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Absorption Cross Sections of the ClO Dimer

K. J. Huder and W. B. DeMore*

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109

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The absorption cross sections of the ClO dimer, ClOOCl, are important to the photochemistry of ozone depletion in the Antarctic. In this work new measurements were made of the dimer cross sections at 195 K. The results yield somewhat lower values in the long wavelength region, compared to those currently recommended in the NASA data evaluation (JPL 94-26). The corresponding solar photodissociation rates in the Antarctic are reduced by about 40%.

Introduction

The ClO dimer is formed by the self-reaction of ClO radicals at the low temperatures of the earth's polar winter. When sunlight is present, the dimer is thought to take part in catalytic ozone destruction by yielding chlorine atoms upon photolysis, followed by attack of the chlorine atoms on ozone.

$$ClOOCl + h\nu \rightarrow Cl + ClOO \quad (1)$$

$$ClOO \rightarrow Cl + O_2 \quad (2)$$

$$Cl + O_3 \rightarrow ClO + O_2 \quad (3)$$

To model the role of ClOOCl in polar photochemistry, it is necessary to know its rate of formation, the photolytic cross sections, and the photolysis products. In addition to the path yielding Cl and ClOO radicals, another path yielding ClO + ClO is possible.

$$ClOOCl + h\nu \rightarrow ClO + ClO \quad (4)$$

This path would not contribute to ozone loss, because ClO is inert to ozone. Although it is normally assumed in atmospheric models that only the Cl + ClOO branch is important, the experimental basis for this assumption is somewhat uncertain. Cox and Hayman[1] concluded that Cl and ClOO are the major dimer photolysis products by modeling the disappearance of Cl_2O and the appearance of dimer in the photolysis of Cl_2O at 254 nm, at temperatures of 203−233 K. However, they placed an uncertainty of approximately a factor of 2 on the result for the Cl + ClOO yield.

In the most direct study at a wavelength appropriate for atmospheric photolysis of the dimer, Molina et al.[2] reported a quantum yield of approximately unity for the Cl + ClOO path at 308 nm. That result was based on measurements of the Cl atom LIF signal in the photolysis of the dimer (235 K, 20 Torr) compared to the Cl atom LIF signal when photolyzing Cl_2 (also at 308 nm). However, the authors used a value of 22 for the ratio of the dimer cross sections at 245 and 308 nm, as determined in their own work. If one takes that ratio from the current NASA recommended dimer cross sections,[3] the value is 13 and the corresponding Cl + ClOO quantum yield would be only 0.6. That would imply that the ClO + ClO path makes a 40% contribution. Thus, there is a direct relationship between the cross sections and the photolysis products.

Eberstein[4] argued that dimer photolysis should proceed by path (4) on the grounds that the O−O bond in ClOOCl is much weaker than the Cl−O bond. However, Eberstein assumed that the Cl−O bond energy in ClOOCl is similar to that of the ClO radical (about 64 kcal/mol). Actually, the Cl−OOCl bond energy is only about 21 kcal/mol, just slightly greater than the ClO−OCl bond (18 kcal/mol).[3] Thus, an argument based on preferential breaking of the weaker bond is not compelling in this case.

Previous studies of the dimer spectrum[1,5,6] (but not that of Molina et al.[2]) have used Cl_2O as the source of ClOOCl. The dimer absorption cross sections are difficult to measure, because the compound is stable only at low temperatures and cannot be prepared in the pure state. The spectrum has only been obtained in the presence of other molecules such as Cl_2, O_3, or Cl_2O, and the net ClOOCl spectrum must be extracted by deconvolution of the composite spectra. This process is somewhat qualitative in nature and is subject to error. The situation is similar to the case of HOCl, for which previous cross section measurements have been erroneous due to contamination with Cl_2O and Cl_2.[7] Some of the largest cross section errors occur in the "tail" region above 300 nm, where the spectrum is weak. The errors arise from the necessity to correct the spectrum for Cl_2 and from base line errors in the total spectrum. This wavelength region is the most important for determining the atmospheric photolysis rates of ClOOCl.

Experimental Section

Apparatus. The ClO dimer was prepared as before[6] by photolysis of Cl_2O mixtures. The Cl_2O was produced by oxidation of Cl_2 over HgO at low temperature.[8] The experiments were performed in a low-temperature, 5 cm path length spectrophotometric cell of quartz construction. The cell was cooled by a surrounding jacket containing a dry ice/methanol mixture. Some early experiments were performed in a metal cell of similar construction, with halocarbon coating on the walls. However, dimer was found to be more stable in the quartz cell. The cell was evacuated and filled with Cl_2O at a pressure of about 10 Torr and then pressurized to about 3 atm with nitrogen to reduce diffusion to the walls. A low-pressure mercury lamp was used for irradiation at 254 nm. The UV absorption spectra were taken from 200 to 400 nm with a Cary Model 4E spectrometer.

Dimer Spectrum. Since it is difficult to obtain reliable cross sections at longer wavelengths by direct experimental measurement (for reasons discussed above), we have concentrated on obtaining accurate data at shorter wavelengths. Those values can then be used for extrapolation above 310 nm. We have looked only at relative cross sections, since the absolute values

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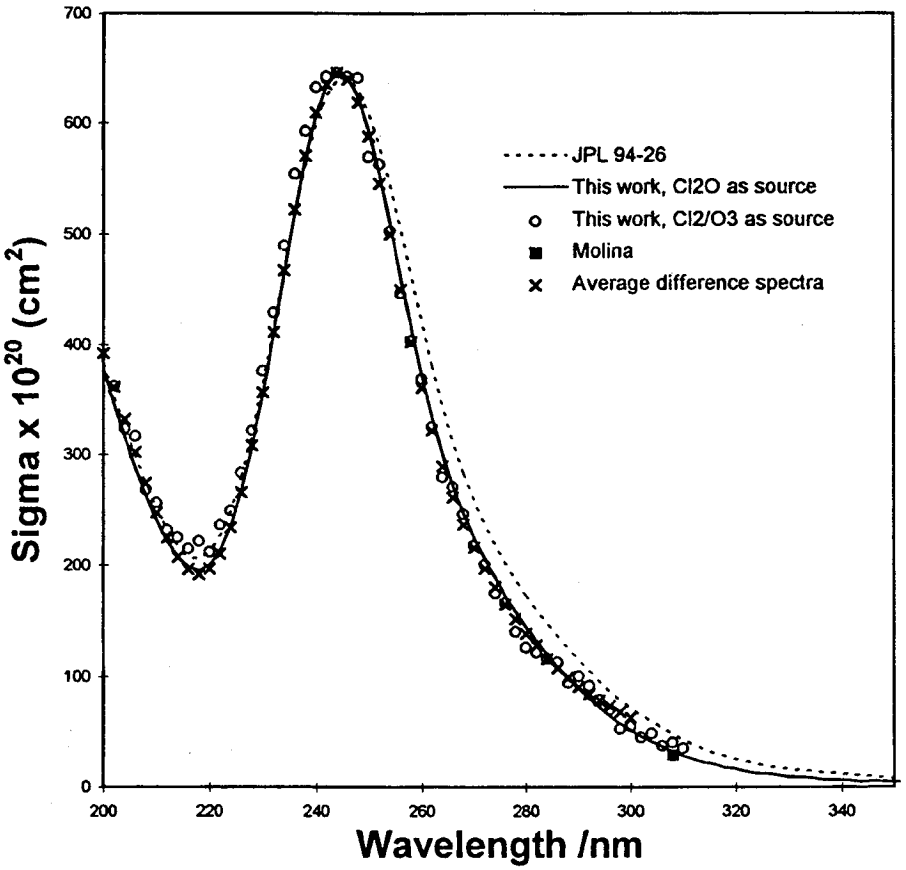

Figure 1. ClOOCl cross sections from this work compared to those of JPL 94-26.

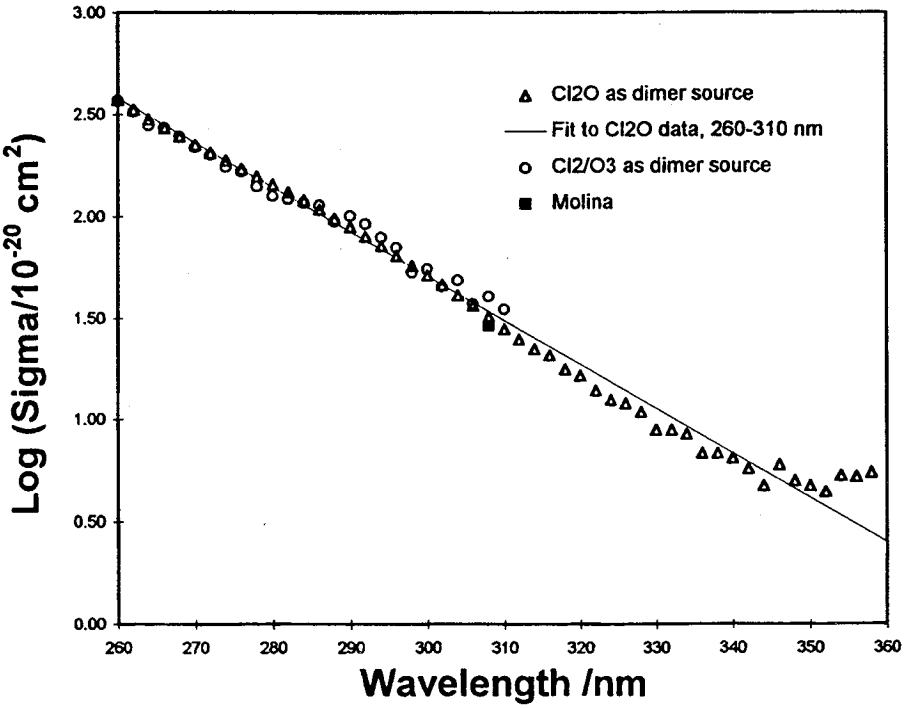

Figure 2. Logarithmic plot of the cross section data.

near the peak are reasonably well established.[3] The basic problem is to determine how much of the Cl_2O spectrum to subtract. Three approaches have been used: (1) From the product spectra for each experiment the individual spectra for each component were subtracted from the total spectrum, using the criterion that the peak in the resultant dimer spectrum should be fixed at 244 nm, as determined in earlier work.[6] (2) Dimer spectra were obtained by taking advantage of the fact that its rate of decomposition in the cell (by wall reactions) is much faster than that of the other components (Cl_2O and Cl_2), and thus the dimer spectrum on a relative basis can be obtained by taking difference spectra. The dimer spectrum obtained by the difference method may be slightly contaminated with the Cl_2O spectrum, to the extent that decomposition of that species occurs

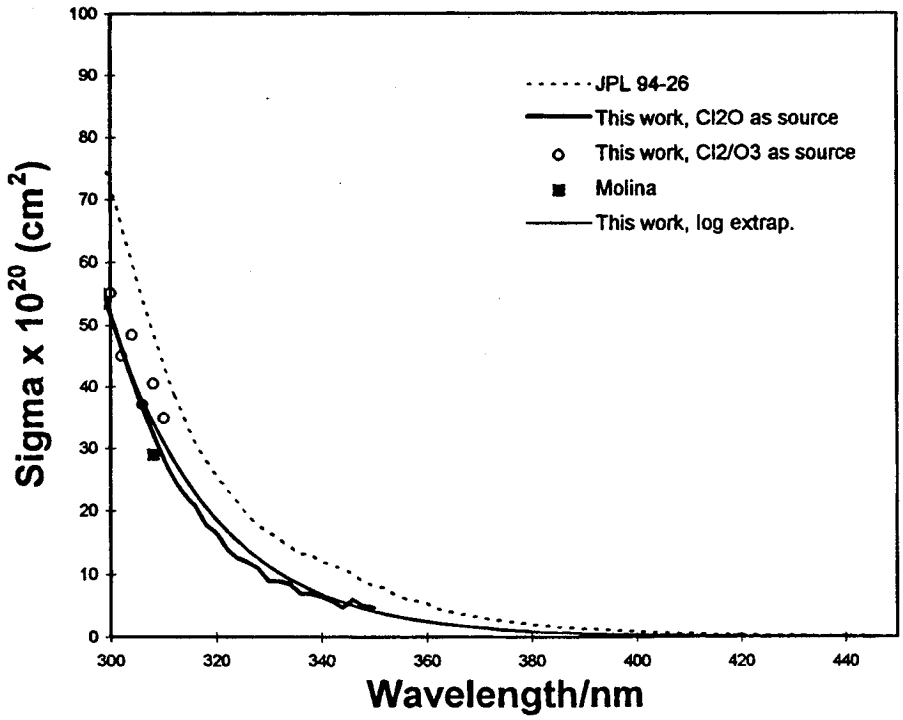

Figure 3. ClOOCl cross sections at longer wavelengths.

during the time of the dimer decomposition. However, that dimer spectrum should correspond to an upper limit for Cl_2O content and thus serve as a useful boundary condition for comparison with spectra obtained by the iterative subtraction method. (3) Difference spectra taken in the course of our earlier work,[6] using Cl_2/O_3 mixtures as the dimer source, were compared with the present spectra. The earlier spectra, although less suitable for the measurement of absolute cross sections because of the much lower dimer concentrations, are nevertheless useful for comparison of the shape of the dimer spectrum obtained from the Cl_2O experiments.

Results

Figure 1 shows dimer spectra as obtained by methods 1−3 above. All have been normalized to 6.4×10^{-18} cm^2 at 244 nm, this being the JPL 94-26[9] recommendation at that wavelength. The NASA recommendation is included for comparison, as is the single measurement at 308 nm by the Molina group (calculated from their ratio $\sigma^{245}/\sigma^{308} = 22$).[2] Our data are in good agreement among themselves and with the Molina measurement but are significantly lower than the JPL 94-26 recommendation in the tail or falloff region.

Figure 2 is a plot of the logarithms of the cross sections vs wavelength. Also shown is a linear fit to the Cl_2O data based on the wavelength range 260−310 nm. Above about 310 nm, the logarithmic extrapolation is considered to be a better estimate of the cross sections than the actual data. The extrapolated data are compared in Figure 3 with the data and with the JPL 94-26 recommendation. The latter is based on an extrapolation (above 360) nm of previous data.[1,5,6] Table 1 lists recommended cross sections based on the present work.

Discussion

The present results strongly suggest that previous measurements of the dimer cross sections, on which the recommendations in JPL 94-26 (also 92-20) are based, were improperly

TABLE 1: Dimer Cross Sections (σ, cm^2 × 10^{20})

λ, nm	σ	λ, nm	σ	λ, nm	σ
200	374.6	284	119.4	368	1.7
202	342.8	286	107.9	370	1.5
204	312.8	288	97.2	372	1.4
206	285.3	290	88.5	374	1.2
208	260.5	292	79.5	376	1.1
210	238.3	294	71.5	378	1.0
212	219.9	296	63.7	380	0.92
214	205.9	298	56.9	382	0.83
216	196.7	300	51.3	384	0.75
218	193.7	302	46.0	386	0.68
220	198.3	304	41.6	388	0.62
222	211.5	306	37.7	390	0.56
224	233.2	308	34.1	392	0.50
226	264.8	310	30.8	394	0.46
228	304.7	312	27.9	396	0.41
230	352.8	314	25.2	398	0.37
232	406.6	316	22.8	400	0.34
234	461.6	318	20.6	402	0.30
236	515.2	320	18.7	404	0.28
238	563.6	322	16.9	406	0.25
240	602.4	324	15.3	408	0.23
242	628.7	326	13.8	410	0.20
244	640.0	328	12.5	412	0.18
246	637.1	330	11.3	414	0.17
248	619.1	332	10.2	416	0.15
250	588.9	334	9.2	418	0.14
252	549.5	336	8.4	420	0.12
254	505.1	338	7.6	422	0.11
256	458.1	340	6.8	424	0.10
258	413.0	342	6.2	426	0.09
260	370.1	344	5.6	428	0.08
262	332.1	346	5.1	430	0.07
264	299.0	348	4.6	432	0.07
266	269.7	350	4.1	434	0.06
268	245.2	352	3.7	436	0.06
270	223.3	354	3.4	438	0.05
272	204.2	356	3.1	440	0.05
274	187.6	358	2.8	442	0.04
276	170.9	360	2.5	444	0.04
278	157.1	362	2.3	446	0.03
280	143.3	364	2.1	448	0.03
282	131.0	366	1.9	450	0.03

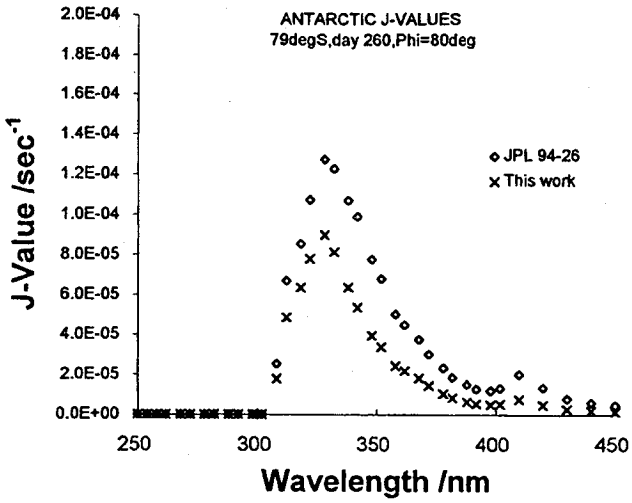

Figure 4. Antarctic J values for ClOOCl.

corrected for Cl_2O and are too high in the "tail" region. The current results also agree well with the 308 nm cross section value of the Molina group.[2] The difference has a significant effect on dimer photolysis rates in the Antarctic atmosphere. Most of the contributions to the photolysis rate occur at wavelengths in the 310−270 nm range (see Figure 4). With the new cross sections the total J value under Antarctic conditions is about 60% of that obtained from the JPL 94-26 cross sections. This change will affect the distribution of ClO between the monomeric and dimeric forms but will not reduce the rate of ozone destruction in the same proportion, because the rate determining step for ozone loss is the ClO association reaction rather than the photolysis process.

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