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Short Communication

Vacuum ultra-violet absorption spectra of halogenated methanes and ethanes

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The current concern about man's release into the atmosphere of chlorofluorocarbons (FCCs) arises from the possibility that stratospheric ozone levels may be diminished by such release. A detailed discussion is given by Molina and Rowland [1]. A catalytic chain decomposition of ozone may be propagated by Cl and ClO in the stratosphere:

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad (1)$$

$$O + ClO \longrightarrow Cl + O_2 \qquad (2)$$

The atomic chlorine can be found in the photolysis of the FCCs: *e.g.* for CF_2Cl_2:

$$CF_2Cl_2 + h\nu \longrightarrow CF_2Cl + Cl \qquad (3)$$

It is therefore important to know the absorption cross-sections, in the atmospheric window† region (180 - 210 nm), for the FCCs, in order to provide a "worst case" (*i.e.* quantum yield set equal to unity) rate of Cl atom production. This communication describes measurements of such cross-sections for several halocarbons.

Experimental

The halocarbons were supplied either by Fluorochem Limited, or by Imperial Chemical Industries Limited. Purity was checked by gas chromatography and mass spectroscopy; all compounds had purity >99.7%, except for CF_3CHCl_2, which had a purity of 98%.

A 0.3 m scanning monochromator (McPherson Model 218) was used with a deuterium lamp as the light source. The bandwidth (FWHM) was $\ngtr$0.5 nm, and the wavelength accuracy is of the same order. An EMI type 9783B photomultiplier, together with appropriate pulse-counting electronics, was used as

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†This spectral "window" is a region where fairly intense u.v. reaches the stratosphere as a result of relatively weak absorption by both atmospheric ozone and oxygen.

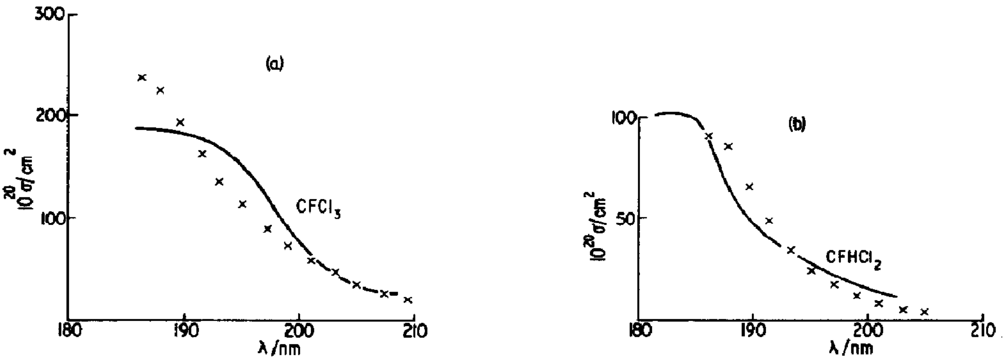

Fig. 1. Absorption cross-sections of (a) $CFCl_3$ and (b) CF_2Cl_2 as a function of wavelength. The solid lines show the data reported by Molina and Rowland [1].

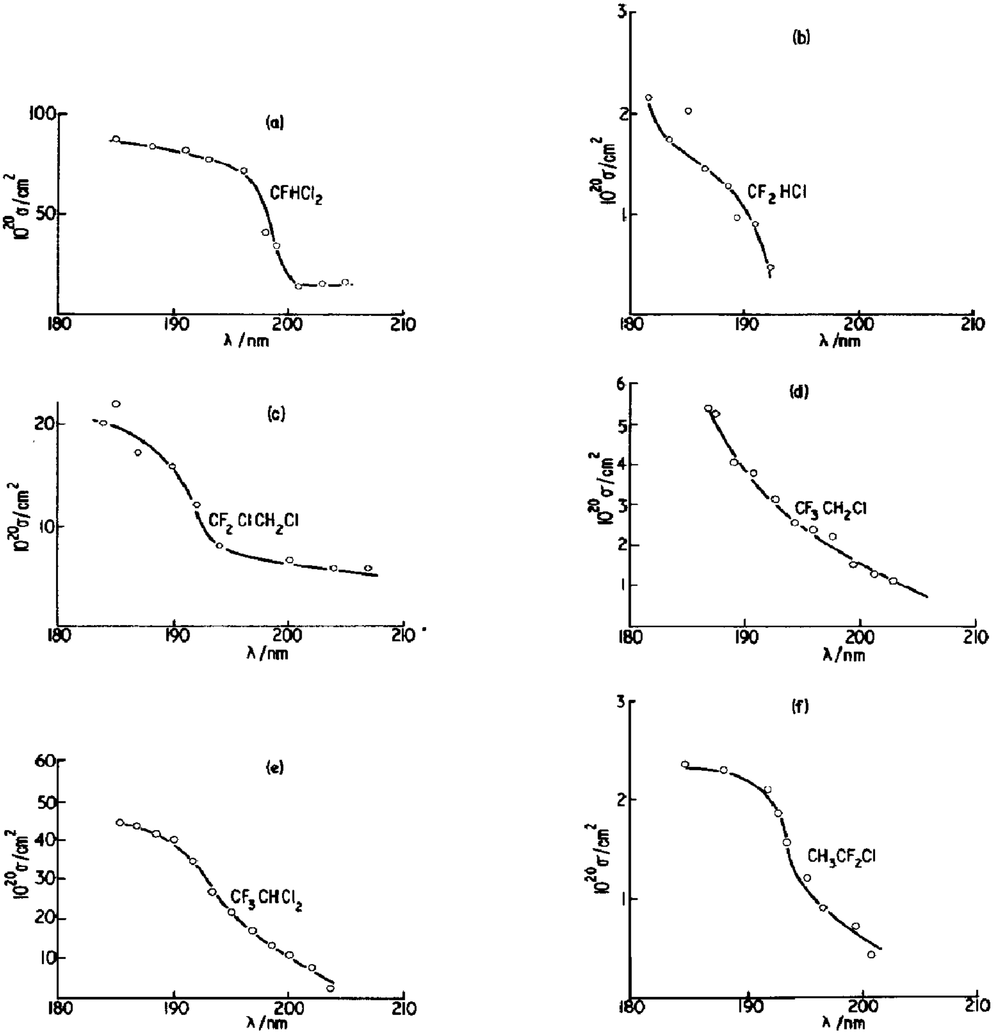

Fig. 2. Absorption cross-sections for six fluorochlorocarbons as a function of wavelength. Solid lines represent smoothed fits. (a) $CFHCl_2$; (b) CF_2HCl; (c) CF_2ClCH_2Cl; (d) CF_3CH_2Cl; (e) CF_3CHCl_2; (f) CH_3CF_2Cl.

detector. The absorption cell was 10 cm in length, and was equipped with Suprasil windows. Sample pressures were measured by an Edwards' Capsulon gauge, cross calibrated against oil manometers; the pressures of sample used ranged from 2 to 50 Torr.

All experiments were carried out at a temperature of ~300 K.

Results and Discussion

The spectra obtained are shown in Figs. 1 and 2. The precision of the measurements is limited largely by noise-on-signal, and ranges from ~ ± 10% at λ = 210 nm to ± 30% at λ = 180 nm.

In all cases, the bands appear diffuse and no fine structure was detected. Spectra for CF_2HCl, $CFHCl_2$, CH_3CF_2Cl, CF_2Cl_2 and $CFCl_3$ have been reported previously [2, 3], although our wavelength range (180 - 210 nm) was not considered of interest since it lies just at the onset of the vacuum u.v. absorption. Other spectra for the specific wavelength region λ = 180 - 230 nm have appeared recently [1, 4, 5] for CF_2Cl_2 and $CFCl_3$. The results of Rowland and Molina [1] are given as solid lines in Figs. 1 and 2 for comparison with our data. The various sets of measurements are, within experimental error, in agreement.

The weak absorptions were assigned [2] to the tail of the band due to the electronic transition of the chlorine lone pair to the antibonding C–Cl orbital. As expected from this assignment, the fluorohydrocarbons (*i.e.* species not containing Cl) CHF_3, CH_2F_2, CF_3CHF_2, CF_3CH_2F, CF_3CH_3 and CF_2HCH_2F showed no measurable absorption in the λ = 180 - 210 nm region. Further, the absorption cross-section at any given wavelength shows a marked dependence on the number of chlorine atoms in the molecule. For example, at λ = 190 nm, the cross-sections for the molecules with two chlorines (CF_2Cl_2, $CFHCl_2$, CF_2ClCH_2Cl, CF_3CHCl_2) are about an order of magnitude greater than those for the molecules with one chlorine (CF_2HCl, CF_3CH_2Cl, CH_3CF_2Cl), while $CFCl_3$ has an absorption cross-section nearly 200 times that of CF_2HCl.

It is also noteworthy that the cross-section (at λ = 190 nm) is appreciably smaller for the molecule with two chlorines attached to different carbons (CF_2ClCH_2Cl) than for the other "two-chlorine" molecules.

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1 M. J. Molina and F. S. Rowland, Rev. Geophys. Space Phys., 13 (1975) 1.
2 J. Doucet, P. Sauvageau and C. Sandorfy, J. Chem. Phys., 58 (1973) 3708.
3 J. Doucet, P. Sauvageau and C. Sandorfy, J. Chem. Phys., 62 (1975) 355.
4 R. H. Huebner and D. L. Bushnell, Nature, 257 (1975) 376.
5 A. M. Bass and A. E. Ledford, 12th Informal Conf. Photochem., (1976).