text{O}_3\) at 245 nm, and \(A(244.7)\) is the measured absorbance at 244.7 nm. Figure 8 shows an example of this procedure applied to a truncated spectrum.

\[
\sigma(\text{total}) = \frac{(640 + 989d_2/\sigma_1)(A(\lambda) - B)}{A(244.7) - B}
\]

(20)

Discussion

The current spectrum of ClOOCl reported in Table 2 agrees best with the spectrum reported previously by Huder and DeMore.\(^7\) Because both have been normalized to 640 at about 245 nm, they can be compared directly. The two spectra agree to within 1% from 240 to 260 nm but diverge at both shorter and longer wavelengths, disagreeing by 9% at 226 nm, 10% at 300 nm, and 30% at 310 nm. At each wavelength, the Huder and DeMore cross sections are larger than those in Table 2. At wavelengths longer than 310 nm, Huder and DeMore proposed a log-linear extrapolation that rapidly diverges from the values in Table 2, becoming 4 times larger by 340 nm. The cross sections reported by Burkholder et al.\(^5\) are even larger than those of Huder and DeMore in the region >245 nm; compared to Table 2, they are twice as large at 300 nm and more than 9 times larger at 340 nm. Because other literature values fall between those of Burkholder et al. and Huder and DeMore, it is clear that the \(\sigma(\text{ClOOCl})\) in Table 2 are significantly below the currently recommended values\(^{18}\) in the region of most importance to the atmosphere, namely for \(\lambda > 300\) nm.

Although there is general agreement in the literature on the features of the ClOOCl spectrum, with a peak near 245 nm and a tail to longer wavelengths, there is only modest agreement on the absolute cross sections. Cox and Hayman\(^5\) used mass balance to derive a cross section at the peak, \(\sigma_{\text{max}}\), of 640 ± 60 (all times 10\(^{-20}\) cm\(^2\)). DeMore and Tschuikow-Roux\(^8\) compared the loss of reactant \(\text{Cl}_2\text{O}\) with the formation of ClOOCl and concluded that \(\sigma_{\text{max}}\) was 680 ± 80. Burkholder et al.\(^5\) used mass balance to determine a \(\sigma_{\text{max}}\) of 650 with unsymmetrical error limits of +80 and −50. For the present study, we have decided to use the \(\sigma_{\text{max}}\) recommended by the JPL/NASA evaluation,\(^{18}\) namely 640, with the understanding that if future studies establish a more reliable value, all of our absolute cross sections should be scaled accordingly. The above error estimates suggest that the uncertainty in all of the cross sections in Table 2 may be as great as +20% or −10%.

Analysis of the spectra measured in this study suggests that the main ClOOCl absorption consists of two electronic transitions, one centered at 244.1 nm (5.08 eV) and the other at 248.5 nm (4.99 eV). Although the energies of the transitions are very similar, the widths of the bands differ by a factor of 2.5, which implies that the slopes of the excited-state potential energy surfaces (PES) differ significantly. One expects the broader band to be a transition to a steep PES because the Franck–Condon overlap will be large over a range of energies. Conversely, the narrower band would involve a flatter PES where good Franck–Condon overlap occurs only within a narrow energy range.

These observations are consistent with several ab initio calculations on ClOOCl. Stanton and Bartlett\(^{41}\) and also Peterson and Francisco\(^{42}\) find a total of eight allowed electronic transitions in the region below 6 eV. These eight are grouped into four pairs, with each pair having similar energies. The pairing occurs because the ClOOCl molecule has a \(C_\text{2}\) axis of symmetry and the excitations are largely to Cl–O antibonding \(\sigma^*\) orbitals. As a result, the excited-state wavefunctions need to be either
symmetric or antisymmetric with respect to the symmetry operation. The splittings between the pairs of symmetric/antisymmetric states in these two studies are calculated to be quite small, in the range 0–0.05 eV. These two studies also calculate oscillator strengths, and they agree that transitions to the third pair of states, \(4(1\text{~A})\) and \(3(1\text{~B})\), are the strongest.

For an absorption that can be fitted to the Gaussian function used here, it is possible to calculate the oscillator strength, \(f\), of the transition using eq 21, where \(e_0\) is the electric constant, \(m_e\) and \(e\) are the mass and charge of an electron, and \(c\) is the speed of light.\(^{29}\) Using the average parameters reported in Table 1 (\(\sigma_{\text{max}} = C_1\) or \(C_2\), \(w = w_1\) or \(w_2\), and \(\lambda_{\text{max}} = L_1\) or \(L_2\)), the oscillator strengths are calculated to be 0.017 and 0.033 for the 244.1 and 248.5 nm bands, respectively. These \(f\) values are similar to those calculated for the \(4(1\text{~A})\) and \(3(1\text{~B})\) states.

Two other theoretical calculations reach slightly different conclusions. Toniolo et al. and Kaledin and Morokuma agree that at least one of the transitions to the third pair of states is strong,\(^{43–45}\) but they both find that the splitting between the \(4(1\text{~A})\) and \(3(1\text{~B})\) states is larger, approximately 0.4–0.6 eV. The PES calculated by Toniolo et al. (Figure 2 of ref 44) indicates several avoided crossings in the vicinity of 5 eV, which give rise to quite different slopes in the excited states. This could account for the different band widths observed. These theoretical results are collected in Table 3 together with the experimental values of the present study. While none of the ab initio studies give perfect agreement with the observed spectra, taken together they provide good theoretical support for the present interpretation that the ClOOCI spectrum consists of two electronic transitions having similar energies but different band widths.

The ClOOCI cross sections of most importance to modeling atmospheric ozone concentrations are those at wavelengths longer than 300 nm. This is just the region that suffers the most interference in the above spectra. Especially troubling is the observation of method 1 spectra that although the Cl\(_2\)/ClOOCl interference in the above spectra. Especially troubling is the atmospheric ozone concentrations are those at wavelengths having similar energies but different band widths. These theoretical calculations have provided good theoretical support for the present interpretation that the ClOOCl spectrum consists of two electronic transitions, and they contribute no more than about 8 units at 330 nm, because \(\sigma(2\text{Gauss})\) contributes about 5 to this upper limit of 13. It is concluded that as an upper limit, the cross sections of ClOOCI at wavelengths longer than 310 nm cannot be much larger than the extrapolation suggested by Huder and DeMore.\(^7\)

Two observations are important in Figure 8. First, when all the known impurities are subtracted, the resulting red line agrees well with \(\sigma(2\text{Gauss})\) derived from method 1; the experimental data are compatible with the assumptions underlying eqs 18 and 19. Second, the results of subtracting out the contributions of Cl\(_2\)O\(_3\), which is very minor in this region, and OCIO, which can be done with the least uncertainty because of the structured nature of its spectrum, should give an upper limit to the cross sections for ClOOCI. As can be seen, the blue line in Figure 8 falls close to the extrapolated cross sections suggested by Huder and DeMore. If ClOOCI has additional electronic transitions in this region, they contribute no more than about 8 units at 330 nm, because \(\sigma(2\text{Gauss})\) contributes about 5 to this upper limit of 13. It is concluded that as an upper limit, the cross sections of ClOOCI at wavelengths longer than 310 nm cannot be much larger than the extrapolation suggested by Huder and DeMore.\(^7\)

The molecular ratio of Cl\(_2\) to ClOOCI suggested by the analysis in Figure 8, 0.28, is a factor of 3–4 lower than the limiting values observed using method 1. It is reasonable that there is some Cl\(_2\) present when using method 2 to generate ClOOCI. Modeling showed that even if the gas mixture was exposed to a single laser pulse, this ratio would be at best about 0.06, due to the overlap between the decaying Cl concentration and the growing ClOOCI concentration. Because of diffusion and non-plug flow at the exit of the photolysis cell, some dimer must remain in the cell when the next laser pulse arrives, allowing reaction 5 to generate additional Cl\(_2\). And, finally, ClOOCI is a fragile molecule, prone to photolysis by the analysis beam and to decomposition on the walls of the absorption cell during its 90 s residence time. We conclude that Figure 8 is strong support for assigning the spectrum of ClOOCI in this wavelength region to \(\sigma(2\text{Gauss})\).

Another approach to the question of additional electronic transitions of ClOOCI is to extend the absorbance measurements to longer wavelengths to establish a more reliable baseline. Figure 9 shows three spectra obtained using method 1. The absorbances have been converted to cross sections by using the measured absorbances at 281 and 330 and assuming that only \(\sigma(2\text{Gauss})\) and \(\sigma(\text{Cl}_2)\) contribute. The resulting molecular ratios of Cl\(_2\)/ClOOCI are 4.46, 1.86, and 1.13 for the top three curves. Subtracting out each of the contributions of chlorine results in the lowest curve, which is actually three overlapping curves. This lower curve coincides with \(\sigma(2\text{Gauss})\), shown as diamonds, within the experimental uncertainties. Additional spectra measuring out to 498 nm show no absorptions except for the long wavelength tail of Cl\(_2\). If there is another electronic transition of ClOOCI in this wavelength region, it must have a shape that is essentially identical to that of Cl\(_2\). The more likely interpretation, in our opinion, is that there is no significant ClOOCI absorption in the long wavelength region except for the tail of \(\sigma(2\text{Gauss})\).

It should be noted here that the middle (blue) spectrum in Figure 9 is based on the same data set as the black spectrum in Figure 4. The blue dots in Figure 9, which result from subtracting 1.86 times \(\sigma(\text{Cl}_2)\) from the blue spectrum, correspond

### Table 3: Comparison of Theoretical Predictions of Energies and Oscillator Strengths of the Third Pair of States with Present Experimental Values

<table>
<thead>
<tr>
<th>references</th>
<th>energies/eV</th>
<th>oscillator strengths, (f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stanton and Bartlett(^{41})</td>
<td>5.42, 5.41</td>
<td>0.014, 0.079</td>
</tr>
<tr>
<td>Peterson and Francisco(^{42})</td>
<td>5.82, 5.78</td>
<td>0.018, 0.092</td>
</tr>
<tr>
<td>Toniolo et al. (^{44})</td>
<td>5.36, 4.92</td>
<td>0.0027, 0.042</td>
</tr>
<tr>
<td>Kaledin and Morokuma(^{45})</td>
<td>5.22, 4.58</td>
<td>0.017, 0.032</td>
</tr>
<tr>
<td>present exptl values</td>
<td>5.08, 4.99</td>
<td>0.017, 0.032</td>
</tr>
</tbody>
</table>
closely to the next to lowest (brown) curve in Figure 4, which corresponds to subtracting the equivalent of 1.8 times \( \sigma(\text{Cl}_2) \) from the black spectrum. Thus the method of least-squares fitting of the data provides a quantitative answer to the question, posed earlier, of how much chlorine to subtract and it avoids the subjectivity of the manual subtraction method.

Atmospheric Implications

To assess the impact of the new chlorine peroxide cross sections, photolysis rates were calculated for the Arctic polar vortex, at a solar zenith angle of 86°, 20 km altitude, and \( \text{O}_3 \) and temperature profiles measured in March 2000. Figure 10 shows the calculated wavelength-dependent partial photolysis rates for this study compared to the work of Burkholder et al., Huder and DeMore, and the current NASA recommendation (JPL 2006). A comparison of these relevant cross sections is given in Figure S1 in the Supporting Information.

Figure 10 illustrates the importance of the long wavelength cross sections. The increasing magnitude of the solar flux at longer wavelengths makes an accurate determination of the increasingly small cross sections essential. The corresponding photolysis rates are given in Table 4, along with their ratios to the current determination.

The results of this study are in major disagreement with recent conclusions of various modeling and field work studies, which find good agreement only when using the extrapolated cross sections of Burkholder et al. The calculated photolysis rate differs between the two studies by a factor of about 9 (Table 4). This difference will be further enhanced at higher solar zenith angles. Because photolysis of ClOOCl is the rate limiting step in the loss of polar ozone, the adoption in atmospheric models of the cross sections determined in the present study will lead to a large reduction in the calculated chemical ozone depletion. New photolytic and/or reactive pathways will be required to obtain closer agreement between models and measurements.

Acknowledgment. The research described in this paper was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract to the National Aeronautics and Space Administration. We thank Ross Salawitch for emphasizing the importance of this problem and Trevor Ingham for sharing with us his attempts to freeze out and re-evaporate ClOOCl. We also thank Y. Yung, T. Canty, D. Natzie, and J. Kendall for assistance in carrying out and analyzing these experiments. This work was supported by the NASA Upper Atmosphere Research and Tropospheric Chemistry Programs.

Supporting Information Available: Figure showing the comparison of the ClOOCl cross sections most relevant for stratospheric modeling. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(15) Ingham, T.; Sander, S. P.; Friedl, R. R.; Pope et al.
(46) Salawitch, R. J.; Canty, T. Personal communication.