

ABSORPTION CROSS SECTIONS OF HALOCARBONS IN THE ULTRAVIOLET

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Abstract

Absorption cross sections of eleven halocarbons (CCl_4 , CHCl_3 , CH_2Cl_2 , CH_3Cl , CFCl_3 , CF_2Cl_2 , CHFCl_2 , CHF_2Cl , $\text{C}_2\text{F}_3\text{Cl}_3$, $\text{C}_2\text{F}_4\text{Cl}_2$ and $\text{C}_2\text{F}_5\text{Cl}$) are being measured between 175 and 240 nm at various temperatures. The largest temperature effects take place near the absorption threshold and are related to the number of hydrogen and (or) fluorine atoms. Numerical values are given.

Introduction

- It is now fully admitted that modelling stratospheric ozone has to consider simultaneously the numerous chemical and photochemical reaction paths involving natural as well as anthropogenic stratospheric constituents. Amongst the minor species present at significant concentration levels a special attention has recently been paid to the widely used chlorofluorocarbons (HUDSON, 1977) : these compounds which reveal almost chemically inert in the low atmospheric layers slowly diffuse up to stratospheric altitudes where they undergo photodissociation in the 170-240 nm wavelength range. The net result of this process is the release of atomic chlorine which in turn initiates the ClO_x chain of catalytic removal of ozone (ROWLAND and MOLINA, 1975 ; NICOLET, 1975 ; RUNDEL and STOLARSKI, 1976). However, in order to assign the exact role displayed by each constituent, it is of primary importance to include in the model photodissociation coefficients corresponding to the actual conditions prevailing in the stratosphere. Under this respect, the role of temperature has generally been neglected, absorption cross sections being taken constant with altitude and equal to those measured at room temperature even if stratospheric temperatures can be as low as 220 K.

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Until now, measurements at low temperature have been carried out only for CF_2Cl_2 and CFC1_3 by REBBERT and AUSLOOS (1975) at one wavelength (213.9 nm) and by BASS and LEDFORD (1976) and CHOU et al. (1977a) between 185 and 230 nm, leading to absorption cross section reduced by a considerable amount for stratospheric temperatures. Consequently it is necessary to take into account the temperature dependance of the ultraviolet absorption cross section of minor stratospheric constituents in the photodissociation calculations.

- The aim of our current work is to measure, in the case of various halocarbons, the ultraviolet absorption cross section between 170 and 240 nm as a function of temperature and to estimate the impact of possible temperature dependance on photodissociation rate coefficients.

Experimental

The measurements have been made with a 3 m focal length Mc Pherson spectrograph used as a monochromator. Continuous wavelength scanning with a bandpass of the order of 0.1 nm have been obtained using as a source a deuterium discharge lamp mounted with a MgF_2 window. The drift of this source is less than 1% for one hour of operation. Light intensities have been measured by means of a solar blind photomultiplier tube EMR-542P-09-18 with a RbTe photocathode having its wavelength cut off around 320 nm. A stainless steel absorption cell with an optical path of 13.5 cm and mounted with MgF_2 window is placed just behind the exit slit of the monochromator. The temperature regulation is achieved by flowing previously cooled nitrogen through a refrigerating jacket and controlled by thermic resistors fixed on the cell walls. Gas pressures are determined independantly by a capacitance manometer MKS Baratron. Each measurement has been performed in the largest wavelength and pressure ranges afforded by the absorption behavior and physical characteristics of the compound itself. At low temperatures, condensation conditions can restrict the use of high gas pressures and consequently the access to fairly low absorption cross sections ; in order to overcome these difficulties, work is now in progress to achieve thermal regulation of a 2 m cell at temperatures as low as 220 K. Determination of the absorption cross section is made in the "single-beam" mode after sequential recording of the incident and absorbed fluxes measured

in the same temperature conditions. The accuracy of our absorption measurements is within 5%.

- All the samples were of analytical grade and were introduced in the absorption cell after prior vacuum distillation and degassing.

Results and discussion

- Absorption cross sections at room temperature have been measured for the following compounds : CCl_4 , CHCl_3 , CH_2Cl_2 , CH_3Cl , CFCl_3 , CF_2Cl_2 , CHFCl_2 , CHF_2Cl , $\text{C}_2\text{F}_5\text{Cl}$, $\text{C}_2\text{F}_4\text{Cl}_2$, $\text{CF}_2\text{Cl-CFCl}_2$. All of these display continuous absorption in the 200 nm region (fig. 1) which is interpreted as an $n \rightarrow \sigma^*$ transition involving excitation to a repulsive electronic state (C-Cl antibonding). In the case of derivatives belonging to the same basic hydrocarbon entity, substitution of fluorine or hydrogen by chlorine atoms leads to a red shift of the average wavelength absorption range, as it was already discussed by MAJER and SIMONS (1964) and SANDORFY (1976). Comparison with the most recently published values shows no significant discrepancy within the limits of experimental errors.

- Until now, data at 279 K and 255 K have been obtained for most of the above cited compounds (fig. 2). With decreasing temperature, the absorption cross section is lowered by a factor which depends both

- i) on the absolute value of the cross section, the temperature effect being maximum near the absorption threshold and vanishing monotonously at lower wavelengths.
- ii) on the chemical nature of the compound itself : molecules highly stabilized by the presence of hydrogen or fluorine atoms display a very small temperature effect, if any, as far as cross sections of an order of magnitude significant to aeronomy purposes are concerned.

Furthermore, for all compounds, the dependance of the absorption cross section with temperature at a given wavelength can be reasonably assumed to be exponential. In the particular case of CF_2Cl_2 whose absorption cross sections at low temperatures have already been measured at 214 nm by different authors (REBBERT and AUSLOOS, 1975, CHOU et al. 1977a), comparison in terms of relative lowerings show no definite discrepancy with our own values down to 270 K.

However, at lower temperatures, values obtained according to an exponential decrease prove to be in very good agreement with REBBERT's ones but significantly lower than those obtained by CHOU et al. (fig. 3).

Figure 4 gives relative absorption cross section for three different temperatures as a function of wavelength, the curves corresponding to a temperature of 220 K being obtained by exponential extrapolation from the values measured at 296, 279 and 255 K. It appears clearly from these curves that the largest reduction factors are achieved in the case of the highly chlorinated species.

- Overall photodissociation rates J_{tot} have been computed as a function of altitude according to the relations

$$J_{\lambda} = \sigma_{\lambda} q^{(\infty)} e^{-\left[\int_{\infty}^z [n(O_2) \sigma_{\lambda}(O_2) + n(O_3) \sigma_{\lambda}(O_3) + n\sigma_{\lambda} \text{ scatt.}] \sec \chi dz \right]}$$

$$J_{tot} = \sum_{\lambda = 170 \text{ nm}}^{\lambda = 240 \text{ nm}} J_{\lambda}$$

$$\sec \chi = 2$$

which take into account the values of solar fluxes as recently selected by SIMON (1977) and the actual halocarbon absorption cross sections corresponding to the temperature conditions prevailing at each definite altitude.

The amplitude of the temperature effect is most easily visualized by resorting to relative photodissociation rates

$$J_{rel} = \frac{J_{\sigma = f(T)}^{tot}}{J_{\sigma = \sigma_{296 K}}^{tot}}$$

Its incidence (fig. 5) appears to be the most significant in the case of compounds which display at the same time a considerable decrease of absorption cross section at low temperature and a wavelength absorption range centered around 210 nm or less, as for example $CFCl_3$ and CF_2Cl_2 , for which photodissociation rate is reduced by a factor close to 2 at the altitude of 20-30 km. It is obvious that this factor cannot be ignored when assigning peak altitude for photodissociation and consequently atmospheric residence times. Photodissociation rate coefficient

for CF_2Cl_2 and CFCl_3 have been calculated at 30 km of altitude for an overhead sun. The use of low temperature cross sections determined in this work reduces their photodissociation rate coefficient respectively by about 35% and 24% from that found if the temperature effect is neglected. For the same conditions but using their own cross section values, CHOU et al. (1977a) have found less important reduction factors, of the order of 28% and 12% respectively. To avoid such uncertainties, our measurements will be extended to the low temperature range for all the compounds already studied. On another hand, it could be useful to enlarge the investigation field to new species being now or in the next future of technological interest. The systematic intercomparison of the data could provide a general picture of the absorption behavior of halocarbons in the 200 nm range, with special emphasis on the relation to the chemical structure (role of H, F, Cl, Br substituents and length of the carbon chain) and the fundamental basis of the temperature effect.

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Fig. 1a : Absorption cross sections vs. wavelength of chloromethane derivatives, and comparison with previously published values.

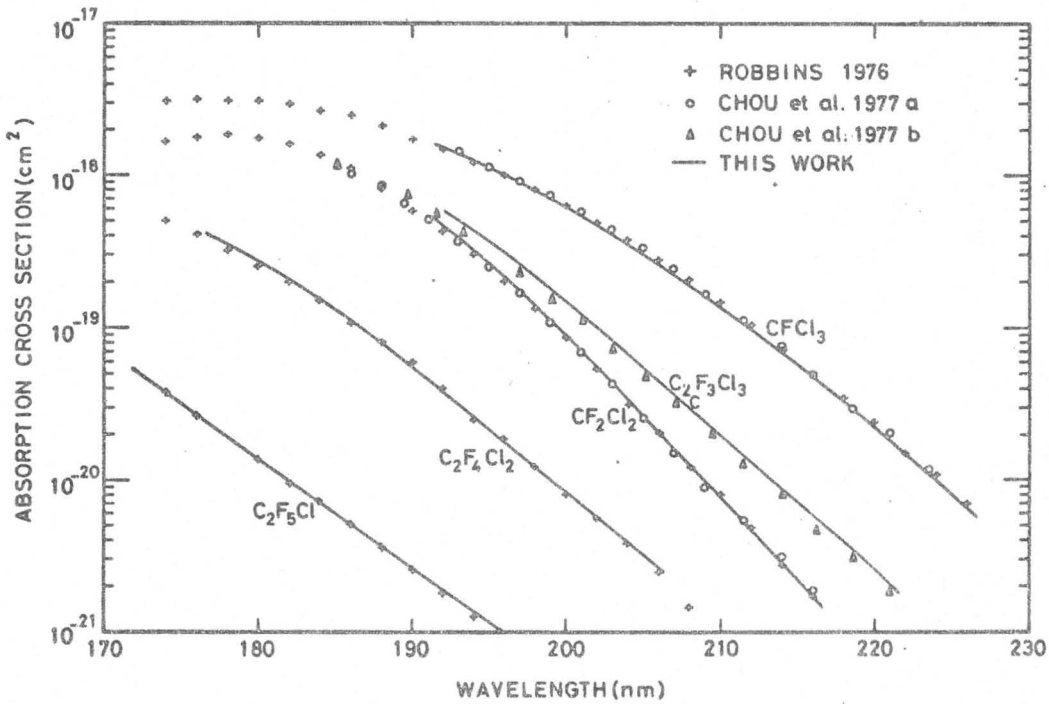
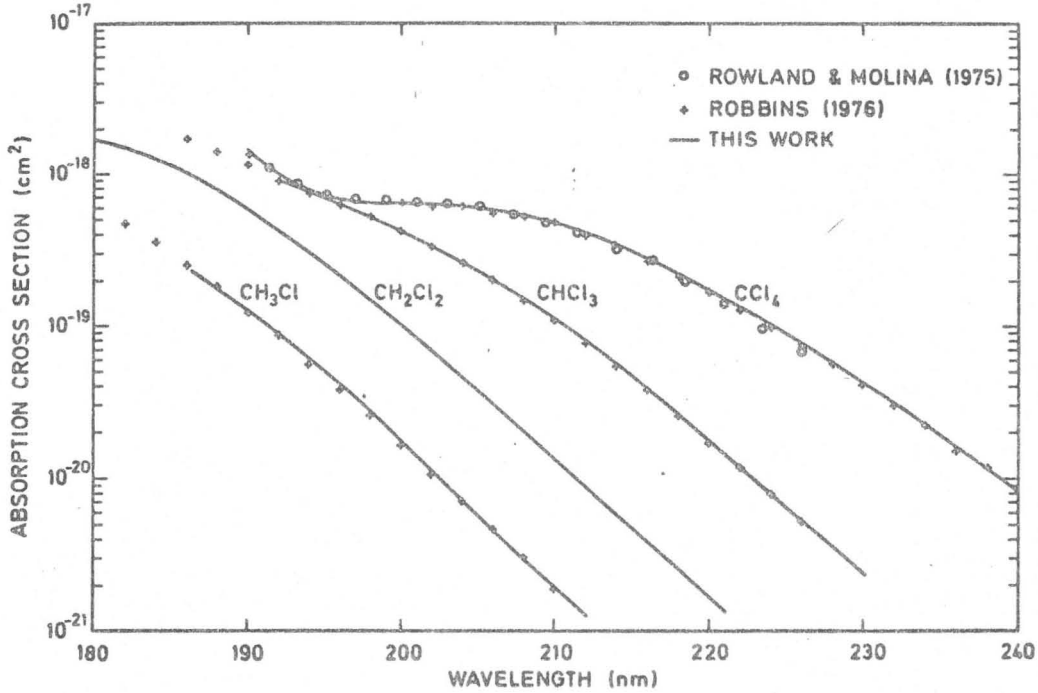


Fig. 1b : Absorption cross sections vs. wavelength of chlorofluoromethane and chlorofluoroethane derivatives, and comparison with previously published values. Results obtained in the case of CHF₂Cl and CHFCl₂ have been omitted for the sake of clarity.

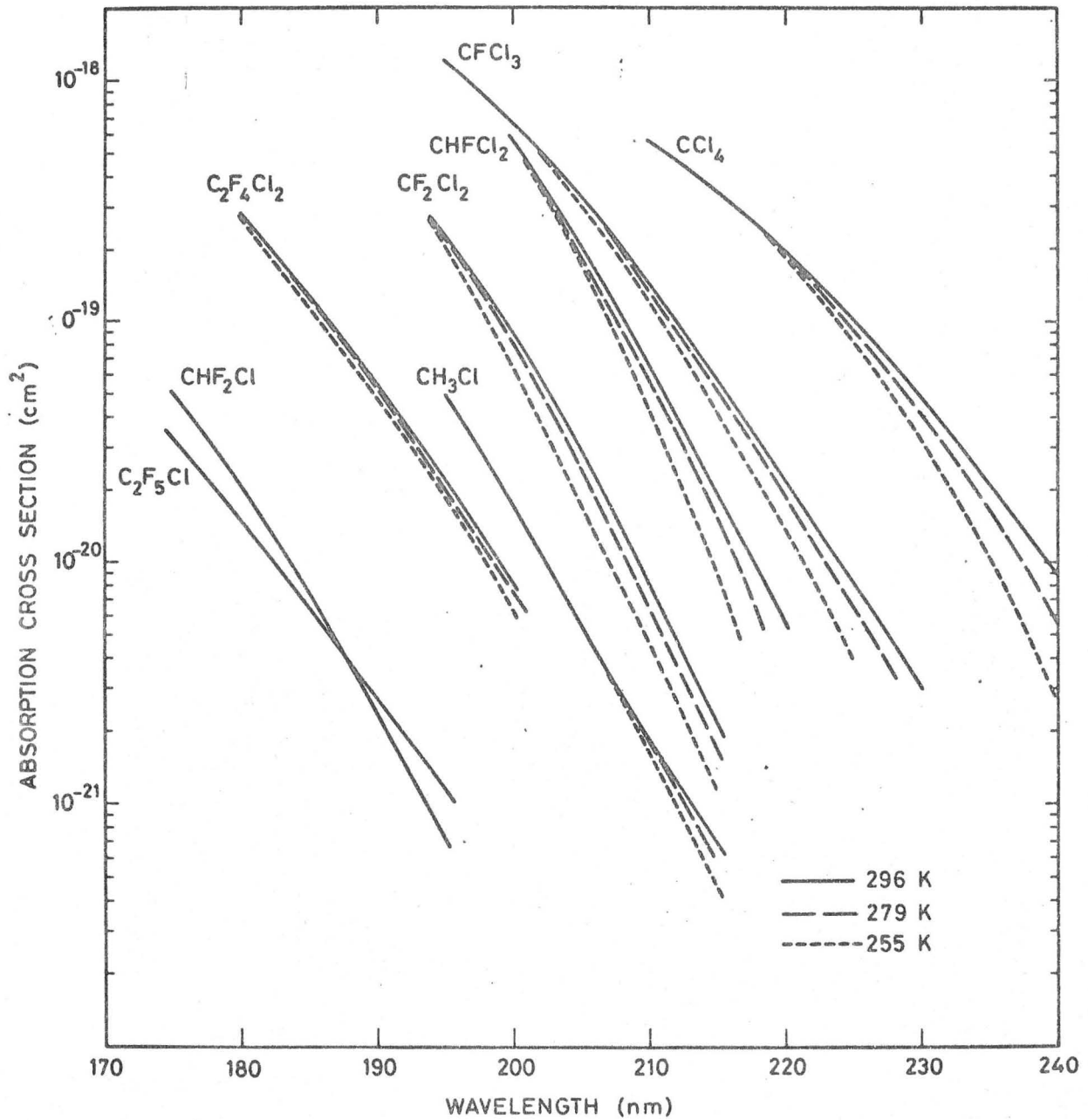


Fig. 2 : Experimental absorption cross sections vs. wavelength at 3 temperatures (296 K, 279 K and 255 K) for various chlorofluorocarbons.

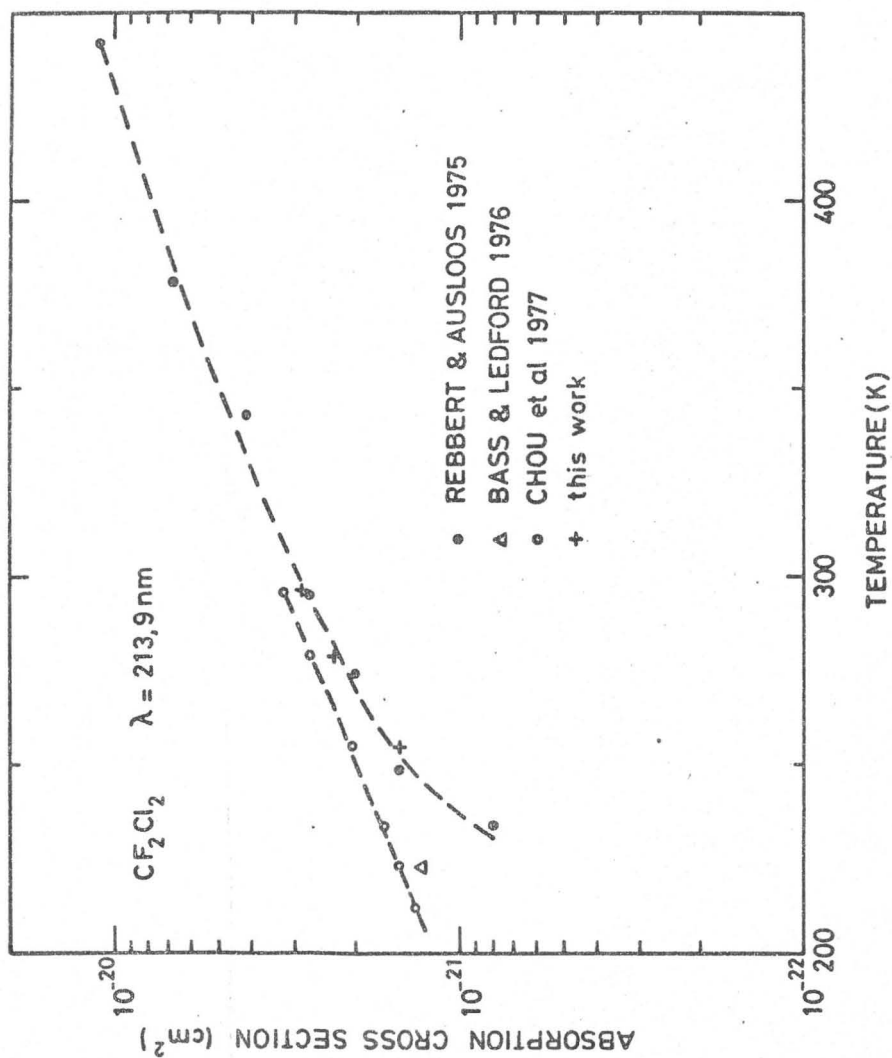


Fig. 3 : Exponential decrease of relative absorption cross sections σ/σ_{296K} with decreasing temperature at 214 nm in the case of CF₂Cl₂, and comparison with previously published values.

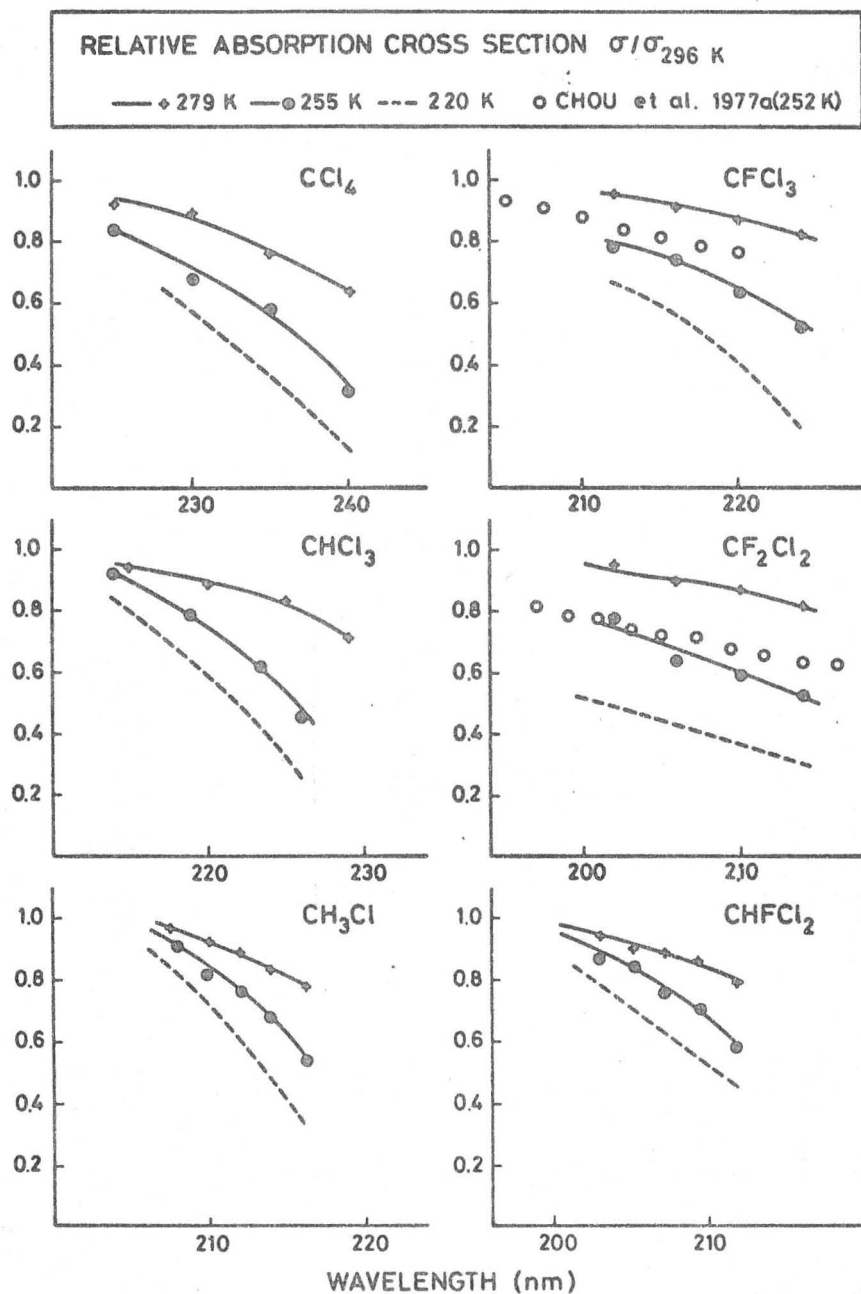


Fig. 4 : Relative absorption cross section $\sigma/\sigma_{296\text{ K}}$ vs. wavelength measured at 279 and 255K and extrapolated at 220 K. Comparison is made with previously published data.

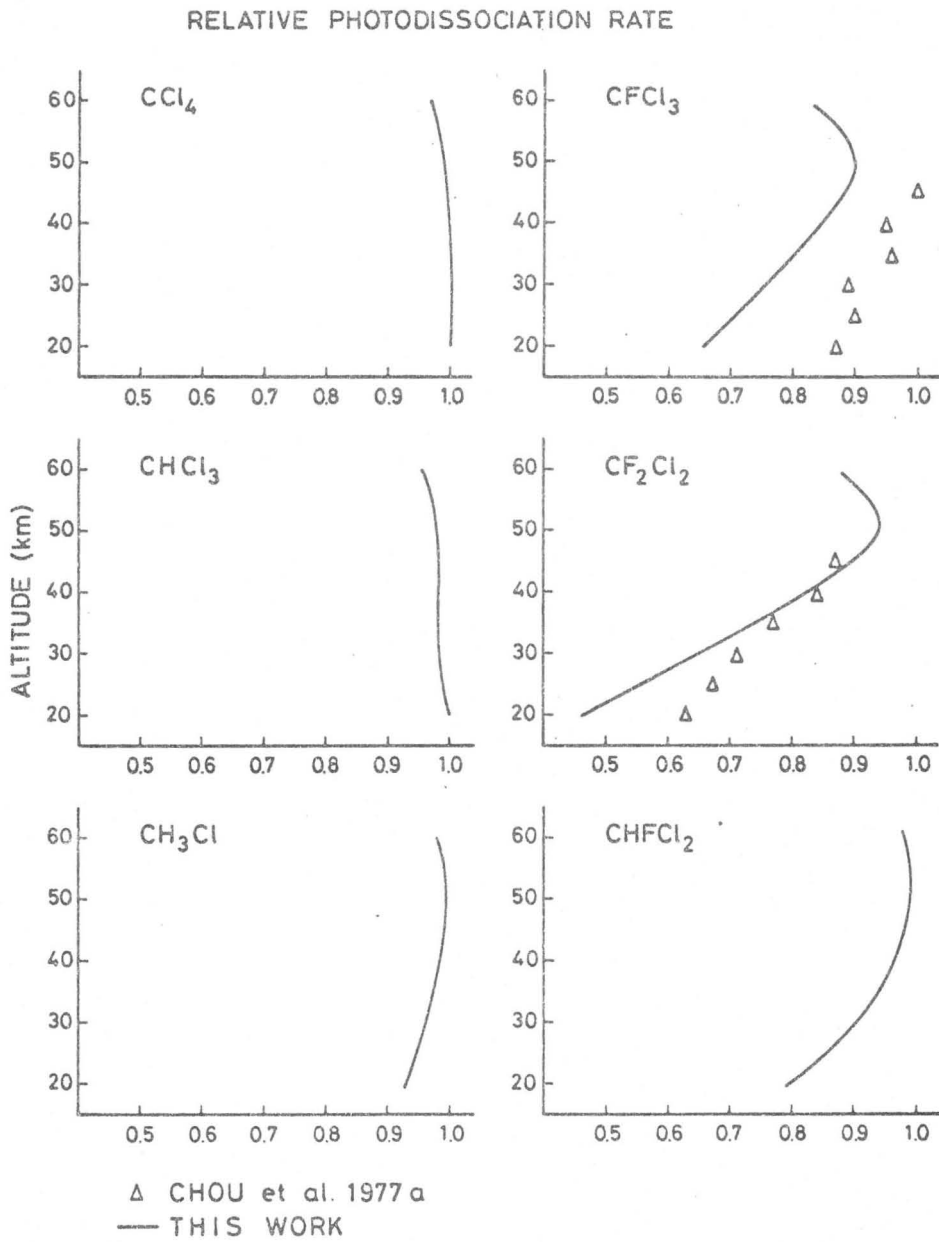


Fig. 5 : Relative photodissociation rates $\frac{J_{\sigma} = f(T)}{J_{\sigma} = \sigma_{296K}}$ at stratospheric altitudes (20 to 60 km) in the case of some halocarbons.