Photodissociation cross sections of ClOOCl at 248.4 and 266 nm

Chien-Yu Lien, Wei-Yen Lin, Hsueh-Ying Chen, Wen-Tsung Huang, Bing Jin, I-Cheng Chen, and Jim J. Lin

Articles you may be interested in

Can theory quantitatively model stratospheric photolysis? Ab initio estimate of absolute absorption cross sections of ClOOCl
J. Chem. Phys. **133**, 174303 (2010); 10.1063/1.3499599

Photodissociation dynamics of Cl N 3 at 193 nm
J. Chem. Phys. **125**, 224304 (2006); 10.1063/1.2400854

An ab initio direct-trajectory study of the photodissociation of ClOOCl
J. Chem. Phys. **113**, 5750 (2000); 10.1063/1.1290606

The ultraviolet photodissociation of Cl 2 O at 235 nm and of HOCl at 235 and 266 nm
J. Chem. Phys. **109**, 1315 (1998); 10.1063/1.476682

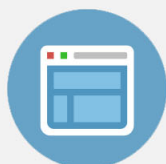Photodissociation of Cl 2 O at 248 and 308 nm
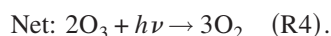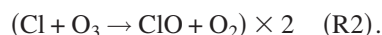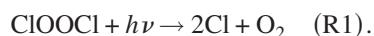J. Chem. Phys. **107**, 3337 (1997); 10.1063/1.474706

Photodissociation cross sections of ClOOCl at 248.4 and 266 nm

Chien-Yu Lien,[1] Wei-Yen Lin,[1,2] Hsueh-Ying Chen,[1] Wen-Tsung Huang,[1,2] Bing Jin,[1,3] I-Cheng Chen,[1] and Jim J. Lin[1,2,4,a)]

[1]*Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan*
[2]*Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan*
[3]*State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics,*
Chinese Academy of Science, Dalian, 116023, China
[4]*Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30010, Taiwan*

This study utilized a mass-resolved detection of ClOOCl to determine its photodissociation cross section, which is the product of the absorption cross section and dissociation quantum yield. An effusive molecular beam of ClOOCl was generated and its photodissociation probability was determined through measuring the decrease in the ClOOCl beam intensity upon laser irradiation. By comparing with a reference molecule, the absolute cross sections of ClOOCl were obtained without knowing its absolute concentration. The determined cross section of ClOOCl at 248.4 nm is $(8.85 \pm 0.42) \times 10^{-18}$ cm^2 at 200 K, significantly larger than previously reported values. The temperature dependence of the cross section was investigated at 248.4 nm in the range of 160–260 K; only a very small and negative temperature effect was observed. Because 248.4 nm is very close to the peak of the UV absorption band of ClOOCl, this work provides a new calibration point for normalizing relative absorption spectra of ClOOCl. In this work, the photodissociation cross section at 266 nm and 200 K was also reported to be $(4.13 \pm 0.21) \times 10^{-18}$ cm^2. © 2009 American Institute of Physics. [doi:10.1063/1.3257682]

I. INTRODUCTION

ClOOCl plays a crucial role in the chemical processes of the ozone hole formation.[1–7] It is known that the photolysis of ClOOCl generates Cl atoms (R1); Cl atoms quickly react with O_3 to form ClO radicals (R2). Two ClO radicals can then dimerize to form ClOOCl again (R3), thus destroying O_3 catalytically.

$$ClOOCl + h\nu \rightarrow 2Cl + O_2 \quad (R1).$$

$$(Cl + O_3 \rightarrow ClO + O_2) \times 2 \quad (R2).$$

$$ClO + ClO + M \rightleftarrows ClOOCl + M \quad (R3).$$

$$\text{Net: } 2O_3 + h\nu \rightarrow 3O_2 \quad (R4).$$

The photolysis rates of ClOOCl are important parameters that control the overall efficiency of the catalytic cycle (R1–R3). However, the large discrepancy in the laboratory data of the absorption cross sections of ClOOCl causes large uncertainty in estimating its photolysis rates. In particular, Pope *et al.*[8] recently reported spectroscopic measurements of ClOOCl with new methods of sample preparation and data analysis. The absorption cross sections reported by Pope *et al.* are much smaller than the 2006 JPL panel recommended values[9] in the critical wavelength region of 300–400 nm. If taking the data by Pope *et al.*,[8] a large portion of the observed ozone loss cannot be explained by current chemical models, which raises questions about the validity of either

the laboratory measurements or model calculations.[3,5] It is therefore extremely important to have accurate laboratory data to resolve the discrepancy and narrow down the uncertainties of the ClOOCl photolysis rates.

It is difficult to prepare a pure ClOOCl sample at a high enough concentration for an absorption measurement. Although many laboratories[2,7,8,10–14] measured the absorption cross sections of ClOOCl, difficulties of subtracting the impurity contributions from the raw spectra may result in larger error bars in the determination of the ClOOCl cross sections. The majority of the ClOOCl spectroscopic studies estimated the concentrations of absorbing species by mass balance. The use of mass balance was mainly based on spectral measurements of the reactants, products, and side products in the synthesis/absorption cell. Only by spectral measurements, it is difficult to estimate accurately the concentrations of all the absorbing species in the case of ClOOCl studies because the spectra of ClOOCl and possible impurities (Cl_2, Cl_2O, etc.) are quite broad and nearly featureless. Uncertainties in the reaction rate constants and possible unknown side reactions might introduce further complications.

Very recently, we reported a method which utilizes mass-selected detection to circumvent the impurity interference.[15] We form an effusive ClOOCl molecular beam and measure the molecular beam intensity before and after the laser irradiation with a mass detector. After photodissociation, the ClOOCl molecular beam is depleted. The probability of photodissociation is proportional to the laser fluence, absorption cross section, and dissociation quantum yield. Absolute cross sections can then be obtained by comparing the molecular depletion signals of ClOOCl with those of a reference mol-

---

a)Author to whom correspondence should be addressed. Electronic mail: jimlin@gate.sinica.edu.tw.

ecule of which the absorption cross sections and dissociation quantum yield are well known. Our reported cross sections of ClOOCl at 308 and 351 nm indicate that higher atmospheric photolysis rates are more reasonable, which is also in line with the observed ClO/ClOOCl concentration ratios and ozone loss rates.[3,5,6]

Instead of investigating the absolute absorption cross sections of ClOOCl, a number of groups only measured relative absorption spectra and normalized their data to the cross section value at 245 nm,[9] the peak of the UV absorption band. As mentioned above, it is difficult to estimate the concentrations of ClOOCl accurately, obstructing precise determination of the absolute peak cross section. Therefore, it is important to revisit the absolute absorption cross section of ClOOCl near the spectral peak.

It is worth mentioning that von Hobe *et al.*[16] reported an absorption spectrum of a "pure" ClOOCl sample which was prepared in a neon matrix at a low temperature of 6 K. The authors performed a careful impurity check with infrared absorption and Raman scattering spectroscopy. Their results confirm that the method 1 reported by Pope *et al.*[8]   [$Cl_2 + h\nu \rightarrow 2Cl$; $Cl + O_3 \rightarrow ClO + O_2$; $2ClO + M \rightarrow ClOOCl + M$; $ClOOCl_{(gas)} \rightarrow ClOOCl_{(solid)} \rightarrow ClOOCl_{(gas)}$] is efficient in producing ClOOCl; the only significant impurity is Cl_2. Possible isomers of Cl_2O_2, like $ClClO_2$ and ClO-ClO, have not been observed. They utilized a low temperature evaporation method to remove the Cl_2 impurity and were able to measure the absorption spectrum of pure ClOOCl. However, the absolute amount of ClOOCl in the matrix sample was unknown, hindering the determination of the absolute absorption cross sections. In addition, based on analysis on a number of reported spectra, the authors suggested that the issue of the absolute cross section should be revisited.

In this work, we report the absolute photodissociation cross sections of ClOOCl at 248.4 and 266 nm using molecular beams with mass detection. Calibrated with the well-known absorption cross sections of ozone, the cross sections of ClOOCl were determined with small error bars. These results may offer new calibration points for normalizing the relative absorption spectra of ClOOCl.

II. EXPERIMENTAL

The experimental apparatus has been described elsewhere.[15,17] Therefore only the relevant setup is given here. The ClOOCl sample was synthesized following the method 1 reported by Pope *et al.*[8] Higher chlorine oxides (e.g., Cl_2O_3) were not observed in the mass scan.[15] The ClOOCl was trapped in a fused silica tube at a low temperature around 150 K. Upon slowly warming up the trap, the solid ClOOCl evaporated, and then an effusive molecular beam of ClOOCl was formed by allowing the low pressure sample to flow through a capillary array (five square holes of 0.5×0.5 mm^2) made of fused silica. The sample pressure was controlled by the trap temperature to ensure an effusive flow, in which the gas mean free path exceeds the nozzle dimensions and the velocity distribution does not depend on the pressure. In such an effusive molecular beam, the mol-

ecules were in thermal equilibrium with the wall. Therefore, the sample temperature mentioned afterwards is the nozzle temperature.

The molecular beam was chopped, collimated, irradiated by an excimer laser beam (KrF, 248.4 nm, 75 Hz; Lambda Physik, LPX210i) or a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser beam (266 nm, 30 Hz; Spectra Physics, GCR290), and eventually monitored with a time-resolved quadrupole mass spectrometer,[17] which utilized electron impact as the ionization method. The repetition rate of the molecular beam pulses was 150 Hz in the case of excimer laser and 90 Hz in the case of Nd:YAG laser. The laser pulse energy was simultaneously monitored by a pyroelectric energy meter (Gentec-EO, QE25) and a thermopile powermeter (Gentec-EO, UP25N-100H, linearity better than 2.5%).

The ozone sample was synthesized by flowing O_2 through a commercial ozonizer, concentrated with a silica gel trap at dry ice temperature, and then stored in a stainless steel cylinder kept at a low temperature of about 190 K. The ozone flow was controlled by a needle valve. Low backing pressure (<0.1 torr) of O_3 was used to generate an effusive molecular beam of O_3. The O_3 molecular beam was very similar to the ClOOCl molecular beam.

III. RESULTS

Under our experimental conditions in which the number of photons greatly exceeds the number of molecules, an alternative form of Beer's law can be written as

$$\ln\frac{N_0}{N} = I\sigma\phi, \tag{1}$$

where N_0 and N are the number of the molecules before and after the laser irradiation, respectively. I is the laser fluence in number of photons per unit area, σ is the absorption cross section, and ϕ is the dissociation quantum yield. By comparing the photodepletion signal of ClOOCl with that of a reference molecule, it only requires the ratio of the laser intensities to obtain the cross section ratio, as in Eq. (2).

$$\frac{[\sigma\phi]_{ClOOCl}}{[\sigma\phi]_{ref}} = \frac{I_{ref}}{I_{ClOOCl}} \frac{\ln\left(\frac{N_0}{N}\right)_{ClOOCl}}{\ln\left(\frac{N_0}{N}\right)_{ref}}. \tag{2}$$

In this work, we chose O_3 as the reference molecule. It is known that the Hartley band (200–300 nm) of O_3 originates from excitation of the strongly repulsive branch of the B state and the involved electronic states are either repulsive or excited above their thresholds.[18] As a result, the lifetimes of photoexcited ozone are short ($<$picosecond), leading to 100% dissociation.[18,19] A similar argument can be applied to ClOOCl because *ab initio* calculations[20–22] and molecular beam experiments[23] suggest fast dissociation. At 266 nm, we may use Cl_2O as a second reference molecule. The near ultraviolet photodissociation of Cl_2O has been investigated in molecular beams[24–27] and in a gas cell;[28] the results indicate unity dissociation yield under low pressure conditions.
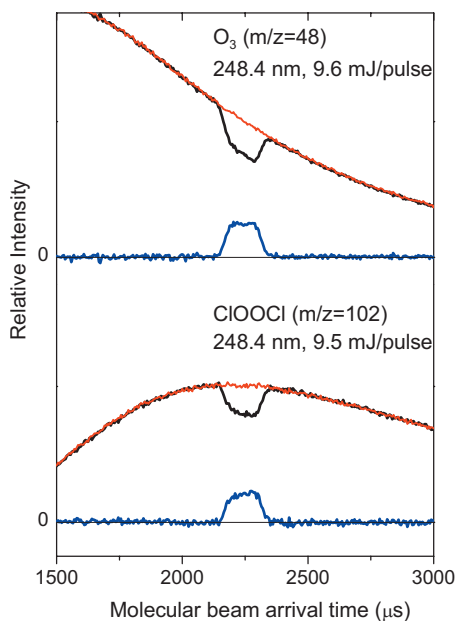
FIG. 1. Intensity profiles of the molecular beams showing the photo-depletion signals at $T = 200$ K. Red and black lines are the molecular beam signals before and after laser irradiation; the blue line is the difference. The laser delay time and spot size were the same for ClOOCl and O_3.
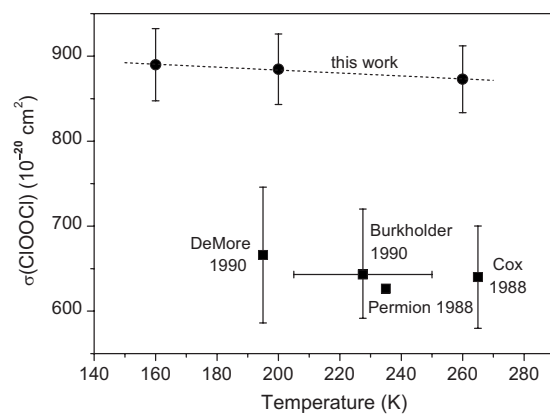

FIG. 2. Comparison of the available absolute cross sections of ClOOCl at 248.4 nm (this work with 1 sigma error bars and Refs. 2, 10, 11, and 13 with the quoted error bars).

Figure 1 shows the molecular beam signals of ClOOCl and O_3 before and after laser irradiation. The experimental conditions for ClOOCl and O_3 were almost identical. In effusive molecular beams, the velocity distributions of ClOOCl and O_3 follow the Maxwell–Boltzmann distributions, such that the majority of O_3 molecules had shorter arrival times. Nevertheless, there was enough overlap in the velocity distributions of these two molecules. Because the intensity of the ClOOCl beam was weaker, the laser delay time was chosen to have a better signal-to-noise ratio in the ClOOCl measurements. The absolute cross sections of ClOOCl could be obtained by analyzing the data with Eq. (2).[15] The results are summarized in Table I.

Figure 2 shows a comparison of our results with the available absolute cross sections of ClOOCl at 248.4 nm. It is obvious that our measured cross sections are larger than all previously reported values. The reason of the discrepancy is not very clear at this point. As mentioned above, concentration estimation in spectroscopic measurements is difficult; it is likely that unknown side reactions lead to overestimates for the concentrations of ClOOCl and underestimates for its cross sections.

IV. POSSIBLE ERROR SOURCES

Our method does not require the knowledge of the absolute concentrations. The accuracy of our measurements is mainly limited by two factors: the energy stability of the pulsed photolysis laser beam and the accuracy of the reference cross sections. The cross sections of O_3 have been very well measured,[9] so we do not have to worry about the later one. Cl_2O can be a second reference molecule at 266 nm. In Table I, we can find that the cross section of O_3 is larger than that of ClOOCl by a factor of 2.23 at 266 nm, while Cl_2O has a smaller cross section than ClOOCl by a factor of 2.45. If the determined ClOOCl cross section is the same by using these two reference molecules, we may eliminate the possibility of any systematic error which is related to the magnitude of the cross sections. However, there are some variations for the cross sections of Cl_2O from different

TABLE I. Summary of the measured photodissociation cross sections of ClOOCl at 248.4 and 266 nm.

Wavelength (nm)	Temperature (K)	Cross section ratio $[\sigma\phi]_{ClOOCl}/[\sigma\phi]_{ref}$			σ_{ref} $(10^{-20}$ cm$^2)$	$[\sigma\phi]_{ClOOCl}$ $(10^{-20}$ cm$^2)$
		Mean value	Standard deviation[a] (%)	Error bar[a] (%)		
248.4	160	0.838	2.7	±4.8	1062[b]	890
	200	0.833	2.5	±4.7	1062[b]	885
	260	0.822	2.0	±4.5	1062[b]	873
266	200	0.449	3.0	±5.0	920[b]	413
	200	2.445	2.2	±4.6	161/168[c]	394/411

[a]Relative to the mean values. The error bar is 1 sigma (one standard deviation) which includes possible systematic errors.
[b]The reference molecule is O_3 at 200 K. The dissociation yield of O_3 is taken as unity. The absorption cross sections of O_3 are taken from the JPL 2006 values (Refs. 9, 29, and 30).
[c]The reference molecule is Cl_2O at 298 K. The Cl_2O cross section is taken as 161×10^{-20} cm^2 from the JPL 2006 value,[9] or 168×10^{-20} cm^2 from the average value of Refs. 31 and 32. The dissociation yield of Cl_2O is assumed to be unity.

references.[9,31-34] At 266 nm, the ClOOCl cross sections determined by using O_3 or Cl_2O as the reference molecule can be very similar ($<1\%$) or slightly different (5%), depending on the value of the Cl_2O cross section chosen (see Table I). Nevertheless, the determined ClOOCl cross sections by using O_3 and Cl_2O reference molecules are consistent within the error bar of the Cl_2O absorption cross section, indicating the related systematic error is insignificant. If the cross section of Cl_2O is revised in the future, the ClOOCl cross section at 266 nm should also be re-evaluated.

Regarding laser stability, we repeated the experiment consecutively for many ClOOCl/reference pairs (seven or more). The average effect of the laser stability would show up in the standard deviations of the cross section ratios, which are less than 3%. Other factors that may affect the accuracy are discussed below.

(i)   Molecular beam stability. The depletion measurements were performed in every other molecular beam pulse and accumulated for 100 000 or more laser shots to average out the fluctuation of the molecular beam which was in a time scale of minutes. In Fig. 1, the red and black lines overlap nicely outside the laser interaction region, indicating the molecular beam stability was good enough.

(ii)   Impurities and/or isomers. Von Hobe *et al.*[16] has done a nice work to demonstrate that ClOOCl is the only isomer formed when using Pope *et al.*'s method 1,[8] which is the same method for our sample preparation. Other impurities such as Cl_2, Cl_2O would not affect our results at all because of the mass-resolved detection.

(iii)   Clusters. Cluster formation is very unlikely in an effusive molecular beam. In addition, we checked the data under quite different backing pressures; very similar results were obtained, indicating the cluster contribution was negligible.

(iv)   Saturation effect. We checked the depletion signals at various laser fluences; the results are shown in Fig. 3. Nice linearity of the depletion signals $\ln(N_0/N)$ versus the laser fluences I was observed, indicating the saturation effect is not significant and the process observed is a single-photon process. To have a better sensitivity for the relative cross section ratio, the magnitudes of the depletion signals were controlled to be only modest $[\ln(N_0/N)<0.5]$. In addition, the cross section of ClOOCl at 248.4 nm is similar to that of O_3, such that the depletion signals of ClOOCl and O_3 are similar and any saturation effects would also be similar and be mostly canceled in the relative cross section determination. At 266 nm, the cross section of O_3 is larger than that of ClOOCl and the cross section of Cl_2O is smaller. In this case, we used a coated optics (Laseroptik GmbH, IVA266) to uniformly attenuate the laser intensities to have similar depletion percentages for the cases of ClOOCl versus O_3 and ClOOCl versus Cl_2O. In this way, any saturation effect would again be similar and thus be cancelled out in the relative cross section determination.
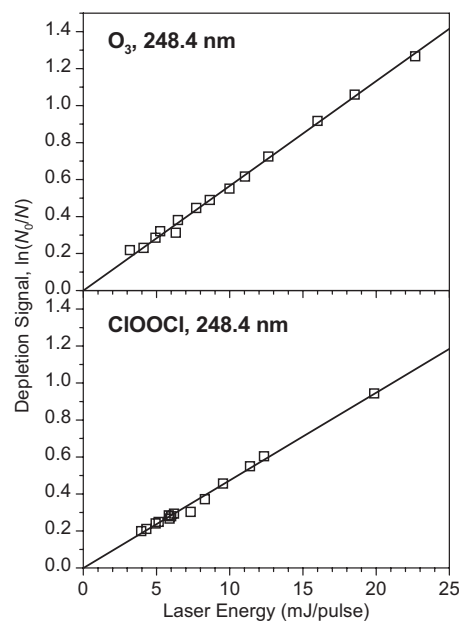

FIG. 3. Depletion signals of O_3 and ClOOCl at various laser fluence I. The laser fluence (linear to the laser pulse energy) was homogenously attenuated by a dielectric-coated optics.

For the final error bars, we think the contribution from possible systematic errors (e.g., nonlinearity of the laser power meter) should be less than 4%. Together with random errors that contribute to the standard deviation of the cross section ratio, we estimate the final percentage error by the expression:

$$\pm \sqrt{(s/\alpha)^2 + (0.04)^2} \times 100\%, \qquad (3)$$

where α is the cross section ratio and s is the standard deviation of α (See Table I).

A systematic error is more important than random errors. To ensure there is no hidden systematic error, great care was taken to ensure the ClOOCl experiment and reference experiment were done under identical or nearly identical conditions. Both molecular beams were effusive and generated from the same source (that is, they had the same spatial distribution). The same laser beam was used in both ClOOCl and reference experiments, except that the fluences were uniformly attenuated to have similar depletion percentages. Every experimental parameter was identical or very similar for the ClOOCl and reference experiments except one thing: the transmitted mass-to-charge ratio (m/z) of the quadrupole mass filter had to be set to m/z=102 for detecting ClOOCl, but m/z=48 for O_3 (m/z=86 for Cl_2O). To check the effect of the mass filter at different m/z setting, we repeated the experiment in which we detected the daughter ions of ClOOCl. The electron impact ionization process in the mass spectrometer usually introduces certain fragmentations (producing daughter ions). After correction for the ion flight times, a daughter ion should exhibit the same arrival time as its parent ion. Figure 4 shows the molecular beam signals at m/z=51(ClO^+), 67(ClO_2^+), 70(Cl_2^+), and 102($Cl_2O_2^+$) recorded under identical conditions. In an effusive molecular beam, the velocity distribution of a molecule is a function of
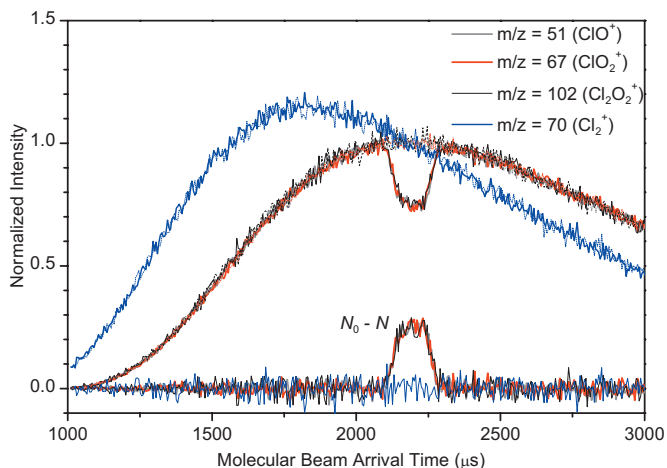
FIG. 4. Normalized molecular beam signals at different ionic masses recorded under nearly identical experimental conditions. The data at 248.4 nm and 200 K are shown. Dotted lines: laser off. Solid lines: laser on and the differences ($N_0 - N$).
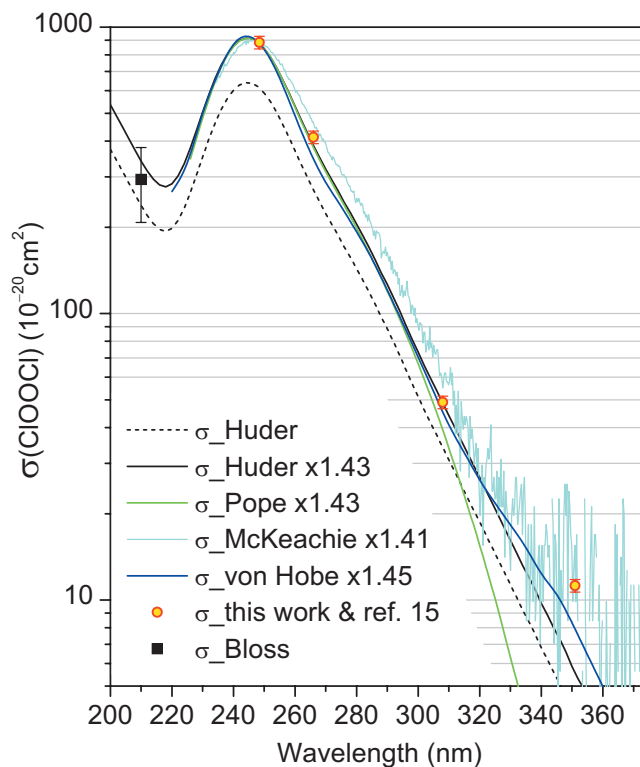

FIG. 5. Comparison of a few relative spectra of ClOOCl which are scaled to the measured cross section at 248.4 nm ($T = 200$ K) of this work. The temperatures for the data are: 195 K [Huder et al. (Ref. 12)], 193 K [Pope et al. (Ref. 8)], 223 K [McKeachie et al. (Ref. 14)], 4–6 K in a neon matrix [von Hobe et al. (Ref. 16)], 200 K (Ref. 15), and 183–245 K [Bloss et al. (Ref. 35)].

the temperature and the neutral mass, $v \propto \sqrt{T/m}$. The perfect overlap of the arrival time distributions at m/z=51, 67, and 102 indicate that these ions are originated from the same neutral molecule, ClOOCl. The m/z=70 signal shows shorter arrival times, indicating it is from a different molecule with a smaller mass. The ratio of the arrival times of the signals at m/z=70 and 102 is consistent with the expected mass ratio between Cl_2 and ClOOCl, confirming that Cl_2 is an inevitable impurity and the absorption cross section of Cl_2 at 248.4 nm is negligible. Most importantly, Fig. 4 shows that the laser depletion signals ($N_0 - N$) at m/z=51, 67, and 102 are almost identical, indicating the m/z setting on the quadrupole mass filter did not affect the cross section measurements at all.

The great similarity among the laser depletion signals at m/z=51, 67, and 102 also supports that there is only one isomer of Cl_2O_2 in the sample. A different isomer usually has different absorption cross section and exhibits different ion fragmentation pattern upon electron impact ionization. Therefore, if two isomers of Cl_2O_2 coexisted in the sample, different depletion signals would usually be observed at different daughter ions.

V. DISCUSSION

Figure 2 shows that there is a small temperature dependence for the cross sections of ClOOCl at 248.4 nm. To our knowledge, our method is the only one of which the error bars are small enough to reveal the temperature effect. At 248.4 nm, the temperature effect is slightly negative. Although differences in the cross sections at 160–260 K are smaller than the error bars, the trend of the temperature dependence is consistent in the measurements which were performed at various days. On the other hand, our previous results[15] indicate that the temperature effect of the ClOOCl cross section at 351 nm is positive and quite significant. *Ab initio* calculations for interpreting the temperature effects will be published elsewhere.

Figure 5 shows a few relative spectra[8,12,14,16] of ClOOCl which are rescaled to our measured cross section at

248.4 nm. Figure 5 also includes the result by Bloss et al.[35] in which the cross section of ClOOCl at 210 nm was determined from time-resolved evolution of ClOOCl absorption and ClO concentration. After the rescaling, the overall consistency among the scaled spectra and the molecular beam results at 266 and 308 nm is significantly improved, except that the spectrum by McKeachie et al.[14] is not consistent with the others[8,12,16] even for $\lambda < 300$ nm. Regarding the cross section at 351 nm, the error bars of the spectroscopic measurements may be still large. It is clear that Pope et al.[8] underestimated the cross sections at wavelengths longer than 300 nm. The ClOOCl sample prepared by Pope et al.'s method 1 contained a significant amount of Cl_2. Pope et al. seemed to subtract out the Cl_2 contribution too much, resulting in too small cross sections of ClOOCl for $\lambda > 300$ nm where Cl_2 absorbs significantly. Although von Hobe et al.[16] prepared a pure ClOOCl sample in a neon matrix, the light scattering from the solid matrix limited their sensitivity in the absorbance determination; as a result, the weak absorption of ClOOCl at $\lambda > 300$ nm could not been determined precisely. The reported relative error bars in the matrix-isolation measurements by von Hobe et al.[16] increase with wavelengths: +3%/−5% at 310 nm, +13%/−21% at 350 nm. It should be noted that although the neon matrix is believed not to significantly affect the UV absorption spectrum, the low temperature of the sample should be concerned because of the significant temperature effect of the cross sections, especially at long wavelengths.[15] The cross sections at

$\lambda > 310$ nm reported by Huder and DeMore[12] were based on an extrapolation of the cross sections at shorter wavelengths. The extrapolation may not well represent the cross sections at long wavelengths about 350 nm.

Because of the importance of the atmospheric photochemistry of ClOOCl, more data of higher accuracy are surely helpful. This work determined the cross sections of ClOOCl at 248.4 and 266 nm without the impurity interference. This experimental method does not require the knowledge of the absolute concentrations of ClOOCl and other impurities. By comparing with the O_3 molecule of which the absorption cross sections and dissociation quantum yields are well determined, the photodissociation cross sections of ClOOCl were determined precisely in this work. Because 248.4 nm is very close to the peak of the UV absorption band of ClOOCl, this work provides a new calibration point for normalizing relative absorption spectra of ClOOCl.

ACKNOWLEDGMENTS

[1] World Meteorological Organization (WMO), "Scientific Assessment of Ozone Depletion: 2006," WMO, Global Ozone Research and Monitoring Project Report No. 50, 2007.

[2] R. A. Cox and G. D. Hayman, Nature (London) **332**, 796 (1988).

[3] M. von Hobe, Science **318**, 1878 (2007).

[4] S. P. Sander, R. R. Friedl, and Y. L. Yung, Science **245**, 1095 (1989).

[5] M. von Hobe, R. J. Salawitch, T. Canty, H. Keller-Rudek, G. K. Moortgat, J. U. Grooss, R. Muller, and F. Stroh, Atmos. Chem. Phys. **7**, 3055 (2007).

[6] R. M. Stimpfle, D. M. Wilmouth, R. J. Salawitch, and J. G. Anderson, J. Geophys. Res. **109**, D03301 (2004).

[7] L. T. Molina and M. J. Molina, J. Phys. Chem. **91**, 433 (1987).

[8] F. D. Pope, J. C. Hansen, K. D. Bayes, R. R. Friedl, and S. P. Sander, J. Phys. Chem. A **111**, 4322 (2007).

[9] S. P. Sander *et al.*, "Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies," Jet Propulsion Laboratory Evaluation No. 15, 2006.

[10] J. B. Burkholder, J. J. Orlando, and C. J. Howard, J. Phys. Chem. **94**, 687 (1990).

[11] W. B. DeMore and E. Tschuikow-Roux, J. Phys. Chem. **94**, 5856 (1990).

[12] K. J. Huder and W. B. DeMore, J. Phys. Chem. **99**, 3905 (1995).

[13] T. Permien, R. Vogt, and R. N. Schindler, in *Mechanics of Gas Phase and Liquid Phase Chemical Transformations,* Air Pollution Report Vol. No. 17, edited by R. A. Cox (Environmental Research Program of the CEC, Brussels, 1988), pp. 149–153.

[14] J. R. McKeachie, M. F. Appel, U. Kirchner, R. N. Schindler, and Th. Benter, J. Phys. Chem. B **108**, 16786 (2004).

[15] H. Y. Chen, C. Y. Lien, W. Y. Lin, Y. T. Lee, and J. J. Lin, Science **324**, 781 (2009).

[16] M. von Hobe, F. Stroh, H. Beckers, T. Benter, and H. Willner, Phys. Chem. Chem. Phys. **11**, 1571 (2009).

[17] J. J. Lin, D. W. Hwang, S. Harich, Y. T. Lee, and X. Yang, Rev. Sci. Instrum. **69**, 1642 (1998).

[18] S. Yu. Grebenshchikov, Z.-W. Qu, H. Zhu, and R. Schinke, Phys. Chem. Chem. Phys. **9**, 2044 (2007).

[19] M. Brouard, A. Goman, S. J. Horrocks, A. J. Johnsen, F. Quadrini, and W.-H. Yuen, J. Chem. Phys. **127**, 144304 (2007).

[20] A. L. Kaledin and K. Morokuma, J. Chem. Phys. **113**, 5750 (2000).

[21] A. Toniolo, G. Granucci, S. Inglese, and M. Persico, Phys. Chem. Chem. Phys. **3**, 4266 (2001).

[22] K. A. Peterson and J. S. Francisco, J. Chem. Phys. **121**, 2611 (2004).

[23] T. A. Moore, M. Okumura, J. W. Seale, and T. K. Minton, J. Phys. Chem. A **103**, 1691 (1999).

[24] R. Aures, K. H. Gericke, C. Maul, G. Trott-Kriegeskorte, M. Kawasaki, and Y. Nakano, J. Chem. Phys. **117**, 2141 (2002).

[25] T. A. Moore, M. Okumura, and T. K. Minton, J. Chem. Phys. **107**, 3337 (1997).

[26] M. Roth, C. Maul, and K. H. Gericke, J. Phys. Chem. A **108**, 7954 (2004).

[27] Y. Tanaka, M. Kawasaki, Y. Matsumi, H. Fujiwara, T. Ishiwata, L. J. Rogers, R. N. Dixon, and M. N. R. Ashfold, J. Chem. Phys. **109**, 1315 (1998).

[28] S. L. Nickolaisen, C. E. Miller, S. P. Sander, M. R. Hand, I. H. Williams, and J. S. Francisco, J. Chem. Phys. **104**, 2857 (1996).

[29] J. Brion, A. Chakir, D. Daumont, J. Malicet, and C. Parisse, Chem. Phys. Lett. **213**, 610 (1993).

[30] J. Malicet, D. Daumont, J. Charbonnier, C. Parisse, A. Chakir, and J. Brion, J. Atmos. Chem. **21**, 263 (1995).

[31] H. D. Knauth, H. Alberti, and H. Clausen, J. Phys. Chem. **83**, 1604 (1979).

[32] L. T. Molina and M. J. Molina, J. Phys. Chem. **82**, 2410 (1978).

[33] C.-L. Lin, J. Chem. Eng. Data **21**, 411 (1976).

[34] G. D. Smith, F. M. G. Tablas, L. T. Molina, and M. J. Molina, J. Phys. Chem. A **105**, 8658 (2001).

[35] W. J. Bloss, S. L. Nickolaisen, R. J. Salawitch, R. R. Friedl, and S. P. Sander, J. Phys. Chem. A **105**, 11226 (2001).