REVIEW OF ULTRAVIOLET
ABSORPTION CROSS SECTIONS OF A SERIES
OF ALTERNATIVE FLUOROCARBONS

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ULTRAVIOLET SPECTRA

The main atmospheric sink for the alternative fluorocarbons (HFC's) is reaction with hydroxyl radicals. Ultraviolet photolysis can, however, be an important additional destruction process in the stratosphere, and it may affect significantly their ozone depletion potential.

There are very few measurements reported in the literature of UV absorption cross sections for the HFC's that are likely to be of industrial importance. This review is focussed on eight of these compounds, namely HFC-123, 141b, 142b, 22, 124, 134a, 152a and 125. There are three sets of very recent measurements which have not been published yet, but which are included in this review. In general, the agreement around the 200 nm wavelength range—the important atmospheric "window" for solar photodissociation-—is good (within 20%) for those species with significant absorptions, namely those containing two chlorine atoms bonded to the same carbon atom (HCFC-123 AND 141b; see Tables 1 and 2). The agreement is equally good for HCFC-124, (Table 3) and it is reasonable for HCFC 142b (Table 4) but it is rather poor for those species not containing chlorine (HFC-134a and 152a). However, it is clear that except for the first

Table 1. Absorption Cross Sections of HCFC-123 ($CHCl_2$-CF_3)

λ (nm)	10^{20} σ (cm²/molecule) (Ref. #)			
	1	2	3	4
185	—	106.7	115*	96.0
190	56.5	55.8	60.3	52.4*
195	26.7	25.5	28.8*	23.6
200	11.3	10.4	12.2	9.95*
205	4.45	3.94	5.2*	3.88
210	1.73	1.47	0.651	1.53*
215	0.651	0.557	0.268*	0.57
220	0.254	0.198	0.112	0.21*
225	0.099	0.073	0.051*	0.079

* Estimated by linear interpolation

1 Orlando et al., 1989
2 Molina and Molina, 1989
3 Gillotay et al., 1989
4 Allied-Signal Corp. (Private Communication) 1989

Table 2. Absorption Cross Sections of HCFC-141b ($CHCl_2-CF_3$)

λ (nm)	10^{20} σ (cm²/molecule) (Ref. #)			
	1	**2**	**3**	**4**
185	—	142.3	137.5*	109
190	79.5	85.8	86.3	70.5*
195	40.4	41.8	43.2*	38.0
200	17.1	16.8	18.3	17.4*
205	6.38	5.96	7.02*	6.78
210	2.38	2.06	2.35	2.86*
215	0.974	0.692	0.804*	1.24
220	0.482	0.235	0.267	0.51*
225	0.326	0.083	0.094*	—

* Estimated by linear interpolation

1 Orlando et al., 1989
2 Molina and Molina, 1989
3 Gillotay et al., 1989
4 Allied-Signal Corp. (Private Communication) 1989

two species, HCFC-123 and 141b, atmospheric photolysis is a minor process and that reaction with hydroxyl radicals occurs much faster throughout the troposphere and stratosphere.

There are no absorption cross section measurements in the 200 nm wavelength region for HFC-125. However, considering that this is a saturated hydrocarbon with only fluorine, hydrogen and carbon atoms, the absorption in that wavelength region should be negligible. In general, at those wavelengths the absorption increases sharply with the number of chlorine atoms per carbon atom, and it decreases with substitution of fluorine for hydrogen.

The absorption cross sections for the HCFC's have a significant temperature dependency in the atmospherically important wavelength range. Only one group has reported measurements at various temperatures (Orlando et al., 1989). Furthermore, for HFC-123, 141b and 124 the room temperature values measured by this same group around 200 nm are close to the average of the values reported in the other studies. Hence, the recommendation at present is to use the values given by Ravishankara el al. at various temperatures (see Tables 5-7). This provides a more consistent set of data than, for example, the average of

Table 3. Absorption Cross Sections of HCFC-124 (CHCIF-CF$_3$)

λ (nm)	10^{20} σ (cm^2/molecule) (Ref. #)		
	1	2	4
185	—	1.82	—
190	0.735	0.799	0.77*
195	0.316	0.331	0.32*
200	0.128	0.129	0.125*
205	0.0482	0.0466	0.04
210	0.0182	0.0168	0.02
215	0.0072	0.0062	—
220	0.0032	0.0023	—
225	0.0020	0.00015	—

* Estimated by linear interpolation

1 Orlando et al., 1989
2 Molina and Molina, 1989
4 Allied-Signal Corp. (Private Communication) 1989

all values, which would then have to be adjusted at each temperature with only one of the data sets contributing to the temperature dependency.

The compound HCFC-142b, namely CCIF$_2$-CH$_3$, appears to absorb UV radiation about as strongly as HCFC 124; both species have a single chlorine atom per molecule, and atmospheric photolysis is unlikely to be of importance. For HCFC-142b there is agreement in the cross section values reported by Orlando et al. (1989), Allied-Signal Corp., Private Communication (1989), (1989), Hubrich and Stuhl (1980), and Gillotay et al. (1989) (see Table 4). The recommendation is, here again, to use the data and the temperature dependency reported by Orlando et al. (Table 8).

For HCFC-22, the recommended cross section values, listed in Table 9, are those obtained by Simon et al. (1988), as a function of temperature. These values are in reasonable agreement with the earlier recommendation in the report of the NASA Panel for Data Evaluation, which was based on room temperature data only. The Allied Co. group reported cross sections for this compound which are also in reasonable agreement with the data of Table 9.

For the HCFC's 123, 141b, 22, 124 and 142b, the error factor in the atmospheric photodissociation rates which arises from uncertainties in the cross section data is estimated as 1.2 (this is the error factor defined in the NASA Panel for Data Evaluation reports). The uncertainty in the cross sections increases rapidly beyond 210 nm, but the available solar intensity in the stratosphere decreases also rapidly. It should be noted that the values given by Orlando et al. beyond 210 nm become significantly larger than the ones

Table 4. Absorption Cross Sections of HCFC-124b ($CHClF_2$-CF_3)

λ (nm)	10^{20} σ (cm²/molecule) (Ref. #)			
	1	3	4	5
185	—	2.57*	2.47	2.79
190	0.853	1.02	1.07*	1.02
195	0.349	0.403*	0.42	0.405
200	0.132	0.150	0.16*	0.158
205	0.046	0.0527*	0.046	0.0618
210	0.015	0.0172	—	0.0254
215	0.0052	0.0051*	—	0.0108
220	0.0018	—	—	0.0040
225	0.0004	—	—	0.0016

* Estimated by linear interpolation
1 Orlando et al., 1989
3 Gillotay et al., 1989
4 Allied-Signal Corp. (Private Communication) 1989
5 Hubrich and Stuhl, 1980

measured by Gillotay et al.; this discrepancy remains to be resolved. Also, the ratio of the cross section value at a given temperature to the corresponding value at 295 K is expected to be a smooth function of wavelength and temperature, and this is not the case for the data given in Tables 5 to 8 for wavelengths longer than about 210 nm; this is another indication of the rapidly increasing uncertainties.

As is the case for the fully halogenated hydrocarbons, the quantum yields for photodissociation for the HCFC's are expected to be unity, given the continuous nature of their UV absorption spectra. Furthermore, the primary products at the atmospherically important wavelengths are most likely a chlorine atom plus the residual organic free radical.

As mentioned above, there are no measurements of the UV spectrum of HFC-125, and there is very significant disagreement in the cross section values for the other two fluorocarbons considered in this review which do not contain chlorine (HFC-134a and 152a). Two groups have measured cross sections around 200 nm for these last two species, Molina and Molina (1989) and Allied-Signal Corp. (1989), with values differing by two orders of magnitude. The most likely explanation is that the small absorptions observed around 200 nm are strongly influenced by impurities, which differ from sample to sample. While this is not at all a satisfactory situation from the point of view of the proper spectroscopic characterization of these compounds, it turns out that the atmospheric implications are minor: photolysis can be neglected even assuming the largest reported cross section values.

A very conservative upper limit for the cross section values for HFC-134a and 152a is given by the cross sections corresponding to HCFC-22 (Table 9), for which solar photolysis is unimportant.

Table 5. Recommended Absorption Cross Sections for HCFC-123 ($CHCl_2-CF_3$), taken from Orlando et al., 1989.

λ (nm)	σ (cm^2/molecule)	
	295K	223K
190	5.65E-19	5.09E-19
191	4.66E-19	4.33E-19
192	4.08E-19	3.76E-19
193	3.48E-19	3.14E-19
194	3.02E-19	2.71E-19
195	2.54E-19	2.25E-19
196	2.14E-19	1.87E-19
197	1.87E-19	1.58E-19
198	1.53E-19	1.3E-19
199	1.27E-19	1.07E-19
200	1.08E-19	8.87E-20
201	8.9E-20	7.25E-20
202	7.35E-20	5.93E-20
203	6.26E-20	4.99E-20
204	5.14E-20	4.08E-20
205	4.21E-20	3.33E-20
206	3.5E-20	2.71E-20
207	2.86E-20	2.21E-20
208	2.4E-20	1.85E-20
209	1.98E-20	1.51E-20
210	1.62E-20	1.24E-20
211	1.32E-20	1.02E-20
212	1.1E-20	8.47E-21
213	9.04E-21	6.94E-21
214	7.44E-21	5.97E-21
215	6.2E-21	4.92E-21
216	5.14E-21	4.12E-21
217	4.1E-21	3.52E-21
218	3.37E-21	3.01E-21
219	2.86E-21	2.48E-21
220	2.41E-21	2.17E-21

UV CROSS SECTIONS

Table 6. Recommended Absorption Cross Sections for HCFC-141b ($CHCl_2$-CF_3), taken from Orlando et al., 1989 .

λ (nm)	σ (cm²/molecule)	
	295K	223K
190	7.95E-19	7.42E-19
191	7.05E-19	6.46E-19
192	6.3E-19	5.71E-19
193	5.4E-19	4.83E-19
194	4.77E-19	4.06E-19
195	4.04E-19	3.47E-19
196	3.43E-19	2.89E-19
197	2.94E-19	2.44E-19
198	2.44E-19	1.97E-19
199	2.02E-19	1.59E-19
200	1.71E-19	1.33E-19
201	1.4E-19	1.06E-19
202	1.15E-19	8.51E-20
203	9.67E-20	7.03E-20
204	7.86E-20	5.61E-20
205	6.38E-20	4.47E-20
206	5.21E-20	3.57E-20
207	4.24E-20	2.84E-20
208	3.56E-20	2.35E-20
209	2.91E-20	1.89E-20
210	2.38E-20	1.52E-20
211	1.95E-20	1.22E-20
212	1.62E-20	1.01E-20
213	1.34E-20	8.14E-21
214	1.16E-20	6.9E-21
215	9.74E-21	5.78E-21
216	8.2E-21	4.82E-21
217	7.11E-21	4E-21
218	6.34E-21	3E-21
219	5.41E-21	2.58E-21
220	4.82E-21	2.21E-21

Table 7. Recommended Absorption Cross Sections for HCFC-124 ($CHClFCF_3$), taken from Orlando, et al., 1989

λ (nm)	σ (cm²/molecule)	
	295K	223K
190	7.35E-21	4.79E-21
191	6.16E-21	4.02E-21
192	5.29E-21	3.52E-21
193	4.41E-21	2.95E-21
194	3.79E-21	2.53E-21
195	3.16E-21	2.09E-21
196	2.61E-21	1.73E-21
197	2.21E-21	1.47E-21
198	1.83E-21	1.21E-21
199	1.51E-21	9.91E-22
200	1.28E-21	8.31E-22
201	1.05E-21	6.77E-22
202	8.6E-22	5.49E-22
203	7.23E-22	4.57E-22
204	5.92E-22	3.71E-22
205	4.82E-22	2.97E-22
206	3.95E-22	2.39E-22
207	3.22E-22	1.93E-22
208	2.62E-22	1.59E-22
209	2.21E-22	1.28E-22
210	1.82E-22	1.03E-22
211	1.48E-22	8.25E-23
212	1.22E-22	6.76E-23
213	1E-22	5.44E-23
214	8.29E-23	4.57E-23
215	7.2E-23	3.8E-23
216	6.05E-23	3.17E-23
217	5.03E-23	2.81E-23
218	4.33E-23	2.42E-23
219	3.77E-23	2.1E-23
220	3.22E-23	1.88E-23

Table 8. Recommended Absorption Cross Sections for HCFC-142b ($CHCl_2F$-CH_3), taken from Orlando et al., 1989

λ (nm)	σ (cm²/molecule)	
	295K	223K
190	8.53E-21	6.38E-21
191	7.16E-21	5.27E-21
192	6.18E-21	4.47E-21
193	5.01E-21	3.61E-21
194	4.29E-21	3.05E-21
195	3.49E-21	2.45E-21
196	2.86E-21	1.98E-21
197	2.39E-21	1.64E-21
198	1.95E-21	1.32E-21
199	1.59E-21	1.06E-21
200	1.32E-21	8.72E-22
201	1.07E-21	6.96E-22
202	8.65E-22	5.53E-22
203	7.18E-22	4.57E-22
204	5.79E-22	3.62E-22
205	4.65E-22	2.87E-22
206	3.71E-22	2.31E-22
207	3.01E-22	1.83E-22
208	2.48E-22	1.51E-22
209	1.97E-22	1.22E-22
210	1.58E-22	9.8E-23
211	1.26E-22	7.94E-23
212	1.01E-22	6.58E-23
213	8.19E-23	5.21E-23
214	6.86E-23	4.46E-23
215	5.41E-23	3.88E-23
216	4.43E-23	3.5E-23
217	3.71E-23	2.93E-23
218	2.98E-23	2.69E-23
219	2.37E-23	2.44E-23
220	2.08E-23	2.17E-23

Table 9. Absorption Cross Section of HCFC-22 ($CHClF_2$), taken from Simon et al., 1988.

λ (nm)	10^{20} σ (cm²/molecule)				
	295K	270K	250K	230K	210K
174	5.72	5.72	5.72	5.72	5.72
176	4.04	4.04	4.04	4.04	4.04
178	2.76	2.76	2.76	2.76	2.76
180	1.91	1.91	1.91	1.91	1.91
182	1.28	1.28	1.28	1.28	1.28
184	0.842	0.842	0.842	0.842	0.842
186	0.576	0.576	0.576	0.576	0.576
188	0.372	0.372	0.372	0.372	0.372
190	0.245	0.245	0.245	0.245	0.245
192	0.156	0.156	0.156	0.152	0.148
194	0.103	0.102	0.099	0.096	0.093
196	0.072	0.069	0.067	0.064	0.062
198	0.048	0.045	0.043	0.041	0.039
200	0.032	0.029	0.0278	0.0259	0.0246
202	0.0220	0.0192	0.0184	0.0169	0.0159
204	0.0142	0.0121	0.0114	0.0104	0.0096

V. TROPOSPHERIC OH AND HCFC/HFC LIFETIMES

Combined Summary and Conclusions

Atmospheric Lifetimes for HCFCs Table

The Tropospheric Lifetimes of Halocarbons and their Reactions with OH Radicals: An Assessment Based on the Concentration of ^{14}CO

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COMBINED SUMMARY AND CONCLUSIONS

The atmospheric lifetime of HCFCs is determined predominantly by reaction with tropospheric OH. Stratospheric loss is secondary and may contribute at most 10% of the total budget.

The lifetimes of HCFCs are determined here by three separate approaches:

(1) 2-D chemical transport model with semi-empirical fit to ^{14}CO;
(2) photochemical calculation of 3-D OH fields and integrated loss;
(3) scaling of the inferred $CH_3 CCl_3$ lifetime by rate coefficients.

Resulting lifetimes from all three independent approaches generally agree within 15%, as shown in the table below. The integrated losses calculated from the global OH fields in the models (1 & 2) are constrained by modelling of the observations and budgets for ^{14}CO and CH_3CDCl_3 (respectively). Method (3) may be expressed simply as

$$\text{lifetime (HCFC)} = 6.3 \text{ yr} \times k(CH_3 CCl_3 \text{ at } 277 \text{ K}) / k(HCFC \text{ at } 277 \text{ K}),$$

where the current estimate of the lifetime for methyl chloroform (6.3 yr) is based on the ALE/GAGE analysis (Prinn et al., 1987). Some of the errors associated with this scaling have been tested with the 3-D OH fields from method (2); method (3) should be reliable for calculating HCFC lifetimes in the range 1 to 30 years.

The calculated local concentrations of OH in these models (1 & 2) are not well tested since there are few observations of OH with which to compare. Based on method (2), the middle tropical troposphere (2-6 km) dominates the atmospheric loss and would be an important region in which to make observations of OH.

Estimated uncertainties in the HCFC lifetimes between 1 and 30 years are $\pm 50\%$ for (1) and $\pm 40\%$ for (2) & (3). Global OH values that give lifetimes outside of these ranges of uncertainty are inconsistent with detailed analyses of the observed distributions for ^{14}CO and CH_3CCl_3. The expected spatial and seasonal variations in the global distribution of HCFCs with lifetimes of 1 to 30 yr have been examined with methods (1) & (2) and found to have insignificant effect on the calculated lifetimes. Larger uncertainties apply to gases with lifetimes shorter than one year; however, for these species our concern is for destruction on a regional scale rather than global accumulation.

Future changes in the oxidative capacity of the troposphere, due to changing atmospheric composition, will affect HCFC lifetimes and introduce additional uncertainties of order $\pm 20\%$.

TROPOSPHERIC LIFETIMES

Atmospheric Lifetimes for HCFCs

HCFC	k (cm³ molec⁻¹ s⁻¹)		lifetime (yr) for method*		
			(1)	(2)	(3)
CH_3CCl_3	5.0×10^{-13}	exp(-1800/T)	5	5.4	6.3
(range)			(3-7)	(4-7)	(5.4-7.5)
CH_3F	5.4×10^{-12}	exp(-1700/T)	3.3	3.8	4.1
CH_2F_2	2.5×10^{-12}	exp(-1650/T)	6.0	6.8	7.3
CHF_3	7.4×10^{-13}	exp(-2350/T)	635.	289.	310.
CH_2FCl	3.0×10^{-12}	exp(-1250/T)	1.26	1.33	1.44
$CHFCl_2$	1.2×10^{-12}	exp(-1100/T)	1.80	1.89	2.10
CHF_2Cl (22)	1.2×10^{-12}	exp(-1650/T)	13.0	14.2	15.3
CH_3CH_2F	1.3×10^{-11}	exp(-1200/T)	0.31	0.25	0.28
CH_2FCH_2F (152a)	1.7×10^{-11}	exp(-1500/T)	0.60	0.58	0.63
CH_3CHF_2	1.5×10^{-12}	exp(-1100/T)	1.46	1.53	1.68
CH_2FCHF_2	2.8×10^{-12}	exp(-1500/T)	3.2	3.5	3.8
CH_3CF_3	2.6×10^{-13}	exp(-1500/T)	40.	38.	41.
CHF_2CHF_2	8.7×10^{-13}	exp(-1500/T)	10.4	11.4	12.3
CH_2FCF_3 (134a)	1.7×10^{-12}	exp(-1750/T)	13.1	14.4	15.5
CHF_2CF_3 (125)	3.8×10^{-13}	exp(-1500/T)	24.9	26.1	28.1
CH_3CFCl_2 (141b)	2.7×10^{-13}	exp(-1050/T)	6.7	6.7	7.8
CH_3CF_2Cl (142b)	9.6×10^{-13}	exp(-1650/T)	16.6	17.8	19.1
CH_2ClCF_2Cl	3.6×10^{-12}	exp(-1600/T)	3.5	4.0	4.2
CH_2ClCF_3	5.2×10^{-13}	exp(-1100/T)	4.1	4.4	4.8
$CHCl_2CF_3$ (123)	6.4×10^{-13}	exp(-850/T)	1.40	1.42	1.59
$CHFClCF_3$ (124)	6.6×10^{-13}	exp(-1250/T)	5.5	6.0	6.6

*Lifetimes from method (1) do not include stratospheric loss; those from method (2) include small additional stratospheric loss. Method (3) is based on scaling the methylchloroform lifetime of 6.3 yrs from Prinn et al. (Science, 238, 945-950, 1988) by the ratio of the rate coefficients at 277 K.