

THE ABSORPTION SPECTRUM OF ClNO BETWEEN 190 AND 350 nmG. S. TYNDALL[†], K. M. STEDMAN[‡], W. SCHNEIDER, J. P. BURROWS and G. K. MOORTGAT*Max-Planck-Institut für Chemie, Air Chemistry Division, D-6500 Mainz, Postfach 3060 (F.R.G.)*

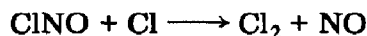
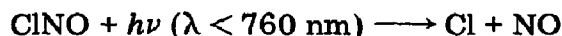
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Summary

The UV spectrum of ClNO has been studied using a microcomputer-controlled scanning spectrometer developed in this laboratory. The absorption cross-sections of ClNO have been determined at 298 K between 190 and 350 nm. These new measurements enable the discrepancies between different determinations of the ClNO absorption cross-sections to be rationalized. They also provide a reliable set of data for actinometric purposes.

1. Introduction

The photochemistry of nitrosyl chloride (ClNO) has been the subject of several detailed investigations [1]. The first measurements of the absorption cross-sections were made by Goodeve and Katz and covered the range 650 - 190 nm [2]. Although measurements of the photolysis quantum yields made by these researchers were not definitive, later determinations have shown that photolysis of ClNO results in a simple cleavage of the Cl-N bond, with formation of both products in their electronic ground states. This leads to an overall quantum yield for ClNO removal at all wavelengths of 2 [2 - 4] proceeding via the mechanism



ClNO therefore offers almost unique possibilities for use as a gas phase actinometer. It is easily prepared and handled and has an unstructured unresolvable absorption spectrum extending from the visible into the vacuum UV. In order that its use as an actinometer can be realised, it is, of course, necessary that accurate cross-sections are available.

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More recently, published spectra from Martin and Gareis [5], Ballash and Armstrong [6] and Illies and Takacs [7], have shown that the measurements by Goodeve and Katz [2] were seriously in error below 350 nm, possibly due to photolysis of ClNO during the course of the measurements. These later measurements all agree to within about 20% above 260 nm, and the discrepancy between the measurements at the absorption maximum at 196 nm [6, 7] is less than 10%. However, the spectrum of Ballash and Armstrong appears to diverge from the other two [5, 7] between 220 and 260 nm.

Current interest in stratospheric ozone depletion has focused attention on the photochemistry of reservoir molecules, such as ClNO₃ and N₂O₅, which reduce the concentration of ozone-destroying free radicals in the stratosphere. Photodecomposition can be an important loss process for such molecules [8]. We are currently carrying out measurements of the primary quantum yields of several reservoir molecules using 254 nm radiation, and considered ClNO as a simple reliable actinometer at this wavelength. It was therefore surprising to find that a discrepancy of a factor of 2.5 exists between the published cross-sections of ClNO in this wavelength region and that recent data compilations offer no recommendation on which to use [9]. ClNO has been used for actinometry in two recent laser photolysis studies of ClNO₃ at 249 nm [10] and 266 nm [11] and errors of this magnitude in the cross-section can obviously seriously affect the results and interpretation of these studies. We therefore consider it necessary to remeasure the ClNO cross-sections. We present here our spectrum and an evaluation of the earlier data.

2. Experimental details

The absorption spectrum of ClNO was measured between 190 and 350 nm. ClNO was prepared by mixing 100 Torr Cl₂ with 250 Torr NO and allowing the gases to stand for several days. The mixture was then frozen at 77 K and the excess NO pumped off. ClNO samples were stored at different pressures in blackened bulbs and degassed at 77 K at regular intervals. The gas was found to be very stable towards decomposition. ClNO exists in equilibrium with Cl₂ and NO, but provided the gas is stored at a pressure greater than 5 Torr the ClNO should be more than 95% pure. For some experiments ClNO purchased from Matheson Co. was used, and no difference in the results was observed. The ClNO was handled in a mercury-free glass vacuum system with Teflon and glass stopcocks. Spectra were taken in a cell of length 114 cm at pressures between 60 mTorr and 9 Torr. The temperature of the cell was stabilized at 25 °C.

The details of the optics and electronics are very similar to those used in our measurements of the NO₂ spectrum [12]. Two different deuterium lamps were used as sources (Heraeus D200F and Hamamatsu L1636). The light was dispersed in a Jobin-Yvon H25 double monochromator with a

resolution of 0.75 nm. The wavelength calibration and resolution of the instrument was checked using a low pressure mercury source (Oriel Penray). The current from the photomultiplier (Hamamatsu R928) was measured on a Keithley 480 picoammeter, which also performed the analogue-digital conversion. The data were transferred to an Apple IIe microcomputer for analysis. The region 200 - 350 nm was scanned in 1000 steps with one reading taken per step. One scan took approximately 9 min. Background scans with the cell empty were taken before and after the data runs and were averaged. The picoammeter and wavelength drive were controlled by the microcomputer.

The long path length and relatively high pressures used were, of course, better suited for the measurement of the lower cross-sections above 240 nm, and the initial part of each spectrum was found to be optically black. A cut-off point had therefore to be chosen, below which the data were no longer usable. By carefully comparing runs at different pressures, it was found that the Beer-Lambert law was observed until optical densities

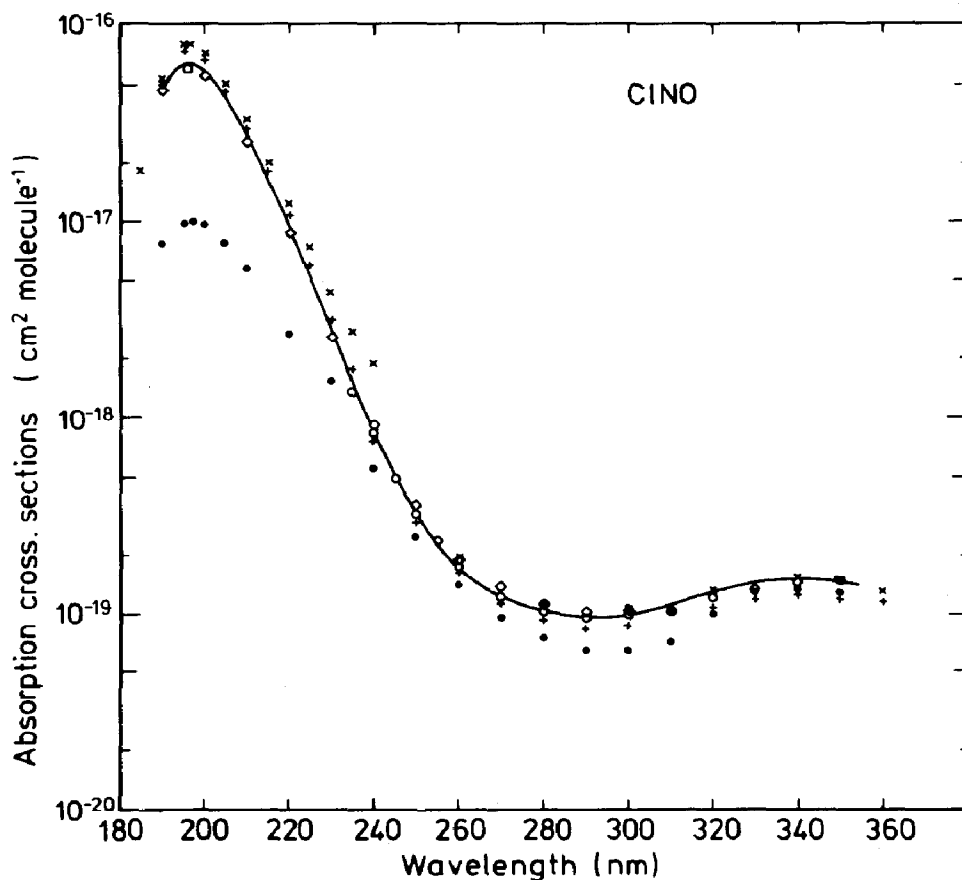


Fig. 1. Absorption spectrum of ClNO: —, this work; +, Illies and Takacs [7]; x, Ballash and Armstrong [6]; ◇, Margitan [13]; □, Lenzi and Okabe [15]; ○, Martin and Gareis [5]; ●, Goodeve and Katz [2].

approached 6 (base e). Although this corresponds to over 99% absorption, measurements to this degree are made possible by the digital measurement technique and the high stability of the lamps and photomultiplier. Photolysis of ClNO by the deuterium lamps was found to occur, but on a time scale much longer than that of the measurements. Ten spectra were taken, varying the pressure over a factor of 200. The region of interest, 235 - 350 nm, was covered by at least seven spectra. The standard deviation of the measurements was at all wavelengths less than 3%.

A few additional measurements were taken with low concentrations of ClNO (5 - 15 mTorr) in order to cover the region 190 - 240 nm. Since the pressures could only be measured with about 10% accuracy, the spectra were normalized at some value (215 or 230 nm) in order to compare the shape of the maximum with other measurements. The combined data are shown in Fig. 1 together with other published data and unpublished measurements from Margitan [13]. In Table 1 we present our data as 1 nm averages at

TABLE 1

Absorption cross-sections^a of ClNO

Wavelength (nm)	<i>This work</i> ^b	<i>From ref. 2</i> ^c	<i>From ref. 5</i> ^c	<i>From ref. 6</i> ^d	<i>From ref. 7</i> ^d
190	432	77.3		537	520
195	636	98.3		792	758
200	586	96.9		720	674
205	420	76.3		514	470
210	263	57.9		337	299
215	157	46.0		202	180
220	89.6	27.1		127	107
225	48.9	19.2		73.8	60.0
230	26.6	15.6		43.6	31.7
235	14.5	8.57	13.5	27.7	17.7
240	8.25	5.55	8.37	19.1	7.68
245	4.95	3.82	4.90		
250	3.17	2.53	3.23		2.99
255	2.24	1.91	2.41		
260	1.75	1.42	1.75	1.99	1.61
270	1.29	0.98	1.24		1.15
280	1.06	0.76	1.05	1.13	0.93
290	0.96	0.65	0.94		0.85
300	1.00	0.65	0.94	1.03	0.87
310	1.15	0.71	1.05		1.05
320	1.34	1.03	1.21	1.34	1.08
330	1.47	1.30	1.33		1.20
340	1.52	1.33	1.45	1.50	1.24
350	1.44	1.21	1.45		1.19

^aCross-sections given in units of 10^{-19} cm² molecule⁻¹.

^b1 nm averages.

^cInterpolated from published graphs.

^dTaken from published tables.

TABLE 2

Absorption cross-sections of ClNO

190	432	230	26.6	270	1.29	310	1.15
191	480	231	23.7	271	1.26	311	1.17
192	534	232	21.2	272	1.23	312	1.19
193	580	233	18.6	273	1.20	313	1.20
194	615	234	16.4	274	1.18	314	1.22
195	636	235	14.5	275	1.15	315	1.24
196	648	236	12.8	276	1.13	316	1.25
197	645	237	11.4	277	1.11	317	1.28
198	631	238	10.1	278	1.07	318	1.30
199	612	239	9.07	279	1.07	319	1.32
200	586	240	8.25	280	1.06	320	1.34
201	558	241	7.42	281	1.04	321	1.35
202	525	242	6.72	282	1.02	322	1.36
203	490	243	6.13	283	1.01	323	1.39
204	454	244	5.51	284	0.999	324	1.40
205	420	245	5.00	285	0.991	325	1.42
206	384	246	4.52	286	0.984	326	1.43
207	351	247	4.15	287	0.973	327	1.46
208	321	248	3.77	288	0.971	328	1.46
209	292	249	3.48	289	0.967	329	1.46
210	263	250	3.17	290	0.964	330	1.47
211	237	251	2.94	291	0.960	331	1.48
212	218	252	2.74	292	0.963	332	1.49
213	195	253	2.56	293	0.961	333	1.49
214	176	254	2.37	294	0.969	334	1.51
215	157	255	2.24	295	0.967	335	1.52
216	140	256	2.13	296	0.971	336	1.53
217	126	257	2.00	297	0.983	337	1.54
218	111	258	1.90	298	0.989	338	1.53
219	100	259	1.82	299	0.992	339	1.53
220	89.6	260	1.75	300	1.00	340	1.52
221	79.1	261	1.70	301	1.01	341	1.53
222	70.7	262	1.65	302	1.03	342	1.53
223	62.7	263	1.59	303	1.03	343	1.53
224	55.2	264	1.53	304	1.05	344	1.51
225	48.9	265	1.49	305	1.07	345	1.49
226	43.6	266	1.44	306	1.08	346	1.51
227	38.5	267	1.40	307	1.10	347	1.49
228	33.9	268	1.36	308	1.11	348	1.49
229	30.4	269	1.33	309	1.13	349	1.48
						350	1.45

The wavelengths (columns 1, 3, 5 and 7) are in nanometres and the cross-sections (columns 2, 4, 6 and 8) are in units of 10^{-19} cm² molecule⁻¹.

5 nm intervals, and in Table 2 as 1 nm averages covering the entire range 190 - 350 nm.

3. Discussion

The earlier data of Goodeve and Katz [2] are known to be in error, as discussed by Ballash and Armstrong [6] and Illies and Takacs [7]. It appears,

however, that the data of Ballash and Armstrong are themselves unreliable between 220 and 240 nm. These researchers measured the spectrum in two parts, from 185 to 240 nm and from 260 to 540 nm, without overlapping the two regions. At the low pressures required to measure the maximum at 196 nm the optical density above 220 nm was very low and the measurements were thus sensitive to noise and to drift. The published values thus seem to be systematically too high by up to a factor of 2.

Outside this region the overall agreement is quite good. Between 260 and 350 nm the data of Illies and Takacs are systematically about 20% lower than those of Ballash and Armstrong. Our results, together with those of Martin and Gareis [5], Margitan [13] and a few measurements at isolated wavelengths by Magnotta [14], tend to support the higher values between 260 and 350 nm. Below 240 nm the spectrum rises very steeply and it appears that both the published works overestimate the cross-section in this region. Our maximum cross-section ($6.5 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$) is approximately 20% lower than the values of Ballash and Armstrong ($8.02 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$) and Illies and Takacs ($7.6 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$). Even though these two studies agree well, the agreement may be a little fortuitous, since the spectrum of Illies and Takacs clearly rises more steeply than any of the others below 240 nm. The tendency towards a lower peak value is also supported by the work of Lenzi and Okabe [15] who measured from 200 nm into the vacuum UV, and whose cross-section at 195 nm is $6.2 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$. We believe that our digital data acquisition and use of a double monochromator to reduce scattered background light leads to a very high precision, under conditions of low analysing light intensity and high absorption.

The lower values for the cross-section around 240 nm particularly affect the results of Marinelli and Johnston [10] for the quantum yield for NO_3 production in the 249 nm photolysis of ClNO_3 . These researchers interpolated between the values of Ballash and Armstrong at 240 and 260 nm, obtaining a cross-section approximately a factor of 2.5 too high. Consequently their quantum yields for NO_3 production should be reduced by a factor of 2.5.

In conclusion, we report new measurements of the absorption spectrum of ClNO between 190 and 350 nm. These allow a rationalization of the discrepancy between previous measurements and offer reliable data for actinometry in the photolysis of other molecules.

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