THE ULTRAVIOLET ABSORPTION OF SOME HALOGENATED METHANES AND ETHANES OF ATMOSPHERIC INTEREST

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Summary

The absorption spectra of some chlorine-containing methanes (CCl_4, CCl_3F, $CClF_3$, $CHCl_3$, CH_2Cl_2 and CH_2ClF) and ethanes (CCl_2FCClF_2, $CClF_2CClF_2$, CF_3CClF_2, CF_3CH_2Cl, CH_3CCl_3, CH_3CClF_2 and CH_3CH_2Cl) and also of N_2O were determined at wavelengths near 220 nm. Some of these spectra were obtained at both 298 and 208 K. Additionally, a chemical method was used to determine the absorption cross section of CCl_3F at $\lambda = 253.7$ nm and the absorption properties at wavelengths above 280 nm. It is concluded from these experiments that the tropospheric decay rate of CCl_3F is less than 10^{-10} s^{-1} for the homogeneous gas phase photolysis.

1. Introduction

Recently we have reported absorption spectra of CCl_3F (Halocarbon 11), CCl_2F_2 (12), $CHCl_2F$ (21), $CHClF_2$ (22) and CH_3Cl (40) in the wavelength range 160 - 275 nm at temperatures of 298 and 208 K [1]. We extended this previous investigation to include the absorption spectra of other halogenated methanes and ethanes such as CCl_4 (10), $CClF_3$ (13), $CHCl_3$ (20), CH_2Cl_2 (30), CH_2ClF (31), CCl_2FCClF_2 (113), $CClF_2CClF_2$ (114), CF_3CClF_2 (115), CF_3CH_2Cl (133), CH_3CCl_3 (140), CH_3CClF_2 (142) and CH_3CH_2Cl (160), and also of N_2O.

Atmospheric investigations have shown that these compounds can play an important role in the determination of stratospheric ozone (see for example ref. 2). In particular, the lack of tropospheric sinks for CCl_3F has been discussed in connection with stratospheric processes which destroy ozone [2, 3].

We have shown previously [1] that CCl_3F has relatively large absorption cross sections at long wavelengths (λ greater than 230 nm). Since, at these wavelengths, it could not be decided whether the measured cross sections were caused by impurities in the sample, by scattering of light or by CCl_3F itself, a tropospheric sink of CCl_3F depleted by photodissociation

could not be excluded [1]. In this work we therefore reinvestigated the absorption of CCl_3F at long wavelengths using a sensitive chemical method.

2. Experimental

The experimental set-up for the absorption measurements has been described previously [1] and only the major features will be repeated here. The light source consisted of a deuterium lamp. A 0.5 m vacuum UV mono-chromator was used to select the desired wavelengths. The resolution was typically 0.3 nm. Suprasil windows were used throughout the experiments and hence the useful range was limited to wavelengths greater than about 160 nm. Two absorption cells were used. The smaller cell had an effective absorption light path of 10 cm and could be cooled to 208 K [1]. The other cell consisted of a glass tube 100 cm in length. It was used for measurements at room temperature only.

For a number of experiments at longer wavelengths (λ = 253.7 nm and λ > 280 nm) a chemical method was used to investigate the photodissociation of CCl_3F. In these experiments small amounts of NO (about 10 ppm by volume) were mixed with large amounts of halogenated methanes and N_2. These mixtures were irradiated in a spherical reaction vessel (4300 cm^3; light path, 24 cm) which was constantly stirred. This vessel consisted of Pyrex glass and had a Suprasil window with an area of about 10 cm^2. The number of radicals which were photolytically produced in this system was estimated from the amount of NO consumed (see Section 4). A chemi-luminescence detector was used as a sensitive monitor for the concentration of NO [4].

The sensitivity of this detector was calibrated for the mixtures and pressures used. In all experiments the pressures were monitored by capacitance manometers (MKS-Baratron, Type 220). A mercury pen lamp (Oriel, Hg(A), 17 mA, Model No. C-13-61) was used to irradiate the mixtures at 253.7 nm. The radiation at shorter wavelengths was cut off in these experiments by a black glass (Schott, UG 5, 1 mm thick, 10% transmission at 220 nm). A 600 W xenon–mercury high pressure lamp (Hanovia, 941 B-1) was used for the experiments at wavelengths greater than 280 nm. A cut-off filter (Schott, WG 305, 1 mm thick, 10% transmission at 280 nm) limited the useful wavelength range. The light flux through the window of the photolysis vessel was roughly estimated, using the typical data given by the manufacturer, to be about 4×10^{16} quanta cm^{-2} s^{-1} for the wavelength range 280 - 375 nm. The photodissociation of CCl_3F to form CCl_2F and chlorine radicals is energetically possible at wavelengths less than 375 nm.

The following gases, together with their gas chromatographic analyses, were provided by Hoechst AG and were used without further purification: CCl_3F, $CClF_3$, CH_2ClF, CCl_2FCClF_2, $CClF_2CClF_2$, CF_3CClF_2, CF_3CH_2Cl and CH_3CClF_2. The following gases were taken from the gas phase of their liquids which were thoroughly degassed at reduced temperatures each time

before they were used: CCl_4 (99.7% minimum purity) and CH_3CH_2Cl (99%, Uvasol quality), both from Merck; $CHCl_3$ (99%), CH_2Cl_2 (99%) and CH_3-CCl_3 (97.0%), all three from Baker, ACS specification. The $CHCl_3$ contained ethanol and the CH_3CCl_3 contained 1,4-dioxane as stabilizers. Therefore their absorption cross sections between 170 and 190 nm were corrected for the extinction coefficients and the concentrations of these stabilizers. These corrections were less than 0.6 and 10.7% respectively. N_2O (L'Air Liquide), N_2 (Messer Griesheim) and NO (Messer Griesheim) were stated to have minimum purities of 99.99%, 99.995% and 99.85% respectively. These three gases were further purified by Oxisorb (Messer Griesheim). Also NO was fed through a trap at 143 K.

3. Results

Absorption cross sections $\sigma(\lambda)$ were determined according to the Lambert–Beer law [1]

$$\ln \frac{I(\lambda)}{I_0(\lambda)} = - \frac{273.15}{1013.3} \frac{N_0 l}{T} p\sigma(\lambda) \tag{1}$$

where I and I_0 are the photomultiplier currents with and without absorbing gas in the cell, T and l are the absolute temperature and the length of the light path in the cell, p is the pressure in mbars and N_0 is the Avogadro constant. The absorption cross section σ at a fixed wavelength was determined by plotting $\ln\{I(\lambda)/I_0(\lambda)\}$ against p and taking into account the stray light of the monochromator. Values of $\sigma(\lambda)$ obtained at 298 K for five chlorinated methanes (CCl_4, $CClF_3$, $CHCl_3$, CH_2Cl_2 and CH_2ClF) and also for N_2O are displayed in Table 1. Values of $\sigma(\lambda)$ obtained at 298 K for seven chlorinated ethanes (CCl_2FCClF_2, $CClF_2CClF_2$, CF_3CClF_2, CF_3CH_2Cl, CH_3CCl_3, CH_3CClF_2 and CH_3CH_2Cl) are shown in Table 2. In Table 3 the absorption cross sections determined for eight gases ($CClF_3$, CH_2ClF, CCl_2F-$CClF_2$, $CClF_2CClF_2$, CF_3CClF_2, CF_3CH_2Cl, CH_3CClF_2 and N_2O) at 208 K are listed.

In this work particular emphasis was placed on the investigation of the absorption cross sections of CCl_3F at longer wavelengths. Table 4 shows a number of measurements of the absorption cross section of CCl_3F at 298 K in the wavelength range 230 - 260 nm. Three different samples of CCl_3F were used to obtain the data given in Table 4. For the run using the small absorption cell ($l = 10$ cm) a limited amount of CCl_3F of very high purity was provided by Hoechst AG. Both the other runs were performed using the larger cell ($l = 100$ cm) and commercially available CCl_3F. The data of our previous study [1] are also included in Table 4 for comparison.

Plots of log σ versus λ (Figs. 1 and 2) clearly demonstrate that, for all the gases investigated in this work and in our previous study [1], the cross sections close to the absorption thresholds can be well approximated by the relationship

TABLE 1

Absorption cross sections $\sigma(\lambda)$ in cm^2 for some halogenated methanes and for N_2O at 298 K[a]

λ (nm)	CCl_4	$CClF_3$	$CHCl_3$	CH_2Cl_2	CH_2ClF	N_2O
160	1.80 (−18)	2.65 (−20)	5.12 (−18)	4.81 (−18)	4.79 (−19)	4.40 (−20)
165	4.49 (−18)	1.98 (−20)	3.67 (−18)	2.24 (−18)	5.59 (−19)	5.77 (−20)
170	6.46 (−18)	1.65 (−20)	3.32 (−18)	1.89 (−18)	4.30 (−19)	8.71 (−20)
175	9.91 (−18)	8.93 (−21)	3.67 (−18)	1.87 (−18)	2.33 (−19)	1.18 (−19)
180	8.92 (−18)	4.88 (−21)	3.56 (−18)	1.77 (−18)	1.25 (−19)	1.42 (−19)
185	4.23 (−18)	2.84 (−21)	2.26 (−18)	1.29 (−18)	4.20 (−20)	1.35 (−19)
190	1.44 (−18)	1.36 (−21)	1.14 (−18)	6.44 (−19)	1.95 (−20)	1.09 (−19)
195	7.77 (−19)	5.59 (−22)	7.21 (−19)	2.67 (−19)	5.44 (−21)	6.23 (−20)
200	6.69 (−19)	1.38 (−22)	4.40 (−19)	9.76 (−20)	2.09 (−21)	3.43 (−20)
205	6.22 (−19)	8.20 (−23)	2.43 (−19)	3.87 (−20)	6.98 (−22)	1.89 (−20)
210	4.99 (−19)	1.72 (−23)	1.05 (−19)	1.62 (−20)	1.88 (−22)	6.44 (−21)
215	3.32 (−19)	5.21 (−24)	4.29 (−20)	6.31 (−21)	5.60 (−23)	2.64 (−21)
220	1.85 (−19)	1.92 (−24)	1.70 (−20)	2.27 (−21)	2.15 (−23)	9.90 (−22)
225	8.80 (−20)	—	6.20 (−21)	7.26 (−22)	4.85 (−24)	3.02 (−22)
230	4.18 (−20)	—	2.40 (−21)	2.65 (−22)	2.57 (−24)	1.15 (−22)
235	1.81 (−20)	—	9.37 (−22)	1.16 (−22)	—	3.45 (−23)
240	7.88 (−21)	—	3.83 (−22)	4.72 (−23)	—	1.29 (−23)
245	3.18 (−21)	—	1.58 (−22)	2.32 (−23)	—	4.25 (−24)
250	1.78 (−21)	—	6.48 (−23)	7.86 (−24)	—	1.36 (−24)
255	6.61 (−22)	—	2.02 (−23)	2.51 (−24)	—	—
260	2.53 (−22)	—	—	—	—	—
265	1.26 (−22)	—	—	—	—	—
270	6.10 (−23)	—	—	—	—	—
275	2.39 (−23)	—	—	—	—	—

[a]The numbers in parentheses represent exponents to the power 10.

TABLE 2

Absorption cross sections $\sigma(\lambda)$ in cm^2 for some halogenated ethanes at 298 K[a]

λ (nm)	CCl_2FCClF_2	$CClF_2CClF_2$	CF_3CClF_2	CF_3CH_2Cl	CH_3CCl_3	CH_3CClF_2	CH_3CH_2Cl
160	2.70 (−18)	1.43 (−18)	2.16 (−19)	5.94 (−19)	4.20 (−18)	6.61 (−19)	1.89 (−18)
165	2.60 (−18)	1.22 (−18)	1.49 (−19)	6.46 (−19)	4.11 (−18)	4.55 (−19)	1.10 (−18)
170	2.18 (−18)	8.37 (−19)	7.07 (−20)	5.64 (−19)	3.80 (−18)	2.96 (−19)	7.05 (−19)
175	1.92 (−18)	5.41 (−19)	3.74 (−20)	3.73 (−19)	3.94 (−18)	1.46 (−19)	4.44 (−19)
180	1.55 (−18)	2.80 (−19)	1.70 (−20)	2.28 (−19)	3.78 (−18)	6.31 (−20)	3.04 (−19)
185	1.07 (−18)	1.63 (−19)	7.03 (−21)	1.16 (−19)	2.96 (−18)	2.79 (−20)	1.36 (−19)
190	5.12 (−19)	7.37 (−20)	3.03 (−21)	6.20 (−20)	2.10 (−18)	1.02 (−20)	6.85 (−20)
195	2.70 (−19)	2.79 (−20)	1.29 (−21)	2.95 (−20)	1.62 (−18)	4.05 (−21)	2.56 (−20)
200	1.23 (−19)	9.82 (−21)	5.07 (−22)	1.14 (−20)	1.01 (−18)	1.58 (−21)	1.17 (−20)
205	4.92 (−20)	3.39 (−21)	1.82 (−22)	5.98 (−21)	5.63 (−19)	6.18 (−22)	3.75 (−21)
210	1.65 (−20)	1.38 (−21)	5.96 (−23)	3.28 (−21)	3.87 (−19)	2.54 (−22)	1.47 (−21)
215	6.61 (−21)	5.32 (−22)	2.09 (−23)	1.69 (−21)	2.02 (−19)	1.08 (−22)	4.33 (−22)
220	2.30 (−21)	1.90 (−22)	7.40 (−24)	8.87 (−22)	1.03 (−19)	4.05 (−23)	1.27 (−22)
225	8.83 (−22)	6.85 (−23)	3.35 (−24)	2.26 (−22)	4.36 (−20)	1.62 (−23)	4.63 (−23)
230	2.82 (−22)	2.61 (−23)	1.14 (−24)	1.47 (−22)	1.75 (−20)	5.65 (−24)	1.17 (−23)
235	1.21 (−22)	8.92 (−24)	—	4.04 (−23)	6.14 (−21)	—	3.95 (−24)
240	4.87 (−23)	—	—	1.81 (−23)	2.11 (−21)	—	1.56 (−24)
245	1.81 (−23)	—	—	5.41 (−24)	8.78 (−22)	—	—
250	8.32 (−24)	—	—	—	4.12 (−22)	—	—
255	—	—	—	—	1.61 (−22)	—	—

[a]The numbers in parentheses represent exponents to the power 10.

TABLE 3

Absorption cross sections $\sigma(\lambda)$ in cm^2 at 208 K[a]

λ (nm)	$CClF_3$	CH_2ClF	CCl_2FCClF_2	$CClF_2CClF_2$	CF_3CClF_2	CF_3CH_2Cl	CH_3CClF_2	N_2O
160	2.54 (−20)	4.70 (−19)	2.60 (−18)	1.37 (−18)	2.20 (−19)	7.33 (−19)	6.30 (−19)	4.30 (−20)
165	1.73 (−20)	5.58 (−19)	2.45 (−18)	1.18 (−18)	1.38 (−19)	6.19 (−19)	4.32 (−19)	5.61 (−20)
170	1.35 (−20)	3.82 (−19)	1.93 (−18)	8.01 (−19)	7.09 (−20)	4.66 (−19)	2.85 (−19)	8.30 (−20)
175	7.49 (−21)	1.98 (−19)	1.98 (−18)	5.31 (−19)	3.33 (−20)	3.18 (−19)	1.40 (−19)	1.10 (−19)
180	4.10 (−21)	8.16 (−20)	1.48 (−18)	2.63 (−19)	1.43 (−20)	1.84 (−19)	5.63 (−20)	1.31 (−19)
185	2.04 (−21)	2.69 (−20)	1.09 (−18)	1.50 (−19)	6.51 (−21)	9.32 (−20)	2.38 (−20)	1.22 (−19)
190	9.95 (−22)	1.15 (−20)	4.93 (−19)	6.70 (−20)	2.66 (−21)	—	9.96 (−21)	9.40 (−20)
195	3.44 (−22)	3.54 (−21)	2.03 (−19)	2.43 (−20)	1.21 (−21)	—	3.88 (−21)	5.11 (−20)
200	1.12 (−22)	9.88 (−22)	9.91 (−20)	9.00 (−21)	4.43 (−22)	—	1.47 (−21)	2.61 (−20)
205	2.12 (−23)	—	3.26 (−20)	3.22 (−21)	1.39 (−22)	—	5.79 (−22)	1.24 (−20)
210	—	—	1.07 (−20)	1.12 (−21)	—	—	—	3.93 (−21)
215	—	—	—	—	—	—	—	1.38 (−21)
220	—	—	—	—	—	—	—	4.30 (−22)
225	—	—	—	—	—	—	—	1.21 (−22)
230	—	—	—	—	—	—	—	3.85 (−23)
235	—	—	—	—	—	—	—	1.12 (−23)

[a]The numbers in parentheses represent exponents to the power 10.

TABLE 4

Absorption cross sections in cm^2 for CCl_3F at 298 K in the wavelength range 230 - 260 nm[a]

λ (nm)	Run 1[b]	Run 2[c]	Run 3[c]	Previously reported data[d]
230	—	3.63 (—21)	3.47 (—21)	3.49 (—21)
235	—	1.32 (—21)	1.31 (—21)	1.26 (—21)
240	4.60 (—22)	4.86 (—22)	4.65 (—22)	4.64 (—22)
245	—	1.74 (—22)	1.73 (—22)	1.84 (—22)
250	5.30 (—23)	7.99 (—23)	6.55 (—23)	9.78 (—23)
255	—	3.09 (—23)	2.64 (—23)	5.86 (—23)
260	1.50 (—23)	1.82 (—23)	1.10 (—23)	2.85 (—23)

[a]The numbers in parentheses represent exponents to the power 10.
[b]10 cm light path, very high purity.
[c]100 cm light path.
[d]Data taken from ref. 1 ; 10 cm light path.
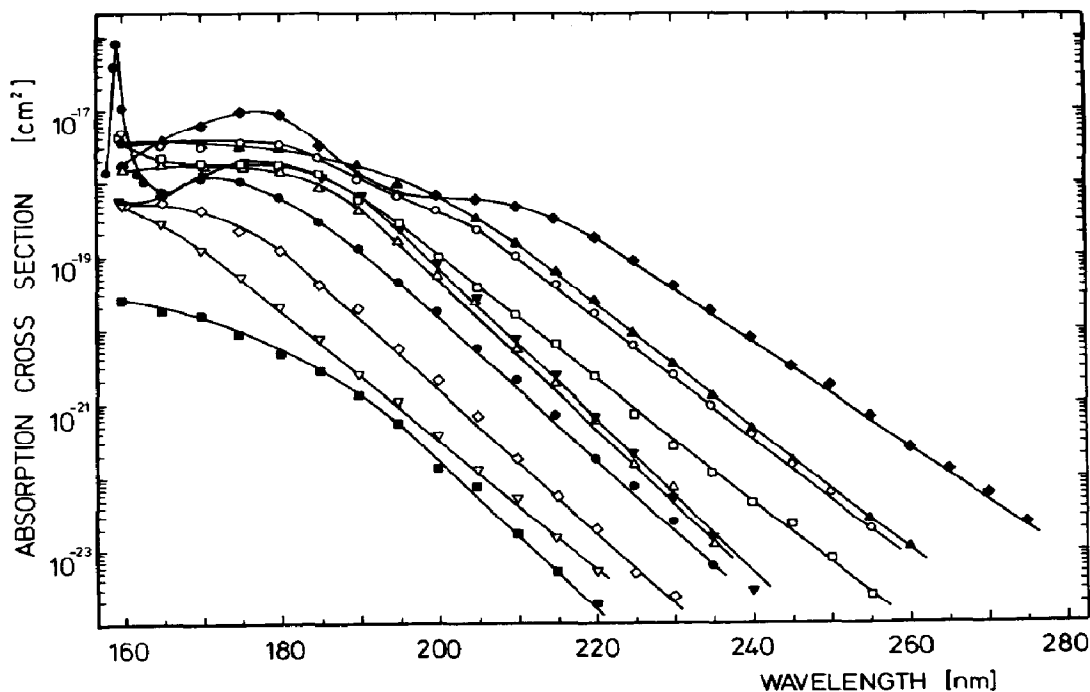
Fig. 1. Semilogarithmic plot of the absorption cross sections of the chlorinated methanes vs. the wavelength at 298 K: ○, $CHCl_3$; △, $CHCl_2F$; ▽, $CHClF_2$; □, CH_2Cl_2; ◇, CH_2ClF; ●, CH_3Cl; ◆, CCl_4; ▲, CCl_3F; ▼, CCl_2F_2; ■, $CClF_3$. Results taken from ref. 1 are included in this figure. For CCl_3F, the data were taken from ref. 1 for $\lambda < 245$ nm and from Table 4 (mean values of runs 1, 2 and 3) for $\lambda \geqslant 245$ nm.
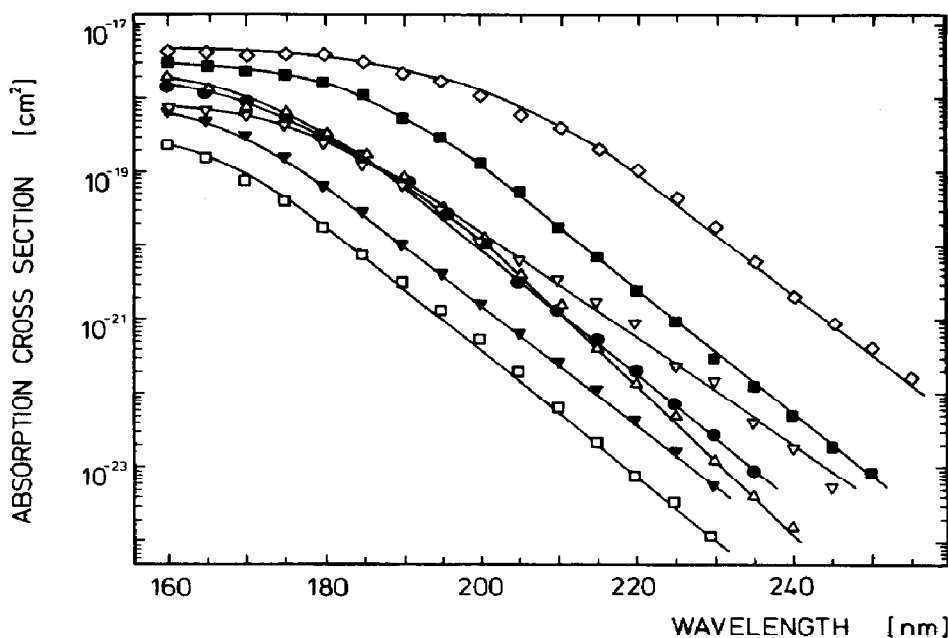
Fig. 2. Semilogarithmic plot of the absorption cross sections of several chlorinated ethanes vs. the wavelength at 298 K: ◇, CH_3CCl_3; ▽, CF_3CH_2Cl; △, CH_3CH_2Cl; □, CF_3CClF_2; ▼, CH_3CClF_2; ●, $CClF_2CClF_2$; ■, CCl_2FCClF_2.

$$\sigma(\lambda) = \sigma(\lambda_0)\exp\{-\kappa(\lambda - \lambda_0)\} \tag{2}$$

The parameters κ and $\sigma(\lambda_0)$, and the shortest wavelengths λ_0 for which this relationship is valid, are summarized in Table 5. The last column of this table gives the longest wavelengths λ_l for which eqn. (2) has been verified in this work.

The precision of the absorption data (expressed as three times the standard deviation) of the present investigation is similar to that given in our previous study (± 50% at the long wavelength limit, ± 20% at the short wavelength limit and as small as ± 3% in the range between these limits) [1]. The error given by the stated impurities is estimated to be less than 2% at the long wavelength threshold.

Several experiments were performed at room temperature in order to estimate at 253.7 nm the photodissociation cross section of CCl_3F relative to those of CCl_4 and $CHCl_3$. Each of these gases was mixed with small amounts of NO and with N_2 and was irradiated by the mercury pen lamp through the UG 5 filter glass. The total pressure of these mixtures was always kept close to 1 atm. Care was taken during the filling of the reaction vessel to avoid condensation of the chlorinated methanes. Figure 3 shows the decrease of NO for such mixtures (in ppm by volume) upon radiation as a function of time. It can be seen that the concentration of NO decreases linearly with time for small amounts of NO consumed. However, it should be noted that no NO was consumed in the absence of CCl_4, $CHCl_3$ or CCl_3F.

TABLE 5

Parameters for the relationship $\sigma(\lambda) = \sigma(\lambda_0)\exp\{-\kappa(\lambda - \lambda_0)\}$ at 298 K

Substance	κ (nm^{-1})	λ_0 (nm)	$\sigma(\lambda_0)$ (cm^2)[a]	λ_l (nm)
CCl_4	0.165	220	1.85 (−19)	275
CCl_3F[b]	0.192	210	1.56 (−19)	260
CCl_2F_2[c]	0.250	190	6.76 (−19)	240
$CClF_3$	0.237	195	5.60 (−22)	220
$CHCl_3$	0.188	205	2.43 (−19)	255
$CHCl_2F$[c]	0.234	190	4.34 (−19)	235
$CHClF_2$[c]	0.204	170	1.30 (−19)	220
CH_2Cl_2	0.191	195	2.70 (−19)	255
CH_2ClF	0.225	180	1.25 (−19)	230
CH_3Cl[c]	0.224	190	1.33 (−19)	235
CCl_2FCClF_2	0.194	200	1.23 (−19)	250
$CClF_2CClF_2$	0.199	185	1.63 (−19)	235
CF_3CClF_2	0.195	175	3.74 (−20)	230
CF_3CH_2Cl	0.162	195	2.95 (−20)	245
CH_3CCl_3	0.187	215	2.02 (−19)	255
CH_3CClF_2	0.186	180	6.31 (−20)	230
CH_3CH_2Cl	0.228	200	1.17 (−20)	240
N_2O	0.213	205	1.90 (−20)	250

[a]The numbers in parentheses represent exponents to the power 10.
[b]For $\lambda < 245$ nm the data were taken from ref. 1; for $\lambda \geqslant 245$ nm the mean values of runs 1, 2 and 3 (Table 4) were used.
[c]Data taken from ref. 1.
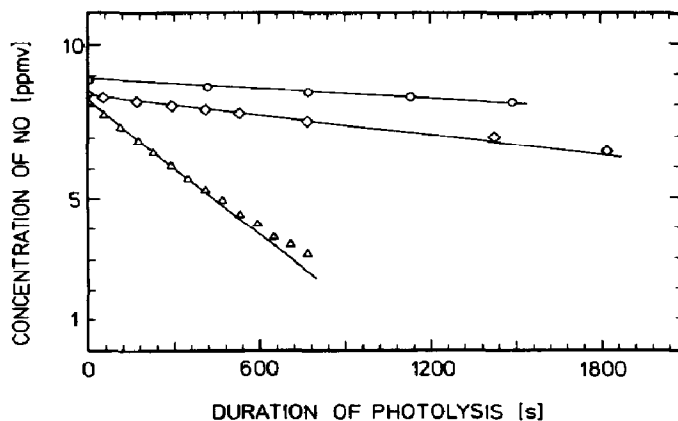
Fig. 3. NO decay upon irradiation with the 253.7 nm mercury line. The gas mixtures consisted of the following: ◇, 483.7 mbar CCl_3F, 530.9 mbar N_2 and contained 8.4 ppm by volume NO; ○, 190.4 mbar $CHCl_3$, 620.0 mbar N_2 and contained 8.9 ppm by volume NO; △, 119.9 mbar CCl_4, 880.1 mbar N_2 and contained 8.2 ppm by volume NO.

Decay rates of NO were hence obtained from the initial linear parts of these curves. These rates are displayed in Table 6 together with the decay rates calculated for a concentration of 1 mbar of chlorinated methane. The last column of this table gives the absorption cross section values which were obtained from these decay rates (see Section 4). For comparison, cross sections calculated using eqn. 2 and data in Table 5 are also given in this last column.

TABLE 6

Decay rates of NO in chlorinated methanes at 298 K upon irradiation with the 253.7 nm mercury line

Substance	Pressure (mbar)	NO decay rate (ppm by volume min^{-1})	Relative decay rate[a] (ppm by volume min^{-1} $mbar^{-1}$)	σ (253.7 nm)[a] (cm^2)
CCl_4	120	0.410	3.4 (—03)	8.0 (—22)[b]
$CHCl_3$	190	0.029	1.5 (—04)	2.8 (—23)[b]
				3.5 (—23)[c]
CCl_3F	484	0.057	1.2 (—04)	3.4 (—23)[b]
				2.8 (—23)[c]

[a]The numbers in parentheses represent exponents to the power 10.
[b]Calculated using eqn. (2) and data in Table 5.
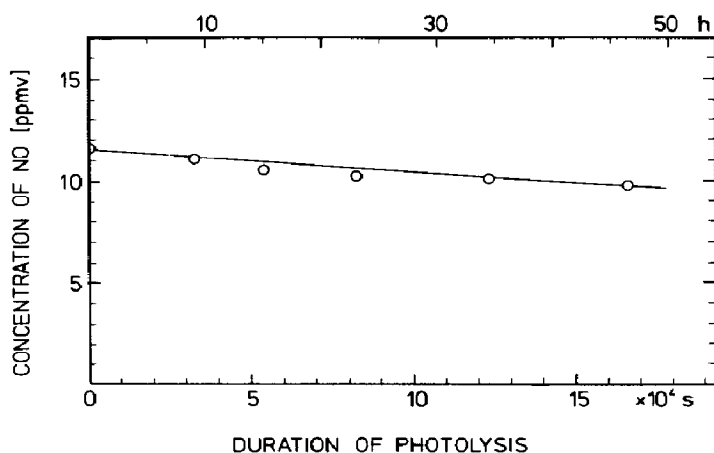[c]Value determined relative to that for CCl_4.

Fig. 4. NO decay upon irradiation with light of wavelengths greater than 280 nm. The gas mixture contained 11.6 ppm by volume NO and consisted of 649.3 mbar CCl_3F and 344.0 mbar N_2.

Some experiments were performed to estimate the absorption cross section for the photodissociation of CCl_3F at wavelengths greater than 280 nm. For this purpose, mixtures of CCl_3F, NO and N_2 at about 1 atm pressure were irradiated using the high pressure xenon—mercury lamp which was equipped with the filter glass WG 305. The samples were irradiated for

up to 150 h, since the removal of NO from this system was very slow. In order to take into account variations in the sensitivity of the chemiluminescence detector during such long periods of time and to avoid the influence of possible dark reactions, the signal obtained with the irradiated sample was always compared with that of an identical sample stored in the dark. Figure 4 shows an NO decay in 649.3 mbar CCl_3F which gives a value of 6×10^{-4} ppm by volume min^{-1} for the decay rate. It should be noted that somewhat smaller decay rates were observed in several runs.

4. Discussion

Absorption cross sections of several halocarbons of atmospheric interest have been summarized by Hudson [5] and by Watson [6] for data published prior to 1977. There is very good agreement between the data reported in this work for the chlorinated methanes CCl_4, CCl_3F, $CClF_3$ and CH_2ClF and the data presented in these summaries (investigated wavelength ranges: CCl_4, 174 - 238 nm; CCl_3F; 174 - 230 nm; $CClF_3$, 184.6 - 203 nm; CH_2ClF, 186 - 211.6 nm) [5, 6].

Also for CCl_2FCClF_2, CF_3CClF_2 and CH_3CCl_3 the data reported in this present work are in accord with those presented in the recent reviews (investigated wavelength ranges: CCl_2FCClF_2, 184.6 - 223.5 nm; CF_3-$CClF_2$, 174 - 198 nm; CH_3CCl_3, 186 - 226 nm) [5, 6]. Although somewhat higher (about 15%), the data for $CClF_2CClF_2$ are in reasonable agreement with those given in the literature for the wavelength range 174 - 218.6 nm [5, 6]. The absorption spectrum of CH_3CH_2Cl has been reported previously by Raymonda et al. [7]; however, the presentation of their data allows no quantitative comparison in the wavelength region investigated in the present work. The values of the absorption cross section obtained in the present work in the gas phase are roughly 30% lower than those obtained previously in alcoholic solution for the range 200 - 220 nm [8].

Recently Baumgärtel [9], Green and Wayne [10] and Vanlaethem-Meuree et al. [11] have determined absorption cross sections for a number of halocarbons. The present data are in good agreement with the data reported by Vanlaethem-Meuree et al. [11] for CCl_4 (170 - 216 nm). Our value for the absorption cross section of CCl_3F at about 190 nm agrees well with that determined by Green and Wayne [10], who investigated the cross sections in the range 187 - 210 nm. Our values are greater, however, at $\lambda <$ 190 nm and are smaller at $\lambda >$ 190 nm. Similarly, for CH_2ClF we observe that the values given by Baumgärtel [9] are smaller than our values for $\lambda <$ 185 nm and are significantly larger than our values for 185 nm $< \lambda <$ 190 nm. The absorption spectra of both CF_3CH_2Cl and CH_3CClF_2 have been studied by Baumgärtel [9] and by Green and Wayne [10]. A comparison of the present data with those of these authors shows that the agreement is not very good. The values for CF_3CH_2Cl presented by Green and Wayne [10] (187 nm $< \lambda <$ 203 nm) are about 50% smaller for $\lambda <$ 195 nm and the

values given by Baumgärtel [9] ($\lambda < 206.6$ nm) are about a factor of five greater than those of the present work. For CH_3CClF_2 there is good agreement with the data measured by Baumgärtel [9] ($\lambda < 200$ nm) for $\lambda > 175$ nm, but the values given by Green and Wayne [10] (185 nm $< \lambda < 201$ nm) are somewhat greater than those of the present study.

At $\lambda > 245$ nm, the reinvestigation of the absorption spectrum of CCl_3F resulted in smaller cross sections than those determined previously in our laboratory [1] (Table 4). We will show later that the present absorption measurements are in good agreement with estimates of the cross sections at $\lambda = 253.7$ nm and for $\lambda > 280$ nm which were obtained for the photodissociation process using the chemical method. These new data indicate the increased accuracy of the present measurements (for $l = 100$ cm) and the higher purity of the samples.

There have been only a few measurements of the temperature dependence of the absorption cross section of halogenated hydrocarbons reported in the literature. In this work we determined the absorption cross sections of $CClF_3$, CH_2ClF, CCl_2FCClF_2, $CClF_2CClF_2$, CF_3CClF_2, CF_3CH_2Cl and CH_3-$CClF_2$ at 208 K. To our knowledge there are no values for the absorption cross sections of these gases reported in the literature for temperatures close to 210 K. For the chlorinated methanes the temperature dependence of the cross sections [1, 5] appears to be less pronounced for molecules containing only one chlorine atom. Those molecules containing two and three chlorine atoms seem to exhibit a similar temperature dependence.

In this work and in our previous study [1] we determined the absorption spectra of all chlorinated methanes at 298 K close to the absorption threshold. The absorption spectra of the non-chlorinated methanes have been reported by Edwards and Raymonda [12]. From this complete set of data the following rules can be deduced for the long wavelength threshold of the absorption spectra: (1) the threshold shifts strongly towards short wavelengths for decreasing numbers of chlorine atoms in the molecules [13]; (2) for a constant number of chlorine atoms in the molecules there is a much weaker trend towards shorter wavelengths for decreasing numbers of hydrogen atoms (i.e. for increasing numbers of fluorine atoms). But there are two exceptions to this rule for molecules with high chlorine content, $CHCl_3/CCl_3F$ and $CCl_2F_2/CHCl_2F$. For these two pairs of molecules the absorption cross sections are not very different.

These two rules can be easily verified by arbitrarily taking $\sigma_{th} = 1 \times 10^{-21}$ cm^2 to indicate the threshold. The corresponding (threshold) wavelengths λ_{th} can be obtained from our previous work [1], from this work and from the work by Edwards and Raymonda [12]; for example $\lambda_{th} = 253$ nm for CCl_4, $\lambda_{th} = 219$ nm for CCl_2F_2, $\lambda_{th} = 141$ nm for CH_4 and $\lambda_{th} < 100$ nm for CF_4. Also, for the chlorinated ethanes, similar trends for the number (and position) of chlorine, fluorine and hydrogen atoms in the molecules are observed. Furthermore, Fig. 1 shows that the cross section of the first absorption maximum increases with the number of chlorine atoms in the chlorinated methanes and, at a constant number of chlorine atoms, decreases

with the number of fluorine atoms. This variation in the cross section takes place over more than three orders of magnitude.

Since the present study extends the investigated range to longer wavelengths (and thus to smaller cross sections) than any other previous study [5, 6, 8 - 11], Rayleigh scattering has to be considered as a limiting process. In order to estimate the contribution of this scattering process to the cross sections of CCl_3F determined in this work, the Rayleigh scattering cross section σ_R of CCl_3F was determined relative to that of CCl_2F_2. For this purpose CCl_3F and CCl_2F_2 were irradiated with an HO resonance lamp ($\lambda \approx 308$ nm) and with the mercury lamp ($\lambda = 253.7$ nm) using an experimental arrangement described previously [14]. The light scattered from both gases was monitored at right angles to the incident light beam. The cross sections for the Rayleigh scattering of CCl_2F_2 have been determined previously for several wavelengths in the range 363.8 - 694.3 nm [15]. The extrapolation of these data according to a λ^{-4} dependence allows estimates for the cross sections of CCl_2F_2 at about 308 nm and at 253.7 nm. Hence the ratio of the light intensities scattered by CCl_3F and by CCl_2F_2 results in values for CCl_3F at these wavelengths; they are $\sigma_R \approx 8 \times 10^{-25}$ cm^2 at about 308 nm and $\sigma_R \approx 2 \times 10^{-24}$ cm^2 at 253.7 nm. Thus, at 253.7 nm Rayleigh scattering contributes about 5% to the measured absorption cross section. We will show that Rayleigh scattering dominates at wavelengths longer than 300 nm.

In the present study the absorption of N_2O was also investigated since this species is of primary interest to stratospheric chemistry. A comparison with the recent data of Selwyn et al. [16] shows very good agreement at both room temperature and stratospheric temperature.

It has been demonstrated recently for several halocarbons, e.g. CCl_4 and CCl_3F, that the quantum yield for the production of atomic chlorine is unity [6] close to the absorption threshold:

$$CCl_4 + h\nu \quad \rightarrow \quad R_3 + Cl \tag{3}$$

$$CCl_3F + h\nu \quad \rightarrow \quad R_4 + Cl \tag{4}$$
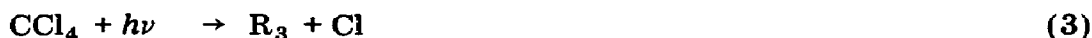
Here R_n is the halogenated methyl radical produced in reaction (n). If the same dissociation process

$$CHCl_3 + h\nu \quad \rightarrow \quad R_5 + Cl \tag{5}$$

is assumed for $CHCl_3$, the relative photodissociation rate of these three gases can be determined by their radical production rate. The radical production rate was estimated from the consumption of small amounts of NO in the photolysis system according to

$$Cl + NO + M \quad \rightarrow \quad ClNO + M \tag{6}$$

$$R_n + NO \,(+M) \rightarrow R_nNO \,(+M) \tag{7}$$

Reaction (6) is relatively fast under the conditions used ([M] $\approx 2.4 \times 10^{19}$ cm^{-3}; [NO] $\approx 2.4 \times 10^{14}$ cm^{-3}; $k_6 \approx 1.5 \times 10^{-31}$ cm^6 s^{-1} [6]) and the initial lifetime τ of chlorine atoms is about 1.3 ms. The resulting product

ClNO is effectively attacked by chlorine atoms ($k_8 = 3 \times 10^{-11}$ cm^3 s^{-1}) [6] and NO is produced:

$$Cl + ClNO \rightarrow Cl_2 + NO \tag{8}$$

Not much seems to be known about reactions such as reaction (7) and the following reactions which can also reproduce NO in this system:

$$R_n + R_nNO \rightarrow R_nR_n + NO \tag{9}$$

$$Cl + R_nNO \rightarrow R_nCl + NO \tag{10}$$

$$R_n + ClNO \rightarrow R_nCl + NO \tag{11}$$

The quantum yield $\phi(NO)$ for the consumption of NO can therefore not be deduced from the reaction mechanism (3) - (11). Since Fig. 3 shows initial decays of NO of zero order, $\phi(NO)$ is constant for small amounts of NO consumed. Assuming that $\phi(NO)$ has the same value for the photolysis of CCl$_4$, CHCl$_3$ and CCl$_3$F at 253.7 nm and that the absorbing gas is optically thin (less than 3% of the incident radiation is absorbed), relative photodissociation cross sections are given by the relative decay rates displayed in the fourth column of Table 6.

Photodissociation cross sections are listed in the last column of Table 6; they are calculated relative to the absorption cross section of CCl$_4$ (Table 1). This column also shows the absorption cross sections of CHCl$_3$ and CCl$_3$F which are estimated from the data in Table 5. The good agreement between the values obtained by these two different methods supports the assumption made earlier.

According to reactions (3) - (11), $\phi(NO)$ will not be greater than two during the initial decay time of NO shown in Fig. 4. However, even for small amounts of NO consumed, $\phi(NO)$ can be much smaller than two depending on the efficiencies of reactions (7) - (11). In order to obtain a rough estimate of the photodissociation cross section of CCl$_3$F for the wavelength region 280 - 375 nm, we assume that $\phi(NO)$ is equal to one. Hence, with the estimated light intensity of the high pressure xenon-mercury lamp, we calculate a cross section of about 10^{-26} cm^2 for the wavelength range 280 - 375 nm. Approximately the same value is estimated simply by averaging the cross sections obtained by extrapolation using the data in Table 5. It should be noted, however, that both these estimates represent at best the order of magnitude of the cross section.

Such a small photodissociation cross section for wavelengths longer than 280 nm indicates that the homogeneous photochemical removal rate of CCl$_3$F in the troposphere is extremely small. Using the data given by Bener [17] and by Peterson [18] for the tropospheric solar flux and the present absorption cross section, the tropospheric decay rate of CCl$_3$F is estimated to be well below 10^{-10} s^{-1} with respect to the homogeneous gas phase photolysis.

Acknowledgments

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