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Ultraviolet absorption cross-sections of chloro-  
and chlorofluoromethanes at stratospheric temperatures

by

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## **FOREWORD**

The paper entitled "Ultraviolet absorption cross-sections of chloro- and chlorofluoro-methanes at stratospheric temperatures" is submitted for publication in "Journal of Atmospheric Chemistry".

## **AVANT-PROPOS**

L'article intitulé "Ultraviolet absorption cross-sections of chloro- and chlorofluoro-methanes at stratospheric temperatures" est soumis pour publication dans le "Journal of Atmospheric Chemistry".

## **VOORWOORD**

Het artikel "Ultraviolet absorption cross-sections of chloro- and chlorofluoro-methanes at stratospheric temperatures" is voorgelegd ter publikatie in het "Journal of Atmospheric Chemistry".

## **VORWORT**

Der Artikel "Ultraviolet absorption cross-sections of chloro- and chlorofluoro-methanes at stratospheric temperatures" ist zur Veröffentlichung vorgelegt im "Journal of Atmospheric Chemistry".

# ULTRAVIOLET ABSORPTION CROSS-SECTIONS OF CHLORO- AND CHLOROFLUORO-METHANES AT STRATOSPHERIC TEMPERATURES

P.C. SIMON, D. GILLOTAY, N. VANLAETHEM-MEUREE and J. WISEMBERG

## Abstract

Absorption cross-sections of nine halomethanes ( $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CFCl}_3$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CF}_3\text{Cl}$ ,  $\text{CHFCl}_2$  and  $\text{CHF}_2\text{Cl}$ ) measured between 174 and 250 nm for temperatures ranging from 225 to 295 K, are presented with uncertainties ranging from 2 to 4 % and compared with previous determinations made for comparable temperature range.

The largest temperature effect which takes place near the absorption threshold, decreases the absorption cross-section up to 50 % for highly chlorinated methanes but is negligible for molecules highly stabilized by hydrogen and/or fluorine.

Extrapolated values for temperatures of aeronomical interest are presented as well as parametrical formulas which give absorption cross-section values for given wavelength and temperature ranges.

## Résumé

Les sections efficaces d'absorption de neuf halométhanes ( $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CFCl}_3$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CF}_3\text{Cl}$ ,  $\text{CHFCl}_2$  et  $\text{CHF}_2\text{Cl}$ ) mesurées entre 174 et 250 nm pour des températures variant entre 225 et 295 K, sont présentées avec une incertitude comprise entre 2 et 4% et comparées à des déterminations antérieures réalisées dans les gammes de températures comparables.

L'effet de température le plus important, qui a lieu près du seuil d'absorption, réduit les sections efficaces d'un facteur pouvant atteindre 50% pour les méthanes fortement chlorées; il devient négligeable pour des molécules fortement stabilisées par des atomes d'hydrogène et/ou de fluor.

Les valeurs extrapolées aux températures d'intérêt aéronomique sont présentées de même que des équations paramétriques permettant de calculer des valeurs de sections efficaces d'absorption pour des intervalles de longueur d'onde et de température données.

## Samenvatting

De werkzame absorptiedoorsneden van negen halomethaanverbindingen ( $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CFCl}_3$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CF}_2\text{Cl}$ ,  $\text{CHFC}_2\text{Cl}$  en  $\text{CHF}_2\text{Cl}$ ) gemeten tussen 174 en 250 nm voor temperaturen variërend tussen 225 en 295 K, worden voorgesteld met onzekerheden die schommelen tussen 2 en 4% en vergeleken met vorige bepalingen opgesteld voor vergelijkbare temperaturen.

Het belangrijkste temperatuurgevolg dat plaats heeft bij de absorptiedrempel leidt tot een vermindering van de werkzame absorptiedoorsneden die wel 50% kan bereiken voor de sterk gechloreerde methaanverbindingen; ze is echter te verwaarlozen voor moleculen die sterk gestabiliseerd worden door waterstof- en/of fluoratomen.

Geëxtrapoleerde waarden voor temperaturen van aëronomisch belang worden voorgesteld, alsook parametrische vergelijkingen die toelaten werkzame absorptiedoorsneden te berekenen voor gegeven temperatuur- en golflengte-intervallen.

## Zusammenfassung

Die Absorptionsdurchschnitten von neun Halomethanverbindungen ( $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CFCl}_3$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CF}_2\text{Cl}$ ,  $\text{CHFC}_2\text{Cl}$  en  $\text{CHF}_2\text{Cl}$ ) gemessen zwischen 174 und 250 nm für Temperaturen die variieren zwischen 225 und 295 K, werden vorgestellt mit Ungewissheiten der wechseln zwischen 2 und 4% und verglichen mit vorigen Bestimmungen aufgesetzt für vergleichbare Temperaturen.

Die wichtigste Temperaturfolge die auftritt an die Absorptionsschwelle, leitet zu einer Verringerung der Absorptionsdurchschnitten der bis 50% erreichen kann für die stark chlorierten Methanverbindungen; sie ist aber zu vernachlässigen für Molekule die stark stabilisiert werden durch Wasserstoff- und/oder Fluoratomen.

Extrapolierte Werten für Temperaturen von aëronomisches Interesse werden vorgestellt, wie auch parametrische Vergleichen die zulassen Absorptionsdurchschnitten zu berechnen für gegeben Temperatur- und Wellenlängeintervallen.

## INTRODUCTION

Odd chlorine ( $\text{Cl}$ ,  $\text{ClO}$ ,  $\text{ClONO}_2$ ,  $\text{HCl}$ ,  $\text{HOCl}$ , ...), which plays a key role in the budget of ozone in the stratosphere, is produced essentially by decomposition of halocarbons released in the troposphere. Organic halocarbons containing hydrogen atoms such as  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CHFCl}_2$ ,  $\text{CHF}_2\text{Cl}$ , may react rapidly with radicals such as  $\text{OH}$  and may thus be largely destroyed in the troposphere. (Singh et al., 1979). Fully halogenated compounds such as  $\text{CFCl}_3$ ,  $\text{CF}_2\text{Cl}_2$ , ..., are not subject to chemical destruction in the troposphere and therefore transported in the stratosphere where they are destroyed by photodissociation. (Molina and Rowland, 1974). Actually, only molecules with appreciable tropospheric residence times are subject to the diffusion up to stratospheric altitudes; when emission data are considered simultaneously, it appears that at least  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCl}_3$ ,  $\text{CCl}_4$ ,  $\text{CH}_3\text{Cl}$  and  $\text{CHFCl}_2$  play a significant role in the stratospheric chemistry. (WMO, 1985; Wuebbles, 1983; Schmidt et al., 1985)

Since a significant fraction of the ozone loss in the 30 - 50 km region is due to active chlorine resulting from the photodecomposition of these halocarbons, the absorption cross-section of these molecules has to be known with high accuracy. Furthermore, their temperature dependence has to be carefully measured because of the temperature condition prevailing at stratospheric altitude. Preliminary measurements of temperature dependence of absorption cross-section of chlorofluoromethanes, published by Vanlaethem-Meuree et al. (1978), have shown some non negligible disagreements in the temperature dependence of cross-section with existing data (Chou et al., 1976, 1977, 1978; Robbins, 1976 a,b,c; Robbins and Stolarski, 1976; Bass and Ledford, 1976). Even at room temperature, discrepancies between some data are larger than the experimental uncertainties.

The purpose of this paper is to report new measurements of ultraviolet absorption cross-section of nine halomethanes, namely :  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ,  $\text{CF}_3\text{Cl}$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCl}_3$ ,  $\text{CHF}_2\text{Cl}$  and  $\text{CHFCl}_2$

performed between 174 and 250 nm., at four different temperatures over the 225 - 295 K temperature range. This new set of data allows a reliable extrapolation down to 210 K. Taking into account the temperature dependence of absorption cross-section and the stratospheric temperature profile, photodissociation coefficients are calculated showing significant departure in these coefficients relative to similar calculations made for 295 K. These data will be helpful to quantitatively estimate the lifetime of these halomethanes and to perform more accurately chlorine and ozone budget evaluations in the stratosphere.

### EXPERIMENTAL

Absorption cross-sections have been determined in the 200 nm wavelength range as a function of temperature, with a classical single beam equipment (deuterium light source, 1 m model 225 Mc Pherson monochromator, absorption cell, an EMR 542 P.09.18 solar blind photomultiplier as detector). A complete description of the experimental device has been given previously by Wisemberg and Vanlaethem (1978) and by Gillotay and Simon (1988).

Two different kinds of absorption cell were used to obtain the U.V. absorption spectra of studied gases:

1. As the condensation conditions restrict the use of fairly high gas pressure at low temperature and then to access to low absorption cross-section determination, a long absorption optical path is required. Most of the measurements have been performed by mean of a thermostatic stainless absorption cell with a 2 m optical path. It can be evacuated down to  $10^{-7}$  torrs by an ionic pump which prevents any contamination. Temperature regulation down to 210 K is achieved by circulation of cooled methylcyclohexane through a double jacket. Thermal equilibrium is obtained usually after 3-4 hours with a maximum temperature gradient between both ends of the cell of 2 K at 220 K. Gas pressure is measured

by capacitance manometers MKS Baratron directly coupled with the absorption cell which allows the measurement of pressure ranging from  $10^{-3}$  to 1000 torrs with a precision better than 0.1 % , and its decrease is followed during a cooling process. The actual gas temperature is determined by considering both the conditions prevailing at the three points of measurement in the cell and the value deduced from the pressure decrease, according to the perfect gases law. Both determinations are in close agreement, better then 2K. Therefore, the accuracy of the final temperature determination is within 2 K over the whole temperature range. For technical reasons, three temperatures have been selected for absorption cross-sections measurements, namely around 270, 255 and 225 K.

2. Some of the experiments were performed at room temperature in a 13.5 cm optical path absorption cell, in order to access to the fairly high absorption cross-sections.

The agreement of the two sets of results is always within the experimental uncertainties defined below (2 % at room temperature) in the overlap wavelength range.

Determination of the absorption cross-sections is based upon at least 15 sequential recordings of continuously scanned spectra of the incident and absorbed fluxes measured for identical temperature conditions, using the Beer-Lambert's law :

$$I(\lambda) = I_0(\lambda) \exp(-\sigma(\lambda) n \cdot d) \quad (1)$$

where :  $I_0(\lambda)$  and  $I(\lambda)$  are respectively the incident and transmitted fluxes, for a given wavelength  $\lambda$ .

$n$  is the number of molecules per volume unit.

$d$  is the optical path.

$\sigma(\lambda)$  is the absorption cross-section at wavelength  $\lambda$ .

The spectral resolution is of 0.15 nm with 100 $\mu$ m slits.

In all cases, measurements were performed in a wide pressure range, for which the validity of Beer-Lambert's law was confirmed.

All samples were of analytical grade and were distilled under vacuum and thoroughly outgassed before use.

According to the error budget, presented in table 1, the accuracy on cross-section measurements is of the order of  $\pm 2\%$ , at ambient temperature. At lower temperatures, the uncertainties increased from  $\pm 3\%$  to  $\pm 4\%$  for the absorption cross-sections values lower than  $2 \times 10^{-21} \text{ cm}^2 \text{ molec}^{-1}$ . Moreover, the standard deviation calculated, at each wavelength, on the observed values of cross-sections (at least 15 values) are lower than  $2\%$  at ambient temperature. At the lowest temperature and for the lowest values of absorption cross-section, the standard deviation is of the order of  $3.5\%$ , after the least squares fit on the four studied temperatures.

## RESULTS

Numerical values of absorption cross-sections for selected wavelengths between 174 and 250 nm and frequency intervals of  $500 \text{ cm}^{-1}$  currently used for aeronomy modelling (Brasseur and Simon, 1981) are respectively given in Tables 2a-10a and 2b-10b. The absorption spectra are also presented in Figures 1-6.

### a) Ambient temperature (295 K).

Cross-sections measurements have been extended to lower values ( $< 2 \times 10^{-21} \text{ cm}^2 \text{ molecule}^{-1}$ ) than those currently available in the literature.

Chloro- and chlorofluoromethanes display continuous absorption in the 174-250 nm region, with absorption cross-sections ranging from  $10^{-17}$  to  $10^{-22} \text{ cm}^2 \text{ molec}^{-1}$ . The progressive substitution of H atoms of the basic methane by Cl atoms leads to increase absorption and to extend the absorption region towards higher wavelengths. On the contrary, the presence of F atoms tends to stabilize the molecule whose absorption spectrum is depressed and shifted towards lower wavelengths.

The results presented in Table 2-10 and Figures 1-3 are in close agreement, within the quoted accuracy, with those generally used in modelling calculations (Codata panel, 1982; DeMore et al., 1985) and confirm the previous published values for  $\text{CH}_3\text{Cl}$  (Robbins 1976,a,b), for  $\text{CHCl}_3$  (Robbins 1976c), for  $\text{CCl}_4$  (Rowland and Molina 1975, Robbins 1976c), for  $\text{CF}_2\text{Cl}_2$  and  $\text{CFCl}_3$  (Rowland and Molina, 1975; Robbins, 1976c; Robbins and Stolarski, 1976; Bass and Ledford, 1976; Chou et al, 1977), and for



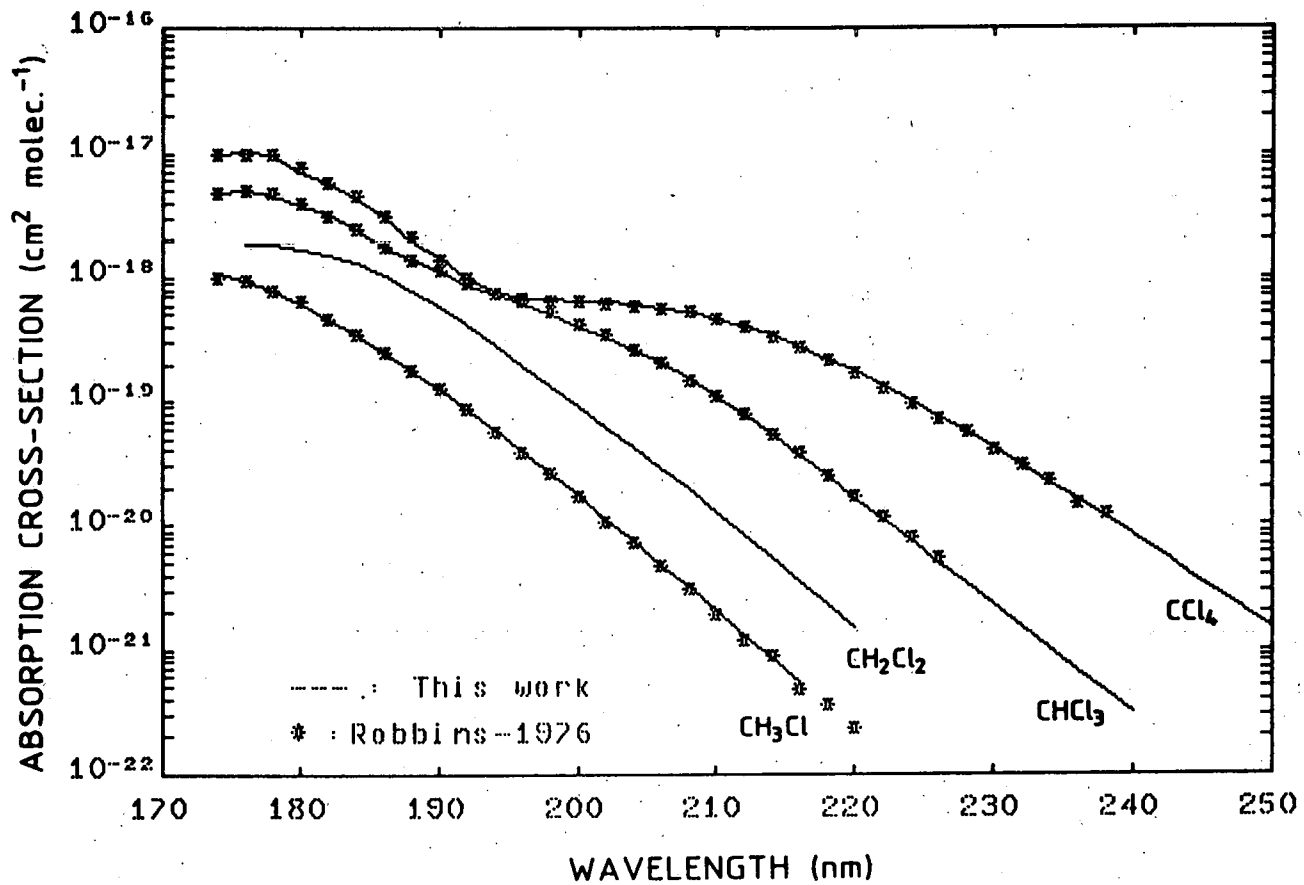


Fig. 1.- Ultraviolet absorption cross sections of CH<sub>3</sub>Cl, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and CCl<sub>4</sub> with respect of wavelength at 295 K.

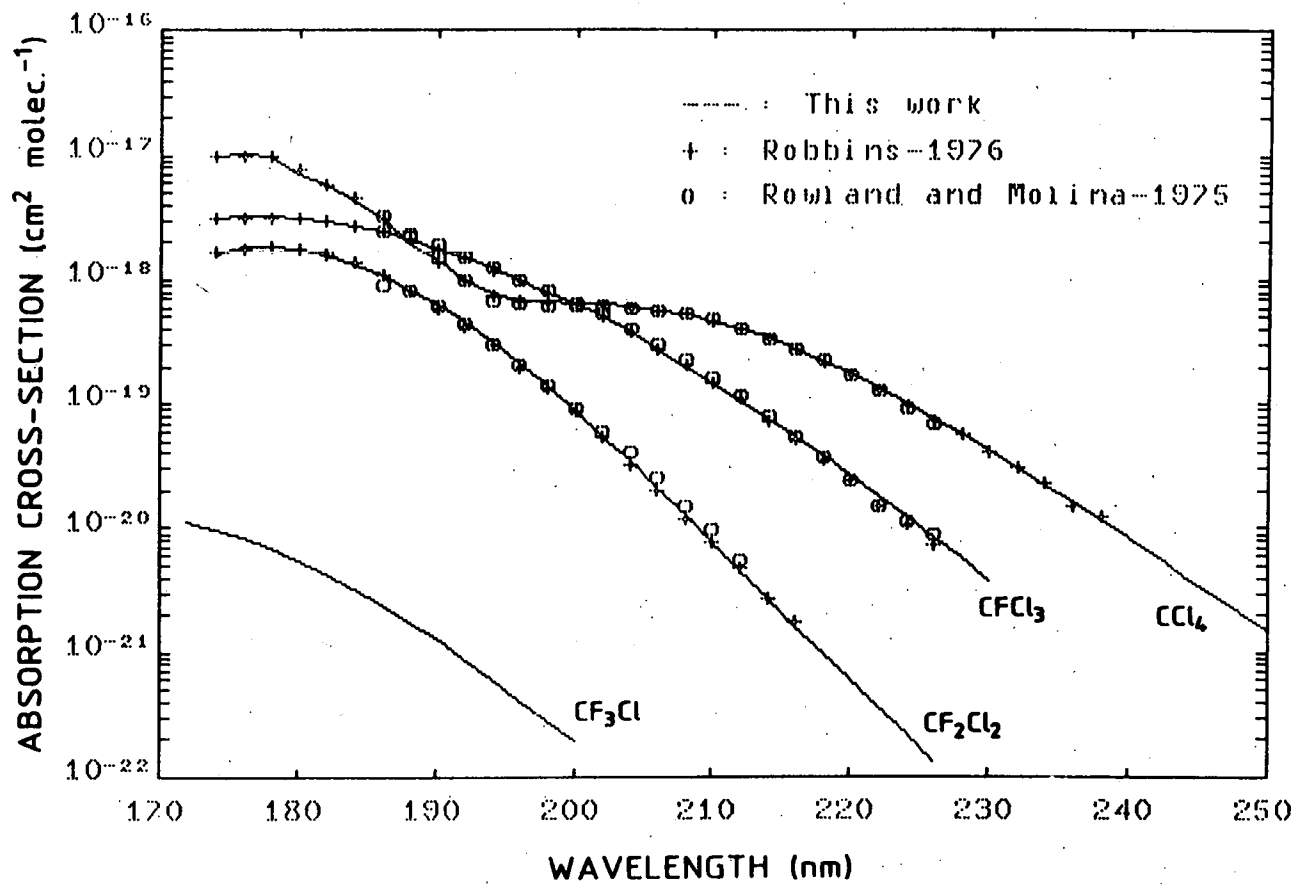


Fig. 2.- Ultraviolet absorption cross-sections of  $CF_3Cl$ ,  $CF_2Cl_2$ ,  $CFCl_3$  and  $CCl_4$  with respect to wavelength at 295 K.

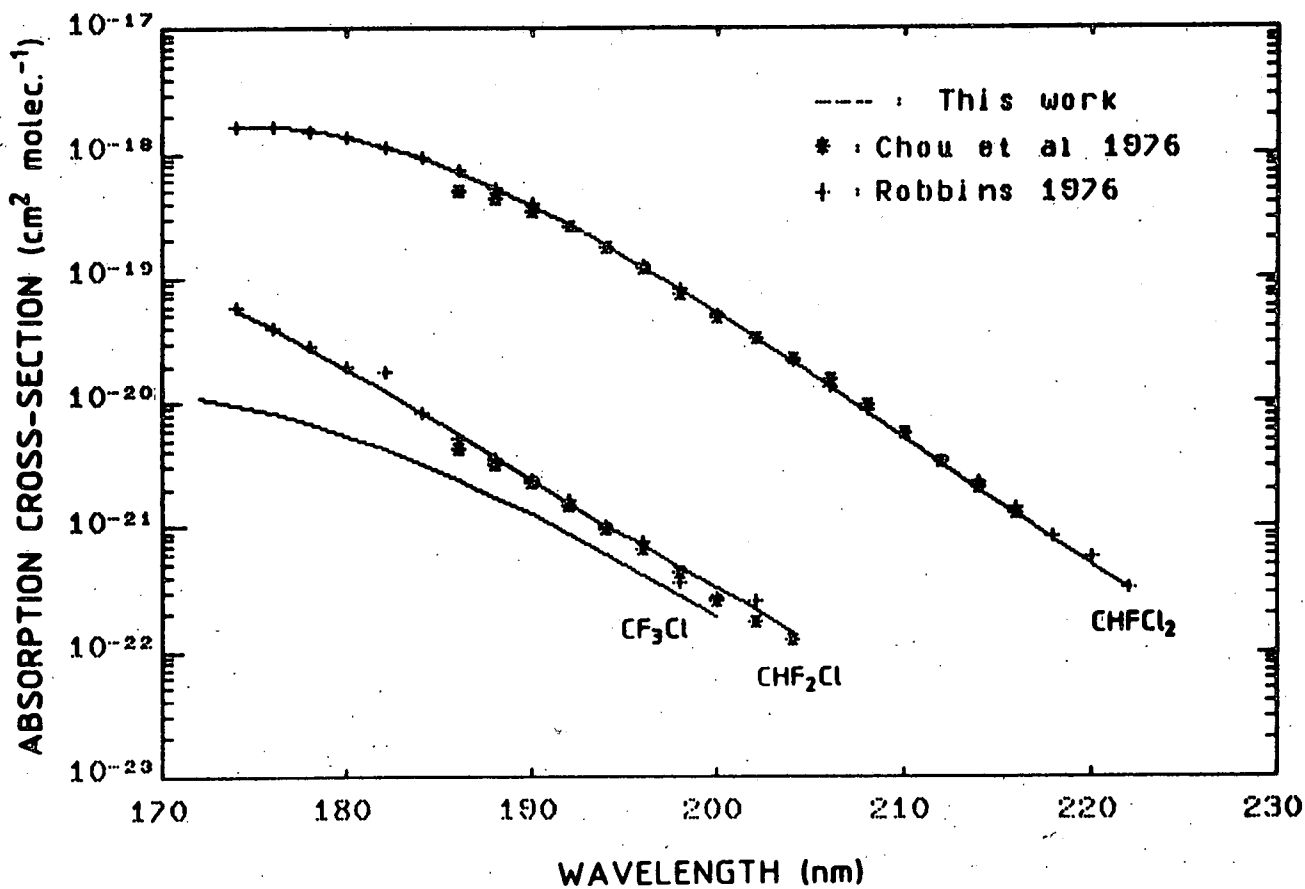


Fig. 3.- Ultraviolet absorption cross-sections of  $\text{CF}_3\text{Cl}$ ,  $\text{CHF}_2\text{Cl}$  and  $\text{CHFCℓ}_2$  with respect to wavelength at 195 K.

$\text{CHF}_2\text{Cl}$  and  $\text{CHFCl}_2$  (Robbins 1976c, Robbins and Stolarski 1976, Chou et al 1976) within the experimental errors. Disagreements between 20 to 30 % at some wavelengths are clearly seen from Figures 2, for  $\text{CF}_2\text{Cl}_2$  between 204 and 210 nm and from Figure 4 for  $\text{CHF}_2\text{Cl}$  between 198 and 204 nm. In the case of methylene chloride ( $\text{CH}_2\text{Cl}_2$ ), if one excepts the data of Gordus and Bernstein (1954) limited to a narrow wavelength range (205-220 nm), the only available data are the values published by Hubrich and Stuhl (1980) which are in average 10% higher those reported here. Values obtained in this work for  $\text{CF}_3\text{Cl}$  are significantly lower in the region of weak absorption (up to 30 % depending of the wavelength) than the ones obtained by Chou et al. 1978 (not plotted on the figure) with a 10 cm absorption cell. It should be pointed out that the use of a 2 m absorption cell allows a more accurate determination specially in the ranges corresponding to low absorption.

With the assumption, in first approximation, of an exponential decrease of absorption cross-sections with the wavelength in this low absorption region, the results presented here substantiate the hypothesis according to which tropospheric photodissociation is negligible compared to the stratospheric contribution ; even in the case of the most absorbing compound ( $\text{CCl}_4$ ), the absorption cross-section does not exceed  $10^{-26} \text{ cm}^2 \text{ molec.}^{-1}$  in the 300 nm region (Rebbert and Ausloos 1976).

b) Low temperature (225\_K - 270\_K).

For each compound, absorption cross-sections have been measured for different temperatures in the largest range afforded by vapor pressure conditions which limit the maximum working pressure. The actual experimental conditions are summarized in Table 11.

As shown in Figures 4-6, absorption cross-sections decrease with temperature by a factor which depends on both the wavelength and the chemical composition of the compound. This effect is the most significant at low temperatures and in spectral regions of low absorptions. The temperature dependence is more important in the case of highly chlorinated substances, but vanishes progressively in the region of

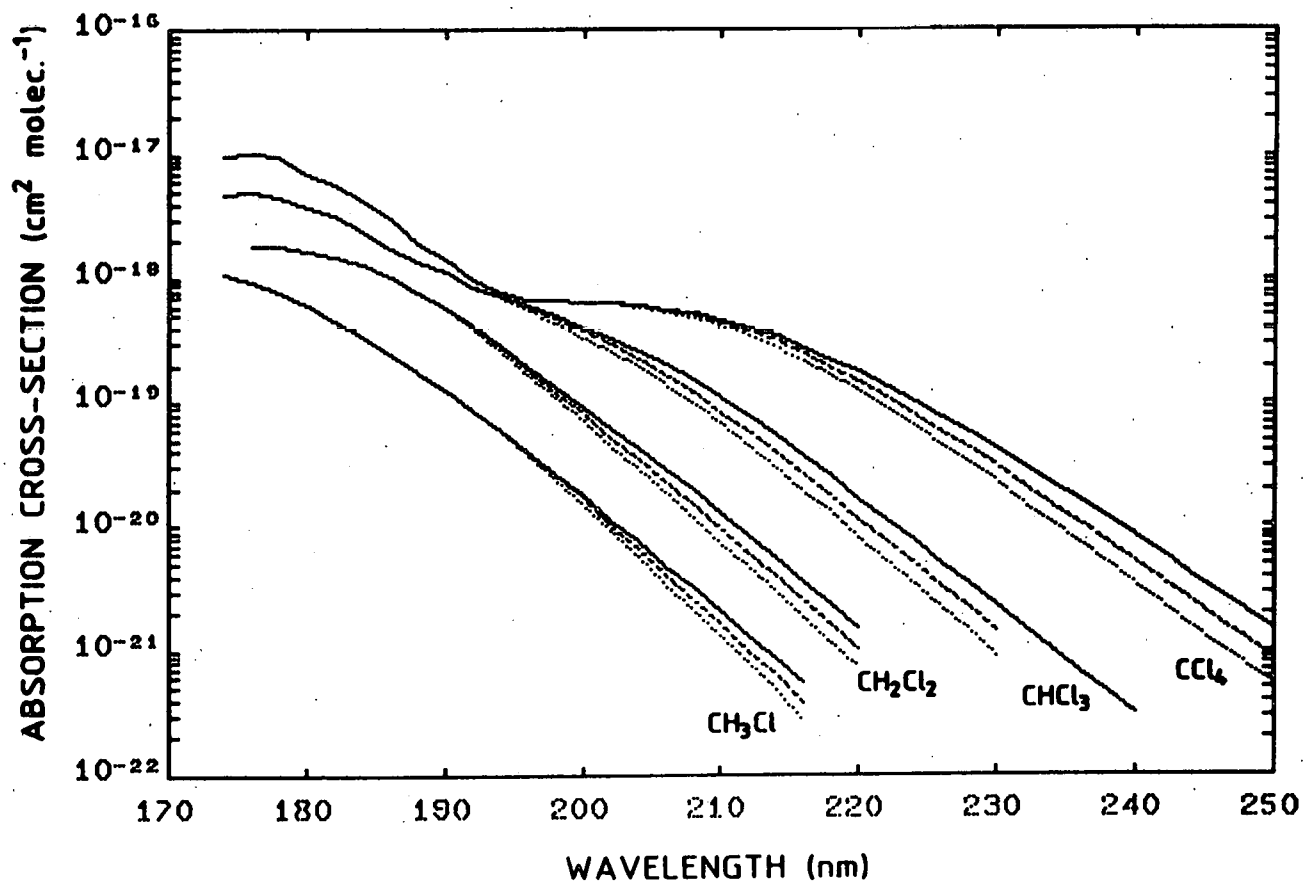


Fig. 4.- Ultraviolet absorption cross-sections of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CCl}_4$  versus wavelength as a function of temperature.

295 K : -----  
 250 K : - . - . -  
 210 K : .....  
 . . . . .

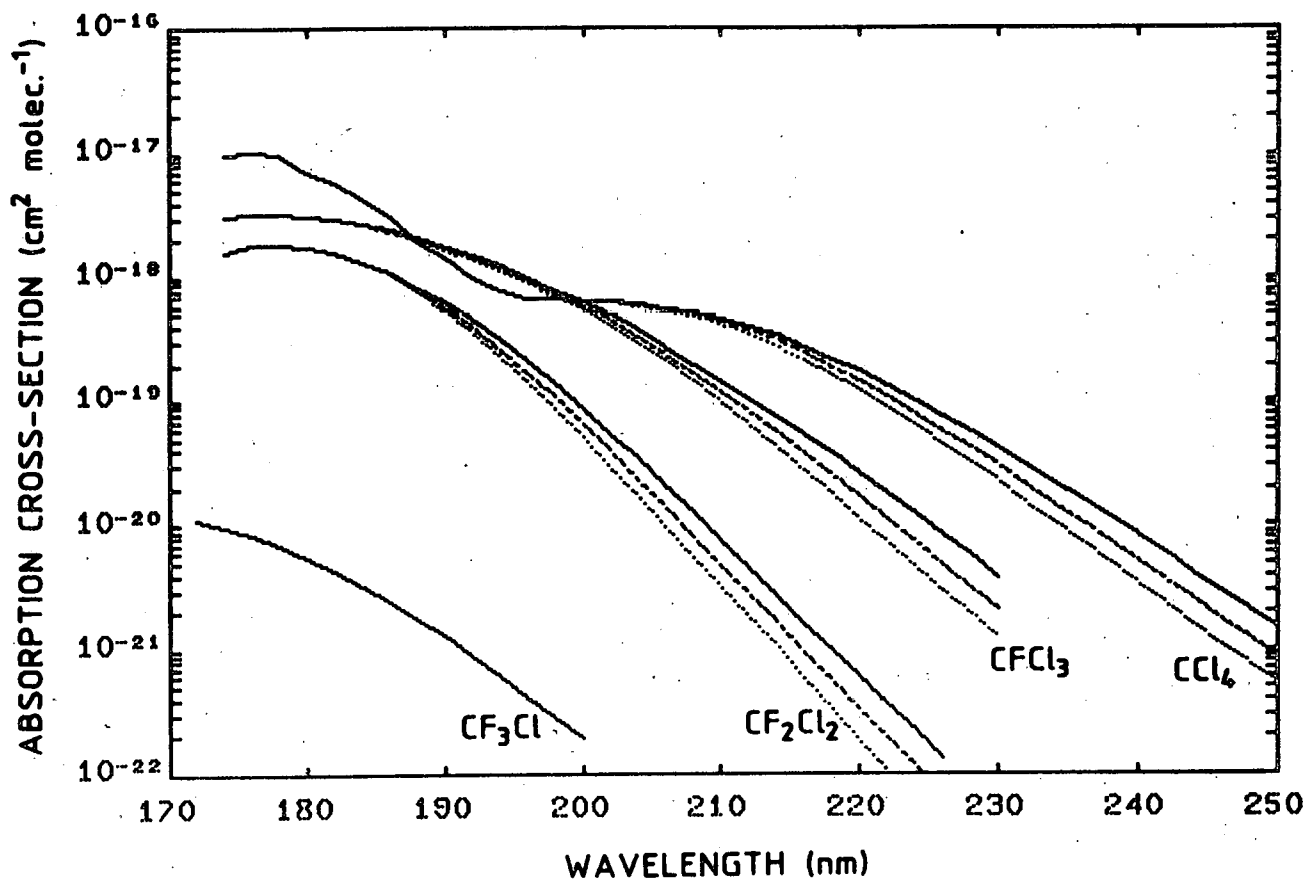


Fig. 5.- Ultraviolet absorption cross-sections of  $\text{CF}_3\text{Cl}$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCl}_3$  and  $\text{CCl}_4$  versus wavelength as a function of temperature.

295 K : ———

250 K : - - -

210 K : .....

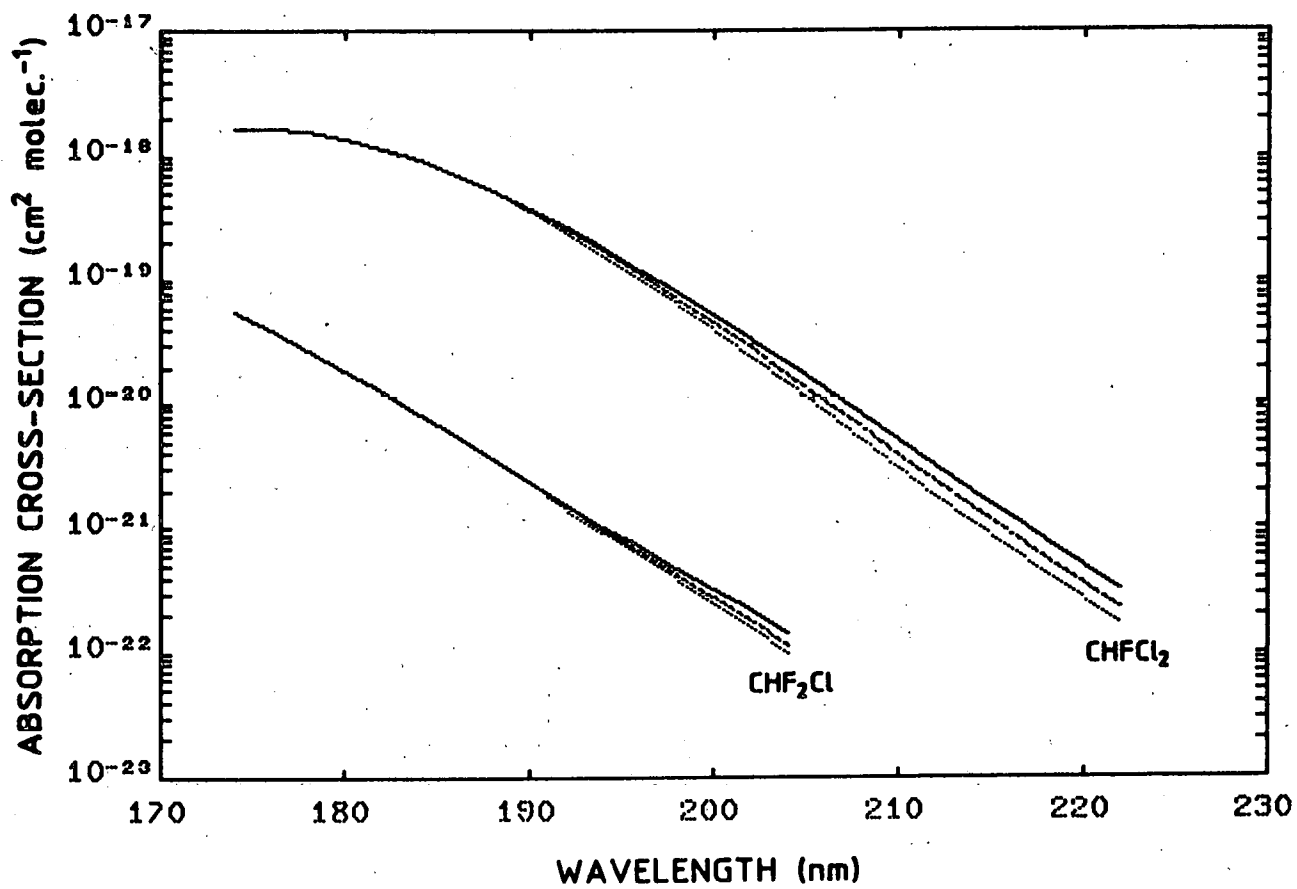


Fig. 6.- Ultraviolet absorption cross-sections of CHF<sub>2</sub>Cl and CHCl<sub>2</sub> versus wavelength as a function of temperature

295 K : ———  
 250 K : - - -  
 210 K : .....

higher absorptions. Temperature effect, if any, was too small to be detected in our experimental conditions in the case of  $\text{CF}_3\text{Cl}$ .

For all compounds, the relationship between the absorption cross-sections and the temperature for a given wavelength is characterized by an exponential decrease depending upon wavelength and temperature values (295 K, 270 K, 255 K and 225 K). Consequently extrapolation based on four temperatures well distributed within the temperature range can easily be made down to 210 K within the accuracy range defined above.

Numerical values are presented in Tables 2-10 for selected temperatures (270, 250, 230, 210 K) which cover the usual stratospheric conditions.

Similar measurements have already been made only at two temperatures, 296 K and 223 K in the particular case of  $\text{CF}_2\text{Cl}_2$  and  $\text{CFCl}_3$  by Bass and Ledford (1976) who used optical paths up to 10 m and by Chou et al. (1977) with a 10 cm absorption cell at several temperatures between 212 and 296 K. Comparison with the available data is given on Figure 7, 8 and 9.

For  $\text{CF}_2\text{Cl}_2$ , values reported in this work confirm the previous results of Bass and Ledford (1976), down to 215 nm. The results published by Chou et al. (1977) give systematically higher values than those reported by Bass and Ledford and in this work. At 220 nm where the absorption cross-sections are below  $10^{-21} \text{ cm}^2 \text{ molec.}^{-1}$ , the agreement between Bass and Ledford and Chou et al. seems better but both give higher values and, consequently, a less pronounced temperature dependence. Actually, this wavelength represents the lower limit in measurements given by both authors.

A similar conclusion can be drawn from Figure 8 giving the comparison between measurements performed for  $\text{CFCl}_3$  and can be extended down to 200 nm.



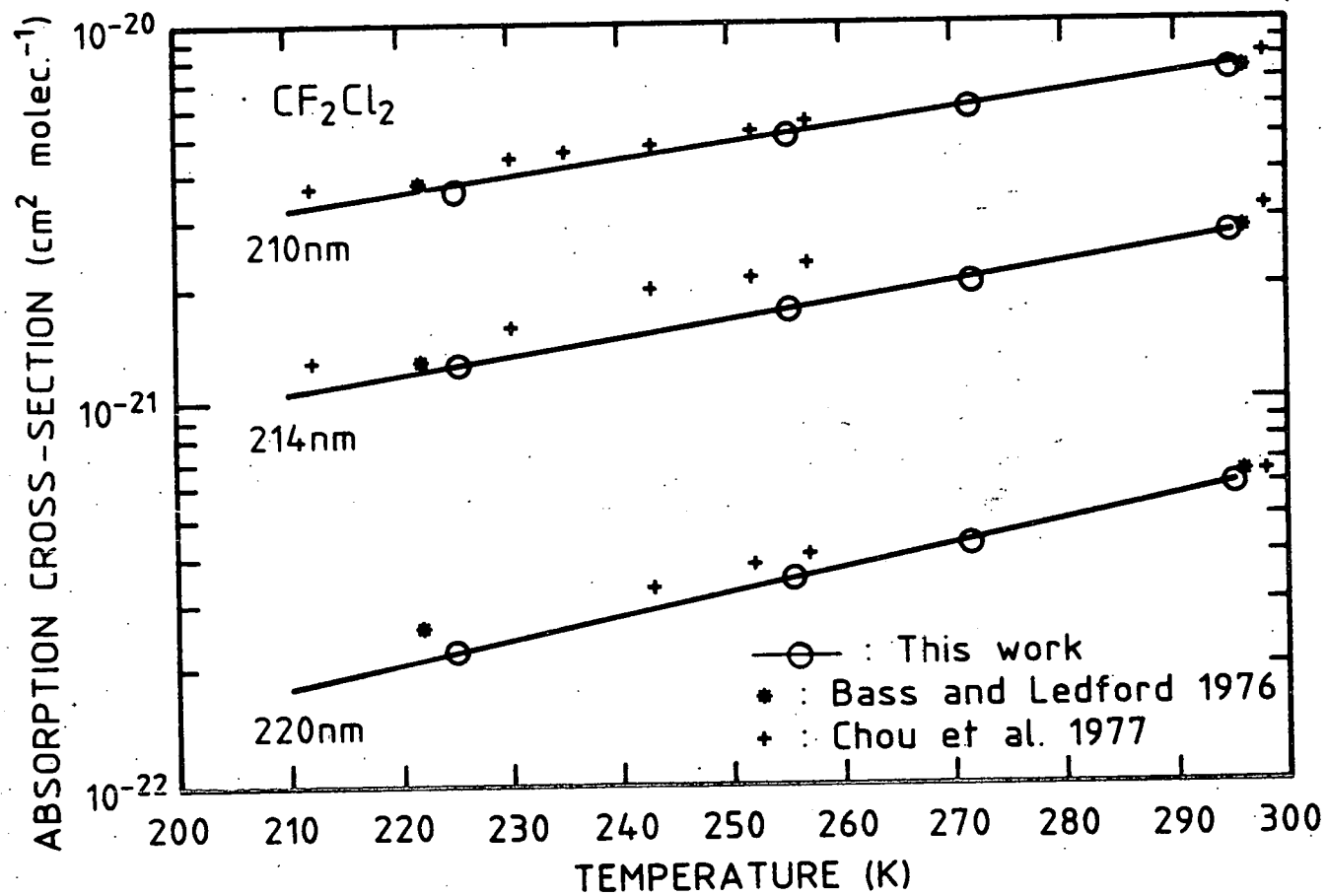


Fig. 7.- Absorption cross-sections of CF<sub>2</sub>Cl<sub>2</sub> versus temperature at three wavelengths (210, 214 and 220 nm).

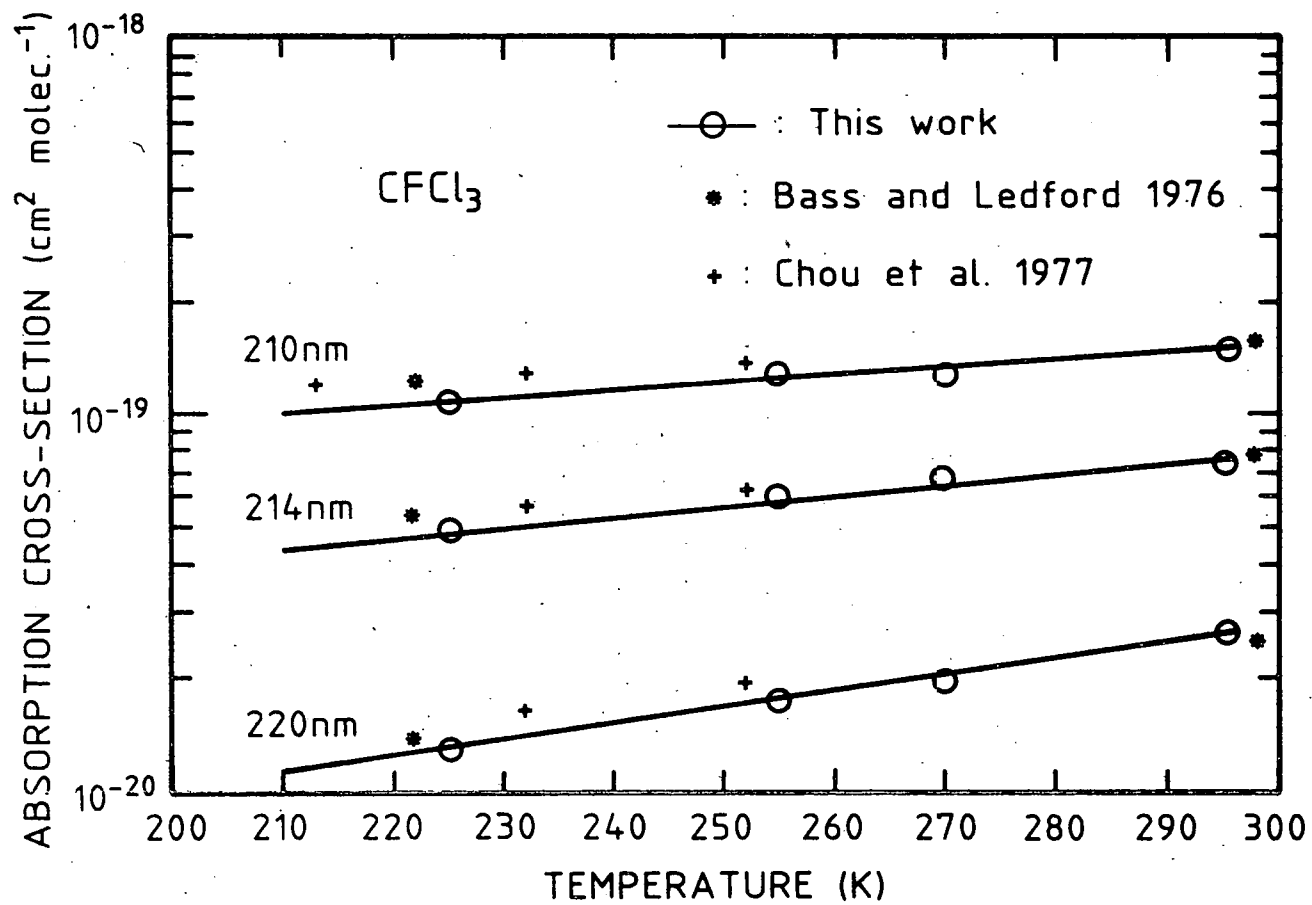


Fig. 8.- Absorption cross-sections of CFCl<sub>3</sub> versus temperature at three wavelengths (210, 214 and 220 nm).

Absorption cross-sections for  $\text{CH}_3\text{Cl}$ ,  $\text{CFCl}_3$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CHF}_2\text{Cl}$  and  $\text{CHFC}_2\text{Cl}$  have also been published by Hubrich et al. (1977) and Hubrich and Stuhl (1980) for only one low temperature, namely 208 K. Their results confirm qualitatively the general conclusions mentioned above. They are in fairly good agreement for  $\text{CF}_2\text{Cl}_2$  between 190 and 205 nm (within the experimental accuracy of 4 %) but diverges from about -5 % at 200 nm up to +40 % at 230 nm for  $\text{CFCl}_3$ . For the other compounds, differences of more than 20 % are observed with their values even at room temperature. Discrepancies can be explained by a critical analysis of the experimental conditions reported by Hubrich et al. (1977) and Hubrich and Stuhl (1980) which reveals that some measurements have been performed in less favourable conditions, namely transmitted fluxes lower than 5 % or higher than 95 %, leading to larger uncertainties than those reported in this work for which experimental measurements for transmission below 10 % and above 85 % have been eliminated in order to stay in a range where the Beer-Lambert law is applicable within the quote accuracy.

As explained above, the absorption cross-sections can be represented by an empirical function of temperature for each wavelength, according to the following expression :

$$\log_{10} \sigma(\lambda) = A(\lambda) + B(\lambda) \times T \quad (2)$$

where the parameters A and B were determined by a polynomial fitting of the available experimental data with respect of temperature and wavelength by means of a least squares fit algorithm developed by The Math Works Inc. (PC MATLAB) to obtain the following polynomial expression :

$$\log_{10} \sigma(\lambda, T) = A_0 + A_1 \lambda + \dots + A_n \lambda^n + (T-273) \times (B_0 + B_1 \lambda + \dots + B_n \lambda^n) \quad (3)$$

The computed values of the A and B parameters are given in Table 12.

The computed values of absorption cross-sections calculated with expression (3) represent all the experimental data with differences lower than  $\pm 4\%$ .

## DISCUSSION

As discussed by Majer and Simons (1964) and Sandorfy (1976), the continuous absorption of chloro- and chloro-fluoromethanes in the 200 nm region corresponds to the less energetic band of their electronic spectrum. It is due to the existence of a  $(C-Cl)^* \leftarrow \overline{Cl}$  transition involving excitation to a repulsive electronic state (C-Cl antibonding). Substitution of hydrogen atoms in the basic hydrocarbon entity by chlorine atoms leads to an increased absorption and a red shift of the average wavelength absorption range, while fluorine atoms play the opposite role and stabilize the molecule. Unfortunately, the complexity of the spectrum features, especially in the case of polychloro-compounds, makes a theoretical analysis of temperature dependence of their absorption cross-sections very difficult.

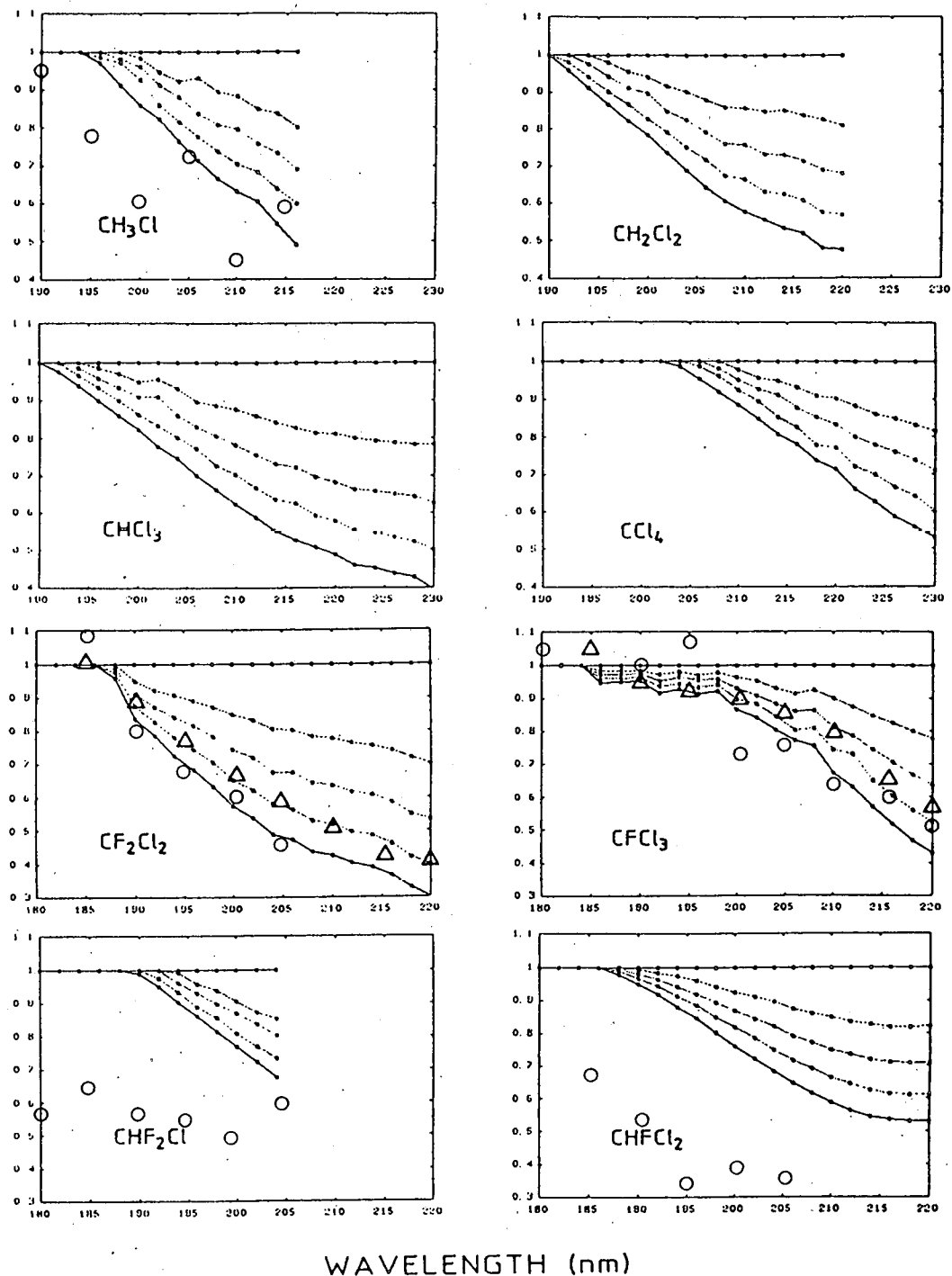
Relative values of absorption cross-sections  $\sigma(T)/\sigma(295)$  versus wavelength relationships, for a given temperature, display very similar features for all highly chlorinated compounds ( $CH_2Cl_2$ ,  $CHCl_3$ ,  $CFCl_3$ ,  $CCl_4$ ) while a greater specificity with the chemical composition is observed in the case of  $CH_3Cl$ ,  $CHF_2Cl$ ,  $CF_3Cl$  and  $CF_2Cl_2$  (Fig 9).

It is currently admitted in the wavelength and pressure ranges of stratospheric interest, that the most important process for the photodissociation of all the halocarbons is the release of one Cl atom with an unitary quantum yield, according to the general scheme :



The immediate reaction of  $RCl_{x-1}$  with atmospheric  $O_2$  releases another Cl atom leaving  $RCl_{x-2}$  which in turn can be subject to photo-

RELATIVE ABSORPTION CROSS-SECTION :  $\sigma_T/\sigma_{295}$



WAVELENGTH (nm)

Fig. 9.- Relative absorption cross-sections  $\sigma(T)/\sigma(295 \text{ K})$  as a function of wavelength for the eighth chloro-fluoro-methanes showing a temperature dependence.

-\*- : This work ( $T = 270\text{K}, 250\text{K}, 230\text{K}$  and  $210\text{K}$ )

$\Delta$  : Bass and Ledford (1976) ( $T = 223 \text{ K}$ )

$\circ$  : Hubrich et al. (1977) ( $T = 208 \text{ K}$ )

Note : values from Chou et al. (1976) are not plotted on this figure for sake of clarity.

lysis. The ultimate fate of such radicals in stratospheric conditions ought to be considered in detail in order to define the production of ClO radicals due to the photodissociation of each halocarbons.

Photodissociation coefficients J for a given altitude z, zenith angle  $\chi$  and wavelength interval have been computed according to the relations:

$$J^Z = \sigma_\lambda q_\lambda (z) \quad (5)$$

$$q_\lambda (z) = q_\lambda (\infty) e^{-\tau_\lambda(z)} \quad (6)$$

$$\tau_\lambda (z) = \int_z^\infty [n(O_2) \sigma(O_2) + n(O_3) \sigma(O_3) + n(\text{air})\sigma_{\text{scatt.}}] \sec \chi dz \quad (7)$$

where :  $\sigma$  are the absorption cross-sections

$q_\lambda (z)$  and  $q_\lambda (\infty)$  are the solar irradiance at altitude z or extraterrestrial. ( $z = \infty$ )

n are the number of particules per volume unit.

for solar zenith angles of  $0^\circ$  and  $60^\circ$  ( $\sec \chi = 1$  and  $2$ )

Taking the values of  $\sigma(O_2)$ ,  $\sigma(O_3)$  from WMO (1985) and Kockarts (1976), of  $\sigma_{\text{scatt}}$  from Nicolet (1984) and the values of q ( $\infty$ ) from WMO (1985) and taking into account the actual values of cross-sections which correspond to the temperature conditions prevailing at a definite altitude. (Tables 13 and 14, Figures 10 and 11).

A comparison of either temperature dependent or independent photodissociation coefficients for different stratospheric altitudes (15 to 50 km) is presented in Table 14 where relative photodissociation coefficients  $J(T)/J(295)$  versus altitude relationships are given for all studied compounds. Obviously, the effect is maximum at low altitudes and gradually decreases, following the temperature profile in the stratosphere. Due to the significant increase of ozone optical depth in

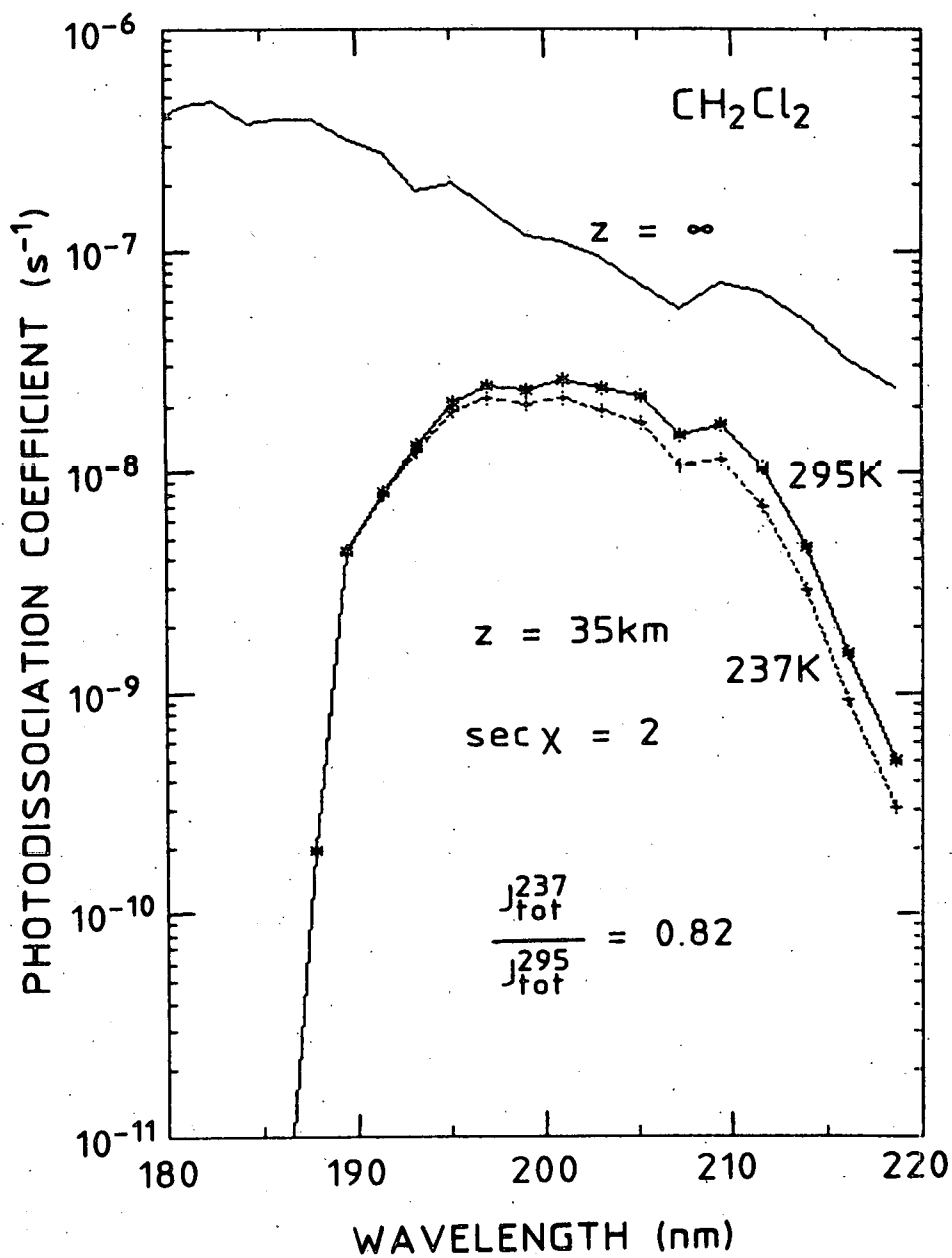
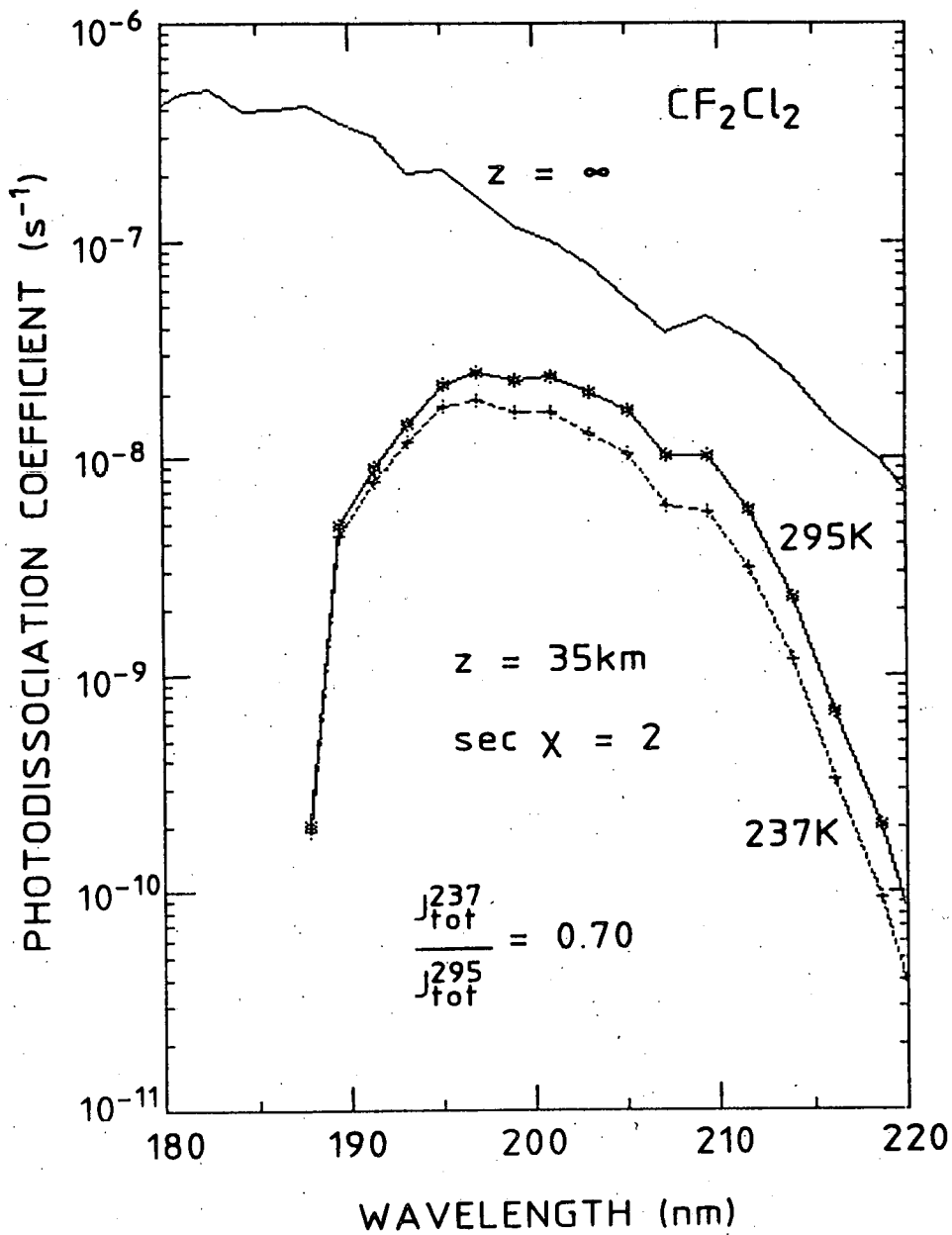


Fig. 10.- Spectral distribution of photodissociation coefficients of  $\text{CH}_2\text{Cl}_2$  for frequency intervals of  $500 \text{ cm}^{-1}$ ,  $z = 35 \text{ km}$  and solar zenith angle =  $60^\circ$  ( $\text{sec } \chi = 2$ ).

(\*) :  $J(295 \text{ K})$ , (+) :  $J(T)$ .



**Fig. 11.-** Spectral distribution of photodissociation coefficients of  $\text{CF}_2\text{Cl}_2$  for frequency intervals of  $500 \text{ cm}^{-1}$ ,  $z = 35 \text{ km}$  and solar zenith angle =  $60^\circ$  ( $\sec \chi = 2$ ).  
 (\*) :  $J(295 \text{ K})$ , (+) :  $J(T)$ .



the stratosphere at wavelength beyond 220 nm, the value of the overall photodissociation coefficients between 20 and 35 km is mainly influenced by the 200-210 nm interval contribution.

In such conditions, a significant reduction of overall photodissociation coefficients is only to be expected in the case of compounds whose absorption cross-sections are strongly temperature dependent in this wavelength interval. Accordingly, important reduction factors are observed for  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CF}_2\text{Cl}_2$  and  $\text{CHFCl}_2$ , and to a lesser extent for  $\text{CH}_3\text{Cl}$ ,  $\text{CHF}_2\text{Cl}$  and  $\text{CFCl}_3$ , while  $\text{CCl}_4$  photodissociation coefficient is almost temperature independent in the stratosphere.

The introduction of lower photodissociation coefficients in atmospheric models increases altitudes of photolysis, and therefore changes the altitude profile of the considered halomethane in the stratosphere.

In conclusion, this work presents a complete and coherent set of experimental data about temperature dependent absorption cross-sections and photodissociation coefficients of chloro- and chlorofluoro-methanes, and gives fairly simple relationships to compute the absorption cross-sections values with respect of temperature and wavelength.

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TABLE 1. Error budget

a) T = 295 K

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optical path (200 cm $\pm$ 0.1 cm)	0.05 %
pressure (in the range $10^3$ - $2 \times 10^{-3}$ torr)	0.1 %
impurities in the sample	0.1 %
temperature ( $\pm$ 0.1 K at 300 K)	0.03 %
absorbance $\ln(I_0/I)$ for $\tau = 1$	2.0 %

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Total r.m.s. error ( $2 \sigma$ )  $\pm$  2.00 %

b) T = 210 K

---

optical path (200 cm $\pm$ 0.1 cm)	0.05 %
pressure (in the range $10^3$ - $2 \times 10^{-3}$ torr)	0.1 %
impurities in the sample	0.1 %
temperature ( $\pm$ 2 K at 210 K)	1 %
cross-section dependence on temperature error	1 %
absorbance $\ln(I_0/I)$ for $\tau = 1$	2.0 %
= 0.6	3.3 %
(min. value considered)	

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total r.m.s. error ( $2 \sigma$ )  $\pm$  2.47 %  $\pm$  3.62%

**TABLE 2.a.** Absorption cross-sections at 2 nm interval at selected temperatures (295 K, 270 K, 250 K, 230 K, 210 K)

CH<sub>3</sub>Cl

$\lambda$ (nm)	$s(\lambda) * 10^{21}$ (cm <sup>2</sup> molec. <sup>-1</sup> )				
	295K	270K	250K	230K	210K
174	1110	1110	1110	1110	1110
176	938	938	938	938	938
178	766	766	766	766	766
180	607	607	607	607	607
182	467	467	467	467	467
184	350	350	350	350	350
186	255	255	255	255	255
188	182	182	182	182	182
190	127	127	127	127	127
192	87.2	87.2	87.2	87.2	87.2
194	58.8	58.8	58.8	58.8	58.8
196	40.1	40.1	40.1	40.1	40.1
198	26.6	26.6	26.1	25.8	24.3
200	17.6	17.3	16.9	16.3	15.1
202	11.3	10.7	10.3	9.70	9.30
204	7.50	6.91	6.60	6.11	5.73
206	4.83	4.50	4.05	3.75	3.45
208	3.18	2.85	2.57	2.35	2.12
210	2.06	1.82	1.64	1.45	1.30
212	1.32	1.12	1.00	0.90	0.80
214	0.86	0.72	0.63	0.55	0.47
216	0.55	0.44	0.38	0.33	0.27

TABLE 2.b. Absorption cross-sections over the spectral intervals used in atmospheric modelling calculations, at selected temperatures (295 K, 270 K, 250 K, 230 K, 210 K)

CH<sub>3</sub>Cl (wavenumber intervals : 500 cm<sup>-1</sup>)

$$\sigma(\lambda) * 10^{21} \text{ (cm}^2 \text{ molec.}^{-1}\text{)}$$

N°	λ (nm)	295K	270K	250K	230K	210K
45	173.9-174.4	1057	1057	1057	1057	1057
46	175.4-177.0	923	923	923	923	923
47	177.0-178.6	787	787	787	787	787
48	178.6-180.2	656	656	656	656	656
49	180.2-181.8	536	536	536	536	536
50	181.8-183.5	429	429	429	429	429
51	183.5-185.2	333	333	333	333	333
52	185.2-186.9	254	254	254	254	254
53	186.9-188.7	188	188	188	188	188
54	188.7-190.5	139	139	139	139	139
55	190.5-192.3	97.8	97.8	97.8	97.8	97.8
56	192.3-194.2	69.3	69.3	69.3	69.3	69.3
57	194.2-196.1	47.7	47.6	47.3	46.8	45.8
58	196.1-198.0	32.5	32.2	31.7	31.2	30.2
59	198.0-200.0	21.6	21.1	20.6	19.9	19.2
60	200.0-202.0	14.2	13.7	13.2	12.6	12.0
61	202.0-204.1	9.27	8.81	8.36	7.90	7.44
62	204.1-206.2	5.91	5.50	5.14	4.77	4.43
63	206.2-208.3	3.76	3.42	3.13	2.86	2.62
64	208.3-210.5	2.33	2.06	1.86	1.67	1.50
65	210.5-212.8	1.44	1.24	1.09	0.973	0.853
66	212.8-215.0	0.874	0.726	0.634	0.555	0.474
67	215.0-217.4	0.525	0.424	0.367	0.320	0.264

TABLE 3.a. Absorption cross-sections at 2 nm interval at selected temperatures (295 K, 270 K, 250 K, 230 K, 210 K)

CH<sub>2</sub>Cl<sub>2</sub>

$\lambda$ (nm)	$\sigma(\lambda) * 10^{21}$ (cm <sup>2</sup> molec. <sup>-1</sup> )				
	295K	270K	250K	230K	210K
176	1850	1850	1850	1850	1850
178	1807	1807	1807	1807	1807
180	1695	1695	1695	1695	1695
182	1509	1509	1509	1509	1509
184	1307	1307	1307	1307	1307
186	1040	1040	1040	1040	1040
188	799	799	799	799	799
190	575	575	575	575	575
192	417	417	417	409	400
194	288	288	281	271	263
196	197	193	186	178	171
198	136	130	124	118	112
200	92.0	86.5	82.5	76.2	72.2
202	62.0	56.8	52.7	49.0	45.6
204	42.2	38.1	34.8	31.7	29.0
206	28.8	25.4	22.8	20.6	18.5
208	19.5	16.8	14.8	13.1	11.8
210	12.8	11.0	9.70	8.50	7.36
212	8.35	7.10	6.10	5.25	4.63
214	5.40	4.60	3.93	3.36	2.87
216	3.55	2.97	2.53	2.15	1.84
218	2.34	1.93	1.61	1.34	1.12
220	1.52	1.23	1.03	0.860	0.720



**TABLE 3.b.** Absorption cross-sections over the spectral intervals used in atmospheric modelling calculations, at selected temperatures (295 K, 270 K, 250 K, 230 K, 210 K)

CH<sub>2</sub>Cl<sub>2</sub> (wavenumber intervals : 500 cm<sup>-1</sup>)

N°	λ (nm)	σ(λ) * 10 <sup>21</sup> (cm <sup>2</sup> molec. <sup>-1</sup> )				
		295K	270K	250K	230K	210K
46	175.4-177.0	1847	1847	1847	1847	1847
47	177.0-178.6	1812	1812	1812	1812	1812
48	178.6-180.2	1783	1783	1783	1783	1783
49	180.2-181.8	1652	1652	1652	1652	1652
50	181.8-183.5	1470	1470	1470	1470	1470
51	183.5-185.2	1252	1252	1252	1252	1252
52	185.2-186.9	1040	1040	1040	1040	1040
53	186.9-188.7	801	801	801	801	801
54	188.7-190.5	621	621	621	621	621
55	190.5-192.3	457	454	450	442	435
56	192.3-194.2	335	330	325	316	309
57	194.2-196.1	238	232	226	218	211
58	196.1-198.0	167	160	155	148	141
59	198.0-200.0	113	108	102	96.5	91.4
60	200.0-202.0	76.7	71.5	67.1	62.4	58.4
61	202.0-204.1	51.6	47.3	43.7	40.1	37.0
62	204.1-206.2	33.9	30.5	27.7	25.0	22.8
63	206.2-208.3	22.2	19.6	17.5	15.6	14.0
64	208.3-210.5	14.2	12.3	10.8	9.48	8.38
65	210.5-212.8	9.07	7.71	6.66	5.77	5.02
66	212.8-215.0	5.64	4.71	4.02	3.43	2.95
67	215.0-217.4	3.47	2.86	2.42	2.04	1.73
68	217.4-219.8	2.06	1.69	1.42	1.18	0.995

TABLE 4.a. Absorption cross-sections at 2 nm interval at selected temperatures (295 K, 270 K, 250 K, 230 K, 210 K)

CHCl<sub>3</sub>

$\lambda$ (nm)	$\sigma(\lambda) * 10^{21}$ (cm <sup>2</sup> molec. <sup>-1</sup> )				
	295K	270K	250K	230K	210K
174	4750	4750	4750	4750	4750
176	4930	4930	4930	4930	4930
178	4650	4650	4650	4650	4650
180	3875	3875	3875	3875	3875
182	3216	3216	3216	3216	3216
184	2425	2425	2425	2425	2425
186	1750	1750	1750	1750	1750
188	1395	1395	1395	1395	1395
190	1122	1122	1122	1122	1122
192	878	878	878	878	878
194	741	741	730	715	696
196	618	609	593	578	556
198	509	494	476	458	438
200	411	390	374	355	339
202	332	317	302	277	259
204	265	247	228	213	198
206	204	183	170	158	143
208	151	134	122	110	100
210	108	95.0	84.8	76.0	67.5
212	77.5	66.8	58.8	51.8	45.5
214	53.8	45.5	39.5	34.3	29.7
216	36.5	30.3	26.4	22.9	19.3
218	24.8	20.2	17.3	14.7	12.6
220	16.7	13.6	11.4	9.68	8.15
222	11.3	9.05	7.50	6.25	5.20
224	7.50	5.95	4.94	4.10	3.40
226	5.00	3.95	3.25	2.67	2.19
228	3.38	2.65	2.18	1.77	1.45
230	2.28	1.79	1.43	1.14	0.900
232	1.52	1.11	0.896	0.711	0.566
234	1.02	0.725	0.581	0.456	0.361
236	0.680	0.472	0.378	0.294	0.231
238	0.460	0.308	0.247	0.190	0.149
240	0.310	0.202	0.162	0.124	0.096

**TABLE 4.b.** Absorption cross-sections over the spectral intervals used in atmospheric modelling calculations, at selected temperatures (295 K, 270 K, 250 K, 230 K, 210 K)

CHCl<sub>3</sub> (frequency intervals : 500 cm<sup>-1</sup>)

N°	λ (nm)	σ(λ) * 10 <sup>21</sup> (cm <sup>2</sup> molec. <sup>-1</sup> )				
		295K	270K	250K	230K	210K
45	173.9-175.4	4850	4850	4850	4850	4850
46	175.4-177.0	4929	4929	4929	4929	4929
47	177.0-178.6	4680	4680	4680	4680	4680
48	178.6-180.2	4145	4145	4145	4145	4145
49	180.2-181.8	3500	3500	3500	3500	3500
50	181.8-183.5	2930	2930	2930	2930	2930
51	183.5-185.2	2340	2340	2340	2340	2340
52	185.2-186.9	1750	1750	1750	1750	1750
53	186.9-188.7	1470	1470	1470	1470	1470
54	188.7-190.5	1180	1180	1180	1180	1180
55	190.5-192.3	920	920	920	920	911
56	192.3-194.2	790	790	790	774	754
57	194.2-196.1	665	658	645	631	608
58	196.1-198.0	560	546	529	515	493
59	198.0-200.0	455	437	419	403	382
60	200.0-202.0	367	347	328	312	295
61	202.0-204.1	295	274	257	242	226
62	204.1-206.2	228	209	193	180	165
63	206.2-208.3	168	151	137	126	114
64	208.3-210.5	118	104	92.6	85.0	75.5
65	210.5-212.8	82.0	70.5	62.3	56.2	49.2
66	212.8-215.0	55.0	46.5	40.1	35.7	30.8
67	215.0-217.4	35.5	29.5	25.2	22.2	18.8
68	217.4-219.8	21.8	17.9	15.1	12.9	10.9
69	219.8-222.2	13.5	10.9	9.11	7.69	6.48
70	222.2-224.7	8.35	6.64	5.51	4.59	3.84
71	224.7-227.3	5.00	3.95	3.25	2.67	2.19
72	227.3-229.9	2.95	2.29	1.87	1.50	1.25
73	229.9-232.6	1.76	1.34	1.08	0.860	0.677

**TABLE 5.a.** Absorption cross-sections at 2 nm interval at selected temperatures (295 K, 270 K, 250 K, 230 K, 210 K)

CCl<sub>4</sub>

$$\sigma(\lambda) * 10^{21} \text{ (cm}^2 \text{ molec.}^{-1}\text{)}$$

$\lambda$ (nm)	295K	270K	250K	230K	210K
174	9900	9900	9900	9900	9900
176	10100	10100	10100	10100	10100
178	9750	9750	9750	9750	9750
180	7200	7200	7200	7200	7200
182	5900	5900	5900	5900	5900
184	4400	4400	4400	4400	4400
186	3100	3100	3100	3100	3100
188	1980	1980	1980	1980	1980
190	1469	1469	1469	1469	1469
192	992	992	992	992	992
194	767	767	767	767	767
196	695	695	695	695	695
198	680	680	680	680	680
200	660	660	660	660	660
202	638	638	638	638	638
204	610	610	610	610	601
206	570	570	570	561	544
208	525	525	514	504	483
210	469	459	446	434	415
212	410	392	380	367	348
214	345	327	315	295	279
216	278	259	244	230	217
218	221	201	189	172	163
220	175	158	146	135	125
222	136	120	109	98.0	90.0
224	102	88.0	79.5	71.4	64.0
226	76.0	64.5	57.8	50.5	44.5
228	56.5	47.0	41.7	36.2	31.6
230	42.8	34.9	30.4	25.7	22.7
232	30.4	24.8	21.1	17.9	15.2
234	22.0	17.7	14.8	12.5	10.5
236	16.0	12.7	10.5	8.72	7.23
238	11.6	9.06	7.43	6.10	5.00
240	8.30	6.40	5.19	4.22	3.42
242	5.90	4.49	3.62	2.91	2.34
244	4.13	3.11	2.48	1.98	1.58
246	2.90	2.17	1.72	1.36	1.08
248	2.10	1.56	1.23	0.968	0.762
250	1.48	1.09	0.858	0.673	0.528

TABLE 5.b. Absorption cross-sections over the spectral intervals used in atmospheric modelling calculations, at selected temperatures (295 K, 270 K, 250 K, 230 K, 210 K)

CCl<sub>4</sub> (wavenumber intervals : 500 cm<sup>-1</sup>)

N°	λ (nm)	σ(λ) * 10 <sup>21</sup> (cm <sup>2</sup> molec. <sup>-1</sup> )				
		295K	270K	250K	230K	210K
45	173.9-175.4	10000	10000	10000	10000	10000
46	175.4-177.0	10000	10000	10000	10000	10000
47	177.0-178.6	9800	9800	9800	9800	9800
48	178.6-180.2	8150	8150	8150	8150	8150
49	180.2-181.8	6550	6550	6550	6550	6550
50	181.8-183.5	5350	5350	5350	5350	5350
51	183.5-185.2	4200	4200	4200	4200	4200
52	185.2-186.9	3100	3100	3100	3100	3100
53	186.9-188.7	1999	1999	1999	1999	1999
54	188.7-190.5	1510	1510	1510	1510	1510
55	190.5-192.3	1076	1076	1076	1076	1076
56	192.3-194.2	868	868	868	868	868
57	194.2-196.1	749	749	749	749	749
58	196.1-198.0	687	687	687	687	687
59	198.0-200.0	670	670	670	670	670
60	200.0-202.0	649	649	649	649	649
61	202.0-204.1	619	619	619	619	619
62	204.1-206.2	598	598	598	594	577
63	206.2-208.3	548	544	537	529	513
64	208.3-210.5	483	472	463	451	435
65	210.5-212.8	413	397	386	371	355
66	212.8-215.0	339	321	308	292	277
67	215.0-217.4	270	251	238	222	209
68	217.4-219.8	207	188	176	162	151
69	219.8-222.2	155	138	127	115	105
70	222.2-224.7	113	98.1	88.9	79.4	71.7
71	224.7-227.3	77.9	66.4	59.1	51.9	46.1
72	227.3-229.9	52.7	44.0	38.4	33.2	29.0
73	229.9-232.6	33.4	27.2	23.4	19.8	17.0
74	232.6-235.3	22.6	18.1	15.3	12.8	10.8
75	235.3-238.1	14.2	11.1	9.23	7.61	6.31
76	238.1-241.0	8.83	6.81	5.56	4.52	3.69
77	241.0-243.9	5.30	4.02	3.23	2.59	2.08
78	243.9-246.9	3.24	2.43	1.93	1.53	1.21
79	246.9-250.0	1.93	1.43	1.13	0.886	0.696

TABLE 6.a. Absorption cross-sections at 2 nm interval at selected temperatures (295 K, 270 K, 250 K, 230 K, 210 K)

CF<sub>3</sub>Cl

$\sigma(\lambda) * (\text{cm}^2 \text{ molec.}^{-1})$

$\lambda(\text{nm})$       295K

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172	11.0
174	9.70
176	8.25
178	6.81
180	5.42
182	4.25
184	3.26
186	2.44
188	1.75
190	1.28
192	0.900
194	0.610
196	0.410
198	0.280
200	0.190

**TABLE 6.b.** Absorption cross-sections over the spectral intervals used in atmospheric modelling calculations, at selected temperatures (295 K, 270 K, 250 K, 230 K, 210 K)

CF<sub>3</sub>Cl (wavenumber intervals : 500 cm<sup>-1</sup>)

$$\sigma(\lambda) * 10^{21} \text{ (cm}^2 \text{ molec.}^{-1}\text{)}$$

N°	λ (nm)	295K
43	169.5-172.4	11.7
44	172.4-173.9	10.3
45	173.9-175.4	9.25
46	175.4-177.0	8.10
47	177.0-178.6	6.95
48	178.6-180.2	5.80
49	180.2-181.8	4.80
50	181.8-183.5	3.90
51	183.5-185.2	3.10
52	185.2-186.9	2.44
53	186.9-188.7	1.80
54	188.7-190.5	1.36
55	190.5-192.3	0.990
56	192.3-194.2	0.700
57	194.2-196.1	0.480
58	196.1-198.0	0.320
59	198.0-200.0	0.220
60	200.0-202.0	0.150

**TABLE 7.a.** Absorption cross-sections at 2 nm interval at selected temperatures (295 K, 270 K, 250 K, 230 K, 210 K)



$\lambda$ (nm)	$\sigma(\lambda) * 10^{21}$ (cm <sup>2</sup> molec. <sup>-1</sup> )				
	295K	270K	250K	230K	210K
174	1620	1620	1620	1620	1620
176	1810	1810	1810	1810	1810
178	1870	1870	1870	1870	1870
180	1790	1790	1790	1790	1790
182	1600	1600	1600	1600	1600
184	1340	1340	1340	1340	1340
186	1070	1070	1070	1070	1070
188	828	828	815	807	793
190	632	600	576	552	529
192	455	419	397	377	358
194	315	286	265	246	228
196	211	188	172	157	144
198	139	121	109	98.1	88.2
200	88.9	75.5	66.3	58.2	51.1
202	55.1	45.9	39.7	34.3	29.7
204	34.4	27.7	23.2	20.0	16.9
206	20.9	16.8	14.1	11.8	9.89
208	12.7	9.94	8.19	6.75	5.57
210	7.59	5.90	4.84	3.96	3.24
212	4.54	3.47	2.80	2.26	1.83
214	2.71	2.05	1.65	1.32	1.06
216	1.58	1.17	0.926	0.731	0.577
218	1.00	0.720	0.550	0.420	0.330
220	0.600	0.420	0.320	0.240	0.180
222	0.360	0.252	0.189	0.140	0.105
224	0.220	0.152	0.112	0.081	0.060
226	0.130	0.092	0.067	0.047	0.034



**TABLE 7.b. Absorption cross-sections over the spectral intervals used in atmospheric modelling calculations, at selected temperatures (295 K, 270 K, 250 K, 230 K, 210 K**

CF<sub>2</sub>Cl<sub>2</sub> (wavenumber intervals : 500 cm<sup>-1</sup>)

N°	λ (nm)	σ(λ) * 10 <sup>21</sup> (cm <sup>2</sup> molec. <sup>-1</sup> )				
		295K	270K	250K	230K	210
45	173.9-175.4	1700	1700	1700	1700	1700
46	175.4-177.0	1822	1822	1822	1822	1822
47	177.0-178.6	1860	1860	1860	1860	1860
48	178.6-180.2	1817	1817	1817	1817	1817
49	180.2-181.8	1700	1700	1700	1700	1700
50	181.8-183.5	1528	1528	1528	1528	1528
51	183.5-185.2	1310	1310	1310	1310	1310
52	185.2-186.9	1070	1070	1070	1070	1070
53	186.9-188.7	847	847	827	816	803
54	188.7-190.5	683	642	621	600	580
55	190.5-192.3	502	470	446	424	403
56	192.3-194.2	365	335	313	293	274
57	194.2-196.1	253	227	209	193	177
58	196.1-198.0	171	150	136	123	112
59	198.0-200.0	111	95.2	84.6	75.4	67.1
60	200.0-202.0	70.1	59.1	51.6	45.2	39.6
61	202.0-204.1	43.6	36.0	31.0	26.7	23.0
62	204.1-206.2	26.1	21.1	17.9	15.2	12.8
63	206.1-208.3	15.5	12.3	10.2	8.53	7.11
64	208.3-210.5	8.84	6.88	5.64	4.63	3.81
65	210.5-212.8	5.03	3.85	3.10	2.51	2.03
66	212.8-215.0	2.79	2.09	1.66	1.32	1.05
67	215.0-217.4	1.55	1.14	0.890	0.694	0.545
68	217.4-219.8	0.846	0.606	0.467	0.357	0.275
69	219.8-222.2	0.467	0.326	0.247	0.184	0.139
70	222.2-224.7	0.262	0.177	0.134	0.0954	0.0704
71	224.7-227.3	0.143	0.0927	0.0672	0.0471	0.0337

**TABLE 8.a.** Absorption cross-sections at 2 nm interval at selected temperatures (295 K, 270 K, 250 K, 230 K, 210 K)

CFC13

$\lambda$ (nm)	$\sigma(\lambda) * 10^{21}$ (cm <sup>2</sup> molec. <sup>-1</sup> )				
	295K	270K	250K	230K	210K
174	3130	3130	3130	3130	3130
176	3240	3240	3240	3240	3240
178	3235	3235	3235	3235	3235
180	3140	3140	3140	3140	3140
182	2960	2960	2960	2960	2960
184	2720	2720	2720	2720	2720
186	2430	2385	2360	2335	2300
188	2130	2090	2070	2045	2020
190	1790	1760	1745	1725	1705
192	1540	1495	1465	1440	1412
194	1243	1218	1198	1174	1151
196	991	959	945	925	905
198	780	762	747	733	718
200	645	622	600	579	558
202	500	476	454	441	420
204	374	348	330	316	300
206	280	256	241	225	216
208	197	182	170	159	149
210	148	133	120	110	99.4
212	105	91.8	82.6	76.7	66.3
214	75.6	64.1	56.2	49.2	43.1
216	53.8	44.3	37.9	32.4	27.8
218	37.9	30.3	25.3	21.2	17.7
220	26.4	20.5	16.8	13.8	11.3
222	18.2	13.8	11.1	8.90	7.14
224	12.4	9.25	7.30	5.76	4.54
226	8.42	6.16	4.79	3.73	2.91
228	5.65	4.08	3.15	2.43	1.88
230	3.75	2.70	2.08	1.60	1.23

TABLE 8.b. Absorption cross-sections over the spectral intervals used in atmospheric modelling calculations, at selected temperatures (295 K, 270 K, 250 K, 230 K, 210 K)

CFCl<sub>3</sub> (wavenumber intervals : 500 cm<sup>-1</sup>)

N°	λ (nm)	σ(λ) * 10 <sup>21</sup> (cm <sup>2</sup> molec. <sup>-1</sup> )				
		295K	270K	250K	230K	210K
45	173.9-175.4	3180	3180	3180	3180	3180
46	175.4-177.0	3240	3240	3240	3240	3240
47	177.0-178.6	3238	3238	3238	3238	3238
48	178.6-180.2	3160	3160	3160	3160	3160
49	180.2-181.8	3050	3050	3050	3050	3050
50	181.8-183.5	2000	2000	2000	2000	2000
51	183.5-185.2	2670	2670	2670	2670	2670
52	185.2-186.9	2430	2385	2360	2335	2300
53	186.9-188.7	2155	2123	2114	2097	2079
54	188.7-190.5	1894	1871	1858	1843	1827
55	190.5-192.3	1612	1590	1577	1563	1548
56	192.3-194.2	1360	1339	1325	1312	1296
57	194.2-196.1	1118	1097	1081	1068	1052
58	196.1-198.0	905	882	865	851	834
59	198.0-200.0	712	689	671	656	638
60	200.0-202.0	552	528	510	494	477
61	202.0-204.1	422	398	380	365	348
62	204.1-206.2	313	291	274	260	244
63	206.2-208.3	229	209	194	181	167
64	208.3-210.5	163	145	132	121	110
65	210.5-212.8	114	99.3	88.7	79.7	71.0
66	212.8-215.0	77.6	65.7	57.4	50.5	44.0
67	215.0-217.4	52.1	42.9	36.6	31.4	26.8
68	217.4-219.8	34.0	27.1	22.6	18.9	15.7
69	219.8-222.2	21.8	16.9	13.8	11.3	9.15
70	222.2-224.7	13.9	10.5	8.33	6.66	5.30
71	224.7-227.3	8.42	6.16	4.79	3.73	2.91
72	227.3-229.9	5.00	3.60	2.77	2.12	1.64

TABLE 9.a. Absorption cross-sections at 2 nm interval at selected temperatures (295 K, 270 K, 250 K, 230 K, 210 K)

CHF<sub>2</sub>Cl

$\lambda$ (nm)	$\sigma(\lambda) \cdot 10^{21}$ (cm <sup>2</sup> molec. <sup>-1</sup> )				
	295K	270K	250K	230K	210K
174	57.2	57.2	57.2	57.2	57.2
176	40.4	40.4	40.4	40.4	40.4
178	27.6	27.6	27.6	27.6	27.6
180	19.1	19.1	19.1	19.1	19.1
182	12.8	12.8	12.8	12.8	12.8
184	8.42	8.42	8.42	8.42	8.42
186	5.76	5.76	5.76	5.76	5.76
188	3.72	3.72	3.72	3.72	3.72
190	2.45	2.45	2.45	2.45	2.42
192	1.56	1.56	1.56	1.52	1.48
194	1.03	1.02	0.99	0.96	0.93
196	0.72	0.69	0.67	0.64	0.62
198	0.48	0.45	0.43	0.41	0.39
200	0.32	0.29	0.278	0.259	0.246
202	0.220	0.192	0.184	0.169	0.159
204	0.142	0.121	0.114	0.104	0.096

TABLE 9.b. Absorption cross-sections over the spectral intervals used in atmospheric modelling calculations, at selected temperatures (295 K, 270 K, 250 K, 230 K, 210 K)

CHF<sub>2</sub>Cl (wavenumber intervals : 500<sup>-1</sup>)

N°	λ(nm)	σ(λ) * 10 <sup>21</sup> (cm <sup>2</sup> molec. <sup>-1</sup> )				
		295K	270K	250K	230K	210K
45	173.9-175.4	51.7	51.7	51.7	51.7	51.7
46	175.4-177.0	38.0	38.0	38.0	38.0	38.0
47	177.0-178.6	28.8	28.8	28.8	20.0	28.8
48	178.6-180.2	21.2	21.2	21.2	21.2	21.2
49	180.2-181.8	15.5	15.5	15.5	15.5	15.5
50	181.8-183.5	11.3	11.3	11.3	11.3	11.3
51	183.5-185.2	8.03	8.03	8.03	8.03	8.03
52	185.2-186.9	5.65	5.65	5.65	5.65	5.65
53	186.9-188.7	3.88	3.88	3.88	3.88	3.88
54	188.7-190.5	2.72	2.72	2.72	2.72	2.72
55	190.5-192.3	1.83	1.82	1.80	1.77	1.72
56	192.3-194.2	1.26	1.24	1.22	1.19	1.15
57	194.2-196.1	0.850	0.825	0.806	0.778	0.747
58	196.1-198.0	0.576	0.548	0.532	0.508	0.484
59	198.0-200.0	0.385	0.357	0.344	0.324	0.307
60	200.0-202.0	0.259	0.233	0.223	0.207	0.194
61	202.0-204.1	0.177	0.153	0.144	0.132	0.123

TABLE 10.a. Absorption cross-sections at 2 nm interval at selected temperatures (295 K, 270 K, 250 K, 230 K, 210 K)

CHFC1<sub>2</sub>

$\lambda$ (nm)	$\sigma(\lambda) * 10^{21}$ (cm <sup>2</sup> molec. <sup>-1</sup> )				
	295K	270K	250K	230K	210K
174	1660	1660	1660	1660	1660
176	1645	1645	1645	1645	1645
178	1550	1550	1550	1550	1550
180	1380	1300	1380	1380	1380
182	1160	1160	1160	1160	1160
184	924	924	924	924	924
186	715	715	715	715	715
188	532	532	529	525	520
190	384	381	376	371	365
192	269	264	259	254	247
194	184	179	173	168	162
196	123	118	113	109	104
198	81.0	76.2	72.4	68.9	65.0
200	52.4	48.5	45.6	42.9	39.9
202	33.5	30.5	28.3	26.3	24.2
204	21.2	19.0	17.4	15.9	14.5
206	13.4	11.7	10.6	9.61	8.67
208	8.36	7.20	6.45	5.78	5.16
210	5.22	4.43	3.92	3.47	3.08
212	3.25	2.72	2.39	2.10	1.84
214	2.03	1.68	1.46	1.27	1.11
216	1.27	1.04	0.904	0.782	0.681
218	0.797	0.654	0.564	0.487	0.423
220	0.503	0.414	0.357	0.308	0.268
222	0.319	0.266	0.229	0.199	0.174

TABLE 10.b. Absorption cross-sections over the spectral intervals used in atmospheric modelling calculations, at selected temperatures (295 K, 270 K, 250 K, 230 K, 210 K)

CHFC1<sub>2</sub> (wavenumber intervals : 500 cm<sup>-1</sup>)

$\sigma(\lambda) * 10^{21}$  (cm<sup>2</sup> molec.<sup>-1</sup>)

N°	$\lambda$ (nm)	295K	270K	250K	230K	210K
45	173.9-175.4	1660	1660	1660	1660	1660
46	175.4-177.0	1640	1640	1640	1640	1640
47	177.0-178.6	1565	1565	1565	1565	1565
48	178.6-180.2	1435	1435	1435	1435	1435
49	180.2-181.8	1270	1270	1270	1270	1270
50	181.8-183.5	1090	1090	1090	1090	1090
51	183.5-185.2	896	896	896	896	896
52	185.2-186.9	715	715	715	715	715
53	186.9-188.7	550	548	544	540	535
54	188.7-190.5	419	415	410	405	398
55	190.5-192.3	301	296	290	285	278
56	192.3-194.2	215	210	204	199	192
57	194.2-196.1	148	143	137	133	127
58	196.1-198.0	100	95.1	90.8	86.9	82.5
59	198.0-200.0	65.2	61.0	57.6	54.5	51.2
60	200.0-202.0	41.9	38.6	36.0	33.7	31.2
61	202.0-204.1	26.7	24.1	22.2	20.5	18.8
62	204.1-206.2	16.4	14.6	13.3	12.1	11.0
63	206.2-208.3	10.1	8.75	7.88	7.09	6.35
64	208.3-210.5	6.01	5.12	4.55	4.04	3.59
65	210.5-212.8	3.58	3.00	2.64	2.31	2.04
66	212.8-215.0	2.08	1.72	1.50	1.30	1.14
67	215.0-217.4	1.21	0.995	0.860	0.744	0.647
68	217.4-219.8	0.695	0.569	0.490	0.423	0.368

TABLE 11. Experimental conditions for the measurement of absorption cross-sections at low temperature.

	Temperature range (K)	Max. working pressure * (torrs)	Wavelength range showing T dependance (nm)
CH <sub>3</sub> Cl	295-225	20	198-216
CH <sub>2</sub> Cl <sub>2</sub>	295-225	3	192-220
CHCl <sub>3</sub>	295-230	2	194-230
CCl <sub>4</sub>	295-225	4	204-250
CF <sub>2</sub> Cl <sub>2</sub>	295-225	700	-
CF <sub>2</sub> Cl <sub>2</sub>	295-225	25	188-220
CFC1 <sub>3</sub>	295-225	5	186-230
CHF <sub>2</sub> Cl	295-225	40	192-204
CHFC1 <sub>2</sub>	295-225	7	188-222

\* : at the lowest working temperature



**TABLE 12.** Parameters A and B for polynomial function (see formula (3) in the text).



$A_0 = -299.80$	:	$B_0 = -7.1727$
$A_1 = 5.1047$	:	$B_1 = 1.4837 \cdot 10^{-1}$
$A_2 = -3.3630 \cdot 10^{-2}$	:	$B_2 = -1.1463 \cdot 10^{-3}$
$A_3 = 9.5805 \cdot 10^{-5}$	:	$B_3 = 3.9188 \cdot 10^{-6}$
$A_4 = -1.0135 \cdot 10^{-7}$	:	$B_4 = -4.9994 \cdot 10^{-9}$

T range : 210 - 300 K

$\lambda$  range : 174 - 216 nm

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$A_0 = -1431.8$	:	$B_0 = -3.1171$
$A_1 = 27.395$	:	$B_1 = 6.7874 \cdot 10^{-2}$
$A_2 = -1.9807 \cdot 10^{-1}$	:	$B_2 = -5.5000 \cdot 10^{-4}$
$A_3 = 6.3468 \cdot 10^{-4}$	:	$B_3 = 1.9649 \cdot 10^{-6}$
$A_4 = -7.6298 \cdot 10^{-7}$	:	$B_4 = -2.6101 \cdot 10^{-9}$

T range : 210 - 300 K

$\lambda$  range : 176 - 220 nm

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$A_0 = 269.80$	:	$B_0 = 3.7973$
$A_1 = -6.0908$	:	$B_1 = -7.0913 \cdot 10^{-2}$
$A_2 = 4.7830 \cdot 10^{-2}$	:	$B_2 = 4.9397 \cdot 10^{-4}$
$A_3 = -1.6427 \cdot 10^{-4}$	:	$B_3 = -1.5226 \cdot 10^{-6}$
$A_4 = 2.0682 \cdot 10^{-7}$	:	$B_4 = 1.7555 \cdot 10^{-9}$

T range : 210 - 300 K

$\lambda$  range : 190 - 240 nm

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TABLE 12. (cont.)

$\text{CCl}_4$

$A_0 = -37.104$	:	$B_0 = 1.0739$
$A_1 = -5.8218 \cdot 10^{-1}$	:	$B_1 = -1.6275 \cdot 10^{-2}$
$A_2 = 9.9974 \cdot 10^{-3}$	:	$B_2 = 8.8141 \cdot 10^{-5}$
$A_3 = -4.6765 \cdot 10^{-5}$	:	$B_3 = -1.9811 \cdot 10^{-7}$
$A_4 = 6.8501 \cdot 10^{-8}$	:	$B_4 = 1.5022 \cdot 10^{-10}$

T range : 210 - 300 K

$\lambda$  range : 194 - 250 nm

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$\text{CF}_3\text{Cl}$

$A_0 = -155.88$	:	$B_0 = 0$
$A_1 = 2.0993$	:	$B_1 = 0$
$A_2 = -1.0486 \cdot 10^{-2}$	:	$B_2 = 0$
$A_3 = 1.6718 \cdot 10^{-5}$	:	$B_3 = 0$

T range : 210 - 300 K

$\lambda$  range : 172 - 200 nm

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$\text{CF}_2\text{Cl}_2$

$A_0 = -711.02$	:	$B_0 = 6.1648$
$A_1 = 12.490$	:	$B_1 = -1.2093 \cdot 10^{-1}$
$A_2 = -8.2865 \cdot 10^{-2}$	:	$B_2 = 8.8587 \cdot 10^{-4}$
$A_3 = 2.4091 \cdot 10^{-4}$	:	$B_3 = -2.8743 \cdot 10^{-6}$
$A_4 = -2.6113 \cdot 10^{-7}$	:	$B_4 = 3.4904 \cdot 10^{-9}$

T range : 210 - 300 K

$\lambda$  range : 174 - 226 nm

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TABLE 12. (cont.)

$\text{CFCl}_3$

$A_0 = -84.611$	:	$B_0 = -5.7912$
$A_1 = 7.9551 \cdot 10^{-1}$	:	$B_1 = 1.1689 \cdot 10^{-1}$
$A_2 = -2.0550 \cdot 10^{-3}$	:	$B_2 = -8.8069 \cdot 10^{-4}$
$A_3 = -4.4812 \cdot 10^{-6}$	:	$B_3 = 2.9335 \cdot 10^{-6}$
$A_4 = 1.5838 \cdot 10^{-8}$	:	$B_4 = -3.6421 \cdot 10^{-9}$

T range : 210 - 300 K

$\lambda$  range : 174 - 230 nm

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$\text{CHF}_2\text{Cl}$

$A_0 = -106.029$	:	$B_0 = -1.3399 \cdot 10^{-1}$
$A_1 = 1.5038$	:	$B_1 = 2.7405 \cdot 10^{-3}$
$A_2 = -8.2476 \cdot 10^{-3}$	:	$B_2 = -1.8028 \cdot 10^{-5}$
$A_3 = 1.4206 \cdot 10^{-5}$	:	$B_3 = 3.8504 \cdot 10^{-8}$

T range : 210 - 300 K

$\lambda$  range : 174 - 204 nm

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$\text{CHFC1}_2$

$A_0 = -514.56$	:	$B_0 = -3.0577$
$A_1 = 8.7940$	:	$B_1 = 6.6539 \cdot 10^{-2}$
$A_2 = -5.6810 \cdot 10^{-2}$	:	$B_2 = -5.3964 \cdot 10^{-4}$
$A_3 = -1.5894 \cdot 10^{-4}$	:	$B_3 = 1.9322 \cdot 10^{-6}$
$A_4 = -1.6345 \cdot 10^{-7}$	:	$B_4 = -2.5754 \cdot 10^{-9}$

T range : 210 - 300 K

$\lambda$  range : 174 - 222 nm

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TABLE 13. Temperature model

Altitude (km)	Temperature (K)
15	217
20	217
25	222
30	227
35	237
40	251
45	265
50	271

TABLE 14. Photodissociation coefficients versus altitude

Z(km)	CH <sub>3</sub> Cl					
	sec χ = 1			sec χ = 2		
	J(s <sup>-1</sup> ) σ(295K) <sup>a</sup>	J(s <sup>-1</sup> ) σ = f(T)	J <sub>rel</sub>	J(s <sup>-1</sup> ) σ(295K) <sup>a</sup>	J(s <sup>-1</sup> ) σ = f(T)	J <sub>rel</sub>
15	1.063 10 <sup>-10</sup>	7.837 10 <sup>-11</sup>	.737	2.686 10 <sup>-13</sup>	2.003 10 <sup>-13</sup>	.746
20	1.412 10 <sup>-9</sup>	1.094 10 <sup>-9</sup>	.775	2.548 10 <sup>-11</sup>	1,932 10 <sup>-11</sup>	.758
25	9.471 10 <sup>-9</sup>	7.895 10 <sup>-9</sup>	.834	6.526 10 <sup>-10</sup>	5.342 10 <sup>-10</sup>	.818
30	3.917 10 <sup>-8</sup>	3.414 10 <sup>-8</sup>	.872	7.206 10 <sup>-9</sup>	6.095 10 <sup>-9</sup>	.846
35	1.095 10 <sup>-7</sup>	9.982 10 <sup>-8</sup>	.912	3.962 10 <sup>-8</sup>	3.527 10 <sup>-8</sup>	.890
40	2.196 10 <sup>-7</sup>	2.075 10 <sup>-7</sup>	.945	1.219 10 <sup>-7</sup>	1.134 10 <sup>-7</sup>	.930
45	3.346 10 <sup>-7</sup>	3.244 10 <sup>-7</sup>	.969	2.277 10 <sup>-7</sup>	2.188 10 <sup>-7</sup>	.961
50	4.444 10 <sup>-7</sup>	4.354 10 <sup>-7</sup>	.980	3.314 10 <sup>-7</sup>	3.230 10 <sup>-7</sup>	.975

Z(km)	CH <sub>2</sub> Cl <sub>2</sub>					
	sec χ = 1			sec χ = 2		
	J(s <sup>-1</sup> ) σ(295K) <sup>a</sup>	J(s <sup>-1</sup> ) σ = f(T)	J <sub>rel</sub>	J(s <sup>-1</sup> ) σ(295K) <sup>a</sup>	J(s <sup>-1</sup> ) σ = f(T)	J <sub>rel</sub>
15	6.225 10 <sup>-10</sup>	4.134 10 <sup>-10</sup>	.664	1.564 10 <sup>-12</sup>	1.049 10 <sup>-12</sup>	.671
20	8.080 10 <sup>-9</sup>	5.620 10 <sup>-9</sup>	.696	1.472 10 <sup>-10</sup>	1.003 10 <sup>-10</sup>	.681
25	5.269 10 <sup>-8</sup>	3.945 10 <sup>-8</sup>	.749	3.694 10 <sup>-9</sup>	2.680 10 <sup>-9</sup>	.725
30	2.121 10 <sup>-7</sup>	1.688 10 <sup>-7</sup>	.796	3.988 10 <sup>-8</sup>	3.068 10 <sup>-8</sup>	.769
35	5.784 10 <sup>-7</sup>	4.899 10 <sup>-7</sup>	.846	2.146 10 <sup>-7</sup>	1.766 10 <sup>-7</sup>	.823
40	1.131 10 <sup>-6</sup>	1.014 10 <sup>-6</sup>	.896	6.474 10 <sup>-7</sup>	5.680 10 <sup>-7</sup>	.877
45	1.673 10 <sup>-6</sup>	1.569 10 <sup>-6</sup>	.938	1.180 10 <sup>-6</sup>	1.091 10 <sup>-6</sup>	.925
50	2.149 10 <sup>-6</sup>	2.055 10 <sup>-6</sup>	.956	1.665 10 <sup>-6</sup>	1.577 10 <sup>-6</sup>	.947

TABLE 14. (cont.)

$\text{CHCl}_3$

Z(km)	sec $\chi = 1$			sec $\chi = 2$		
	$J(\text{s}^{-1})$	$J(\text{s}^{-1})$	$J_{\text{rel}}$	$J(\text{s}^{-1})$	$J(\text{s}^{-1})$	$J_{\text{rel}}$
	$\sigma(295\text{K})^a$	$\sigma = f(T)$		$\sigma(295\text{K})^a$	$\sigma = f(T)$	
15	$4.521 \cdot 10^{-9}$	$3.170 \cdot 10^{-9}$	.701	$1.117 \cdot 10^{-11}$	$7.948 \cdot 10^{-12}$	.712
20	$5.325 \cdot 10^{-8}$	$3.838 \cdot 10^{-8}$	.721	$1.017 \cdot 10^{-9}$	$7.298 \cdot 10^{-10}$	.718
25	$3.062 \cdot 10^{-7}$	$2.318 \cdot 10^{-7}$	.757	$2.323 \cdot 10^{-8}$	$1.741 \cdot 10^{-8}$	.749
30	$1.094 \cdot 10^{-6}$	$8.601 \cdot 10^{-7}$	.786	$2.264 \cdot 10^{-7}$	$1.761 \cdot 10^{-7}$	.778
35	$2.704 \cdot 10^{-6}$	$2.222 \cdot 10^{-6}$	.822	$1.108 \cdot 10^{-6}$	$9.024 \cdot 10^{-7}$	.814
40	$4.921 \cdot 10^{-6}$	$4.261 \cdot 10^{-6}$	.866	$3.107 \cdot 10^{-6}$	$2.657 \cdot 10^{-6}$	.855
45	$6.773 \cdot 10^{-6}$	$6.132 \cdot 10^{-6}$	.905	$5.294 \cdot 10^{-6}$	$4.755 \cdot 10^{-6}$	.898
50	$8.050 \cdot 10^{-6}$	$7.457 \cdot 10^{-6}$	.926	$6.878 \cdot 10^{-6}$	$6.327 \cdot 10^{-6}$	.920

$\text{CCl}_4$

Z(km)	sec $\chi = 1$			sec $\chi = 2$		
	$J(\text{s}^{-1})$	$J(\text{s}^{-1})$	$J_{\text{rel}}$	$J(\text{s}^{-1})$	$J(\text{s}^{-1})$	$J_{\text{rel}}$
	$\sigma(295\text{K})^a$	$\sigma = f(T)$		$\sigma(295\text{K})^a$	$\sigma = f(T)$	
15	$1.490 \cdot 10^{-8}$	$1.387 \cdot 10^{-8}$	.930	$3.381 \cdot 10^{-11}$	$3.200 \cdot 10^{-11}$	.946
20	$1.630 \cdot 10^{-7}$	$1.523 \cdot 10^{-7}$	.934	$3.020 \cdot 10^{-9}$	$2.857 \cdot 10^{-9}$	.946
25	$8.752 \cdot 10^{-7}$	$8.206 \cdot 10^{-7}$	.938	$6.520 \cdot 10^{-8}$	$6.194 \cdot 10^{-8}$	.950
30	$3.075 \cdot 10^{-6}$	$2.870 \cdot 10^{-6}$	.933	$6.169 \cdot 10^{-7}$	$5.850 \cdot 10^{-7}$	.948
35	$7.950 \cdot 10^{-6}$	$7.368 \cdot 10^{-6}$	.927	$3.121 \cdot 10^{-6}$	$2.942 \cdot 10^{-6}$	.943
40	$1.593 \cdot 10^{-5}$	$1.471 \cdot 10^{-5}$	.924	$9.748 \cdot 10^{-6}$	$9.121 \cdot 10^{-6}$	.936
45	$2.331 \cdot 10^{-5}$	$2.181 \cdot 10^{-5}$	.936	$1.835 \cdot 10^{-5}$	$1.725 \cdot 10^{-5}$	.940
50	$2.774 \cdot 10^{-5}$	$2.618 \cdot 10^{-5}$	.944	$2.454 \cdot 10^{-5}$	$2.316 \cdot 10^{-5}$	.944

TABLE 14. (cont.)

$\text{CF}_3\text{Cl}$

Z(km)	sec $\chi = 1$			sec $\chi = 2$		
	$J(\text{s}^{-1})$	$J(\text{s}^{-1})$	$J_{\text{rel}}$	$J(\text{s}^{-1})$	$J(\text{s}^{-1})$	$J_{\text{rel}}$
	$\sigma(295\text{K})^a$	$\sigma = f(T)$		$\sigma(295\text{K})^a$	$\sigma = f(T)$	
15	$4.579 \cdot 10^{-14}$			$6.410 \cdot 10^{-18}$		
20	$3.380 \cdot 10^{-12}$			$1.976 \cdot 10^{-14}$		
25	$4.341 \cdot 10^{-11}$			$1.892 \cdot 10^{-12}$		
30	$2.385 \cdot 10^{-10}$			$3.462 \cdot 10^{-11}$		
35	$7.700 \cdot 10^{-10}$			$2.412 \cdot 10^{-10}$		
40	$1.675 \cdot 10^{-9}$			$8.444 \cdot 10^{-10}$		
45	$2.690 \cdot 10^{-9}$			$1.717 \cdot 10^{-9}$		
50	$3.701 \cdot 10^{-9}$			$2.647 \cdot 10^{-9}$		

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$\text{CF}_2\text{Cl}_2$

Z(km)	sec $\chi = 1$			sec $\chi = 2$		
	$J(\text{s}^{-1})$	$J(\text{s}^{-1})$	$J_{\text{rel}}$	$J(\text{s}^{-1})$	$J(\text{s}^{-1})$	$J_{\text{rel}}$
	$\sigma(295\text{K})^a$	$\sigma = f(T)$		$\sigma(295\text{K})^a$	$\sigma = f(T)$	
15	$4.477 \cdot 10^{-10}$	$2.253 \cdot 10^{-10}$	.503	$1.146 \cdot 10^{-12}$	$5.789 \cdot 10^{-13}$	.505
20	$6.238 \cdot 10^{-9}$	$3.345 \cdot 10^{-9}$	.536	$1.105 \cdot 10^{-10}$	$5.704 \cdot 10^{-11}$	.516
25	$4.385 \cdot 10^{-8}$	$2.628 \cdot 10^{-8}$	.599	$2.946 \cdot 10^{-9}$	$1.674 \cdot 10^{-9}$	.568
30	$1.867 \cdot 10^{-7}$	$1.235 \cdot 10^{-7}$	.662	$3.364 \cdot 10^{-8}$	$2.101 \cdot 10^{-8}$	.625
35	$5.297 \cdot 10^{-7}$	$3.909 \cdot 10^{-7}$	.738	$1.889 \cdot 10^{-7}$	$1.329 \cdot 10^{-7}$	.703
40	$1.065 \cdot 10^{-6}$	$8.698 \cdot 10^{-7}$	.817	$5.886 \cdot 10^{-7}$	$4.651 \cdot 10^{-7}$	.790
45	$1.610 \cdot 10^{-6}$	$1.425 \cdot 10^{-6}$	.885	$1.105 \cdot 10^{-6}$	$9.584 \cdot 10^{-7}$	.867
50	$2.099 \cdot 10^{-6}$	$1.925 \cdot 10^{-6}$	.917	$1.597 \cdot 10^{-6}$	$1.443 \cdot 10^{-6}$	.903

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TABLE 14. (cont.)

CFC1<sub>3</sub>

Z(km)	sec $\chi = 1$			sec $\chi = 2$		
	$J(s^{-1})$	$J(s^{-1})$	$J_{rel}$	$J(s^{-1})$	$J(s^{-1})$	$J_{rel}$
	$\sigma(295K)^a$	$\sigma = f(T)$		$\sigma(295K)^a$	$\sigma = f(T)$	
15	$6.240 \cdot 10^{-9}$	$4.701 \cdot 10^{-9}$	.753	$1.532 \cdot 10^{-11}$	$1.178 \cdot 10^{-11}$	.769
20	$7.480 \cdot 10^{-8}$	$5.797 \cdot 10^{-8}$	.775	$1.406 \cdot 10^{-9}$	$1.090 \cdot 10^{-9}$	.775
25	$4.403 \cdot 10^{-7}$	$3.557 \cdot 10^{-7}$	.808	$3.278 \cdot 10^{-8}$	$2.636 \cdot 10^{-8}$	.804
30	$1.607 \cdot 10^{-6}$	$1.334 \cdot 10^{-6}$	.830	$3.263 \cdot 10^{-7}$	$2.701 \cdot 10^{-7}$	.828
35	$4.033 \cdot 10^{-6}$	$3.443 \cdot 10^{-6}$	.854	$1.627 \cdot 10^{-6}$	$1.388 \cdot 10^{-6}$	.853
40	$7.408 \cdot 10^{-6}$	$6.525 \cdot 10^{-6}$	.881	$4.631 \cdot 10^{-6}$	$4.070 \cdot 10^{-6}$	.879
45	$1.021 \cdot 10^{-5}$	$9.342 \cdot 10^{-6}$	.915	$7.963 \cdot 10^{-6}$	$7.253 \cdot 10^{-6}$	.911
50	$1.206 \cdot 10^{-5}$	$1.125 \cdot 10^{-5}$	.932	$1.037 \cdot 10^{-5}$	$9.618 \cdot 10^{-6}$	.927

CHF<sub>2</sub>Cl

Z(km)	sec $\chi = 1$			sec $\chi = 2$		
	$J(s^{-1})$	$J(s^{-1})$	$J_{rel}$	$J(s^{-1})$	$J(s^{-1})$	$J_{rel}$
	$\sigma(295K)^a$	$\sigma = f(T)$		$\sigma(295K)^a$	$\sigma = f(T)$	
15	$1.944 \cdot 10^{-13}$	$1.449 \cdot 10^{-13}$	.727	$5.261 \cdot 10^{-17}$	$3.865 \cdot 10^{-17}$	.735
20	$9.692 \cdot 10^{-12}$	$7.416 \cdot 10^{-12}$	.765	$7.935 \cdot 10^{-14}$	$5.926 \cdot 10^{-14}$	.747
25	$1.020 \cdot 10^{-10}$	$8.196 \cdot 10^{-11}$	.803	$5.363 \cdot 10^{-12}$	$4.177 \cdot 10^{-12}$	.779
30	$5.053 \cdot 10^{-10}$	$4.262 \cdot 10^{-10}$	.844	$8.131 \cdot 10^{-11}$	$6.629 \cdot 10^{-11}$	.815
35	$1.558 \cdot 10^{-9}$	$1.386 \cdot 10^{-9}$	.889	$5.108 \cdot 10^{-10}$	$4.421 \cdot 10^{-10}$	.866
40	$3.360 \cdot 10^{-9}$	$3.126 \cdot 10^{-9}$	.930	$1.708 \cdot 10^{-9}$	$1.562 \cdot 10^{-9}$	.915
45	$5.471 \cdot 10^{-9}$	$5.256 \cdot 10^{-9}$	.961	$3.441 \cdot 10^{-9}$	$3.272 \cdot 10^{-9}$	.951
50	$7.743 \cdot 10^{-9}$	$7.541 \cdot 10^{-9}$	.974	$5.369 \cdot 10^{-9}$	$5.192 \cdot 10^{-9}$	.967



TABLE 14. (cont.)

CHFC1<sub>2</sub>

Z(km)	sec $\chi = 1$			sec $\chi = 2$		
	J(s <sup>-1</sup> )	J(s <sup>-1</sup> )	J <sub>rel</sub>	J(s <sup>-1</sup> )	J(s <sup>-1</sup> )	J <sub>rel</sub>
	$\sigma(295K)^a$	$\sigma = f(T)$		$\sigma(295K)^a$	$\sigma = f(T)$	
15	2.884 10 <sup>-10</sup>	1.932 10 <sup>-10</sup>	.670	7.330 10 <sup>-13</sup>	4.936 10 <sup>-13</sup>	.673
20	3.929 10 <sup>-9</sup>	2.756 10 <sup>-9</sup>	.701	7.015 10 <sup>-11</sup>	4.798 10 <sup>-11</sup>	.684
25	2.706 10 <sup>-8</sup>	2.041 10 <sup>-8</sup>	.754	1.836 10 <sup>-9</sup>	1.338 10 <sup>-9</sup>	.728
30	1.140 10 <sup>-7</sup>	9.145 10 <sup>-8</sup>	.802	2.068 10 <sup>-8</sup>	1.598 10 <sup>-8</sup>	.773
35	3.228 10 <sup>-7</sup>	2.756 10 <sup>-7</sup>	.854	1.154 10 <sup>-7</sup>	9.559 10 <sup>-8</sup>	.829
40	6.507 10 <sup>-7</sup>	5.875 10 <sup>-7</sup>	.903	3.590 10 <sup>-7</sup>	3.175 10 <sup>-7</sup>	.884
45	9.898 10 <sup>-7</sup>	9.325 10 <sup>-7</sup>	.942	6.746 10 <sup>-7</sup>	6.278 10 <sup>-7</sup>	.931
50	1.305 10 <sup>-6</sup>	1.252 10 <sup>-6</sup>	.960	9.809 10 <sup>-7</sup>	9.332 10 <sup>-7</sup>	.951

<sup>a</sup> Temperature independant cross-section.

J<sub>rel</sub> : relative values J(T)/J(295K)