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Received for review August 18, 1975. Accepted July 10, 1976. Financial support was provided by the National Science Foundation, the Monsanto Company, and Rice University.

Extinction Coefficients of Chlorine Monoxide and Chlorine Heptoxide

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The ultraviolet and visible extinction coefficients of Cl_2O and Cl_2O_7 were measured from 180 to 800 nm. The results are comparable in shape with literature values, but different in magnitude. The approximate extinction coefficients at the peaks of infrared absorption lines are also given.

Recent laboratory measurements and model atmospheric calculations (*8, 10, 13, 15*) point to possible adverse effects of chlorine-containing compounds in the stratosphere, particularly the destruction of ozone. As part of our study of chlorine–ozone chemistry (*8*), we have synthesized various chlorine oxides and have measured their extinction coefficients. Some of these oxides may be products or intermediates in the chlorine–ozone reaction system. We report here the extinction coefficients of Cl_2O and Cl_2O_7 in the ultraviolet, visible, and infrared spectral regions.

The extinction coefficients ϵ were defined as

$$\log I_0/I = \epsilon c l$$

where the concentration c is in moles/liter, the optical path length l is in cm, and $\log I_0/I$ is the absorbance.

The absorption spectra in the ultraviolet and visible regions were taken with a Cary 15 spectrophotometer (Applied Physics) using a quartz absorption cell of 10-cm path length. Wavelength calibrations were accomplished by using O_2 Shumann-Runge absorption bands (*1, 3*) near 180 nm, and mercury low pressure lines at longer wavelengths.

The ir absorption spectrum was recorded with a Perkin-Elmer Model 21 double beam spectrophotometer from 650 to 5000 cm^{-1} with resolution set at 927. At this setting, the spectral band-passes at different wavelengths are known and supplied by the manufacturer. The absorption cell was made of Pyrex glass with NaCl windows.

A fused quartz precision pressure gauge (Texas Instruments) was used for pressure measurements. The accuracy of the pressure measurements was better than 1%.

(A) Cl_2O

The chlorine monoxide was prepared (*11*) by slowly passing Cl_2 (Matheson research grade) through a reaction tube packed with mercuric oxide (Allied Chemical) which had been previously heated under vacuum to about 250 °C. Chlorine monoxide was condensed in a U-tube surrounded by a solid–liquid slurry of ethanol at ca. −117 °C. Trap-to-trap purification was performed at −117 °C to ensure purity. Since Cl_2O absorption extends into the visible region, special caution was taken to guard against possible photodecomposition resulting from exposure of the purified sample to room light. The purity of chlorine monoxide used in the extinction coefficient measurements was estimated from its stoichiometric ratio determination using pressure measurements before and after complete decomposition into Cl_2 and O_2. This ratio is 2:0.986 compared to the theoretical value of 2:1, indicating that Cl_2O purity is better than 98.5%. Cl_2O was readily decomposed into Cl_2 and O_2 by low pressure mercury lamp irradiation. The amount of Cl_2 produced after decomposition could also be calculated from its peak absorption near 330 nm, with known extinction coefficient (*12*), and the amount of O_2 could be roughly measured from the Shumann-Runge absorption bands. These absorption measurements confirmed the correctness of the aforementioned purity estimate. The absence of absorption characteristic of other chlorine oxides attested further to the purity of the Cl_2O.

Six samples of Cl_2O with pressures ranging from 1 to 165 Torr were used for extinction coefficient measurements. No absorption was recorded for wavelengths greater than 650 nm when the samples were scanned from 800 to 180 nm. Little effect was observed when Cl_2O samples were pressurized to 760 Torr with N_2 gas. These results in the uv and visible are summarized in Table I and plotted in Figure 1 along with the values of Goodeve and Wallace (*6*) and of Finkelnburg, Schumacher, and Stieger (*4*) for comparison. Although all three data sets are of the same shape, the differences in value at various wavelengths are apparent. The accuracy of the uv extinction coefficients measured in the present work is estimated to be about 5% in the region of main interest, between 180 and 330 nm. In the region between 330 and 470 nm it is 10% and at wavelengths greater than 470 nm, the uncertainty is probably greater than 10% because of weak absorption.

The ir approximate extinction coefficients at the peaks (*9*) of absorption lines along with their spectral band-passes are given in Table II. Again, little effect on extinction coefficient was observed when the Cl_2O sample was pressurized to 760 Torr with N_2 gas.

Table I. Extinction Coefficients (l. mol^{-1} cm^{-1}) of Cl_2O Uv and Visible Absorption

Wavelength (nm)	This work	Goodeve and Wallace	Finkelnburg, Schumacher, and Stieger
180	2030		
185	904		
190	444		
195	278		
200	175		
205	110		
210	60.9		
215	35.0		
220	24.2		29.7
225	33.3		
230	74.0	48.3	59.5
235	146		
240	257	150	223
245	381		
250	476	223	372
255	506		
260	478	223	372
265	423		
270	372		
275	338		
280	316	186	297
285	287		
290	256		
295	218		
300	176	130	186
305	135		
310	100		
315	70.6		
320	48.5	50.2	74.3
325	33.6		
330	23.5		
335	17.4		
340	10.8	14.9	10.4
345	7.50		
350	5.23		
355	3.96		
360	2.61	5.76	1.49
365	1.85		
370	1.46	3.72	0.60
375	1.41		
380	1.43	2.42	0.84
385	1.56		
390	1.74		
395	2.02		
400	2.29	2.97	4.65
405	2.61		
410	2.84	3.72	5.95
415	3.04		
420	3.15	4.27	4.65
425	3.10		
430	3.04		
435	2.85		
440	2.77	3.35	2.42
445	2.41		
450	2.13		
460	1.62	2.23	1.17
470	1.18		
480	0.80	1.23	0.74
490	0.60		
500	0.54	0.56	0.60
510	0.55		
520	0.56	0.47	0.65
530	0.62		
540	0.67	0.43	0.65
550	0.67		
560	0.58	0.41	0.41
570	0.53		
580	0.46	0.10	0.13
590	0.39		
600	0.32	0.04	0.07
610	0.25		
620	0.18		
630	0.09		0.09
640	0.04		
650	0.0		0.02
670	0.0		0.0

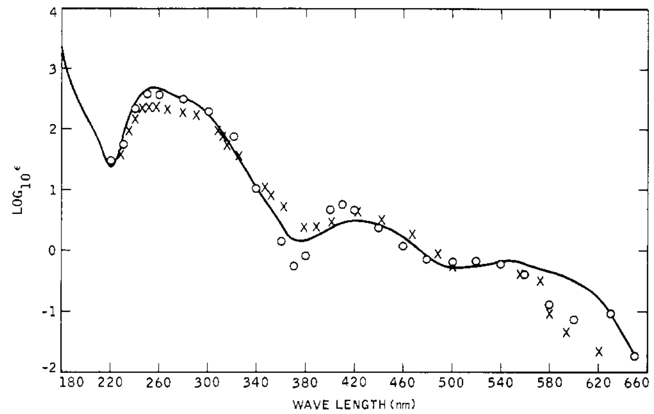

Figure 1. The extinction coefficient of chlorine oxide: —, this work; X, Goodeve and Wallace; O, Finkelnburg et al.

Table II. Approximate Extinction Coefficients (l. mol^{-1} cm^{-1}) at the Peak Ir Absorption Lines (*9*) of Cl_2O

Peak freq (cm^{-1})	Approx spectral slit width (cm^{-1})	ϵ
972	2.8	0.6 ± 0.1
692	4.8	2.8 ± 0.5
686	4.8	3.2 ± 0.5
677	4.9	3.0 ± 0.6

(B) Cl_2O_7

The chlorine heptoxide was made by a method similar to that of Goodeve and Powney (*5*). Briefly a 70% A.C.S. reagent perchloric acid (Matheson, Coleman and Bell) solution was first concentrated by pumping off the excess water. The concentrated acid was then surrounded with a dry ice trap and P_2O_5 slowly added through a side arm. The pressure was then lowered by pumping and the mixture allowed to warm up slowly. The $HClO_4$ was thus dehydrated and Cl_2O_7 freely evolved, which was further dried by passing through a tube filled with P_2O_5 and condensed in a trap at dry ice temperature. The Cl_2O_7 produced was further purified by vacuum fractionation until a pure colorless sample was obtained. The Cl_2O_7 sample was found to be better than 99% pure by methods similar to those used in estimating the purity of Cl_2O. The main impurity of the sample was ClO_2, which was estimated to be less than 0.1% by its absorption centered at 351.5 nm. The ClO_2 extinction coefficient at 351.5 nm = 3090 l. mol^{-1} cm^{-1} was given by Basco and Dogra (*2*). Cl_2O_7 was easily decomposed into Cl_2 and O_2 thermally. An explosive decomposition with a bright flash occurred when the sample in a quartz cell was warmed by a heat gun (to about 250 °C). The pressure ratio before and after thermal decomposition is 1:4.53, close to the pure sample theoretical ratio of 1:4.5 ($Cl_2O_7 \rightarrow Cl_2 + 3.5O_2$). This, coupled with a quantitative Cl_2 concentration determination by its absorption near 330 nm (*12*), further confirmed its purity.

Table III. Extinction Coefficients (l. mol^{-1} cm^{-1}) of Cl_2O_7 Uv Absorption

Wavelength (nm)	ε	Wavelength (nm)	ε
180	3100	250	45.6
185	2370	255	31.2
190	1760	260	20.2
195	1240	265	14.0
200	840	270	9.84
205	604	275	6.69
210	442	280	4.43
215	344	285	3.13
220	266	290	1.84
225	208	295	1.36
230	159	300	0.96
235	119	305	0.53
240	90.2	310	0.27
245	64.5		

Tables III and IV list the uv and ir extinction coefficients, respectively, which were determined using six Cl_2O_7 samples with pressures ranging from 1 to 56 Torr. No absorption was observed for wavelengths greater than 320 nm when the samples were scanned from 800 to 180 nm. The accuracy for the extinction coefficients in Table III is better than 6% between 180 and 255 nm where the absorption is strong. In the region between 255 and 295 nm the uncertainty is larger, being about 11%, and at wavelengths greater than 295 nm the uncertainty is greater than 11%. A comparison with results of Goodeve and Windsor (*7*) was attempted as shown in Figure 2. Although there is agreement near 290 nm, the deviation at the lower wavelengths is more pronounced. At 225 nm, our value was lower by a factor of more than 4. The reason for this large discrepancy is not known; however, Goodeve and Windsor's results were only approximate, especially in the regions of high and low absorption.

Acknowledgment

The author is indebted to Dr. W. B. DeMore for supervising this study, and to Dr. P. Perkins for supplying us the spectral band-pass curve of the Perkin-Elmer Model 21 ir spectrophotometer.

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Table IV. Approximate Extinction Coefficients (l. mol^{-1} cm^{-1}) at the Peak Ir Absorption Lines (*14*) of Cl_2O_7

Peak freq (cm^{-1})	Approx spectral slit width (cm^{-1})	ε
1300	4.7	1090 ± 130
1057	3.1	24 ± 3.0
1025	3.0	282 ± 17
876	2.8	7.3 ± 0.9
798	3.2	12 ± 1.5
698	4.7	65 ± 16

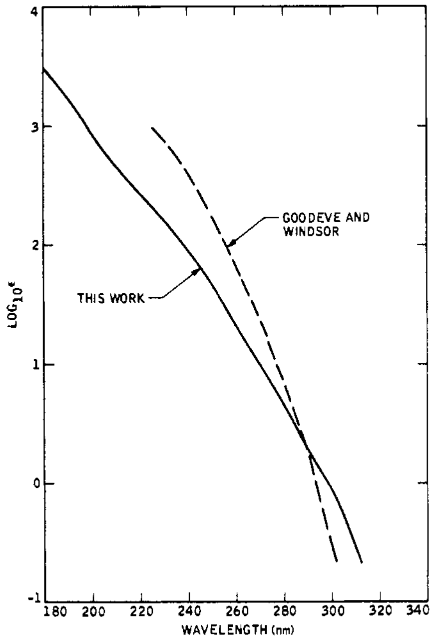

Figure 2. The extinction coefficient of chlorine heptoxide.

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Received for review September 28, 1975. Accepted June 14, 1976. This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS7-100, sponsored by the National Aeronautics and Space Administration.