

CHAPTER 3 – SUPPLEMENT 4

Evaluation of Atmospheric Loss Processes: Photochemistry Supplement

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The UV absorption cross-section data for the compounds included in the SPARC Lifetime report have, for the most part, been evaluated in the NASA/JPL data evaluation.¹ In this supplement, the VUV and UV absorption cross-section data for the compounds included in the SPARC Lifetime report are critically reviewed, evaluated, and compared with the NASA/JPL recommendations. For each compound, cross-section data for Lyman- α (121.567 nm) and at UV wavelengths >170 nm are presented graphically and critically evaluated. In addition, the UV cross-section temperature dependence has been evaluated where data are available.

In many cases, Lyman- α cross sections were not included in the NASA/JPL data evaluation. The UV cross-section parameterizations for the spectra of CFCl_3 (CFC-11), CF_2Cl_2 (CFC-12), $\text{CFCl}_2\text{CF}_2\text{Cl}$ (CFC-113), $\text{CF}_2\text{ClCF}_2\text{Cl}$ (CFC-114), CH_3CCl_3 , CH_3Cl , and CHF_2Cl (HCFC-22) reported in literature and quoted in JPL10-6¹ are corrected here. Recent cross-section value studies for CCl_4 , N_2O , the Halons CF_2Br_2 (Halon-1202), CF_2ClBr (Halon-1211), and $\text{CF}_2\text{BrCF}_2\text{Br}$ (Halon-2402), and NF_3 that were reported following the JPL10-6 NASA/JPL evaluation are included here. In many cases, the UV room temperature cross sections recommended in JPL10-6 are recommended here. Uncertainties in the cross sections in 5 key wavelength ranges were evaluated and the recommended uncertainties reported in Table 3.4 (reproduced here).

Reference

Sander, S., J. Abbatt, J. R. Barker, J. B. Burkholder, R. R. Friedl, D. M. Golden, R. E. Huie, C. E. Kolb, M. J. Kurylo, G. K. Moortgat, V. L. Orkin, and P. H. Wine, *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 17, JPL Publication 10-6*, Jet Propulsion Laboratory, California Institute of Technology, <http://jpldataeval.jpl.nasa.gov>, 2011.

Table 3.4. Summary of Lyman- α (121.567 nm) absorption cross sections, $\sigma(L-\alpha)$, at 298 K and estimated cross-section value uncertainties at Lyman- α and in the 169- to 190-, 190- to 230-, 230- to 286-, and >286-nm wavelength regions. *

Compound	Chemical Formula	Lyman- α (121.567 nm)		$p(298\text{ K})/w$				Footnotes
		$\sigma(L-\alpha, 298\text{ K})^{**}$	$p(298\text{ K})$	169-190 nm	190-230 nm	230-286 nm	>286 nm	
1. CFC-11	CCl ₃ F	9.8	1.2	1.10/60	1.10/120	1.30/-	-/-	1
2. CFC-12	CCl ₂ F ₂	2.07	1.15	1.10/40	1.08/40	1.30/-	-/-	1
3. CFC-113	CCl ₂ FCFClF ₂	10	2.0	1.10/120	1.06/120	1.20/-	-/-	2
4. CFC-114	CClF ₂ CClF ₂	3.6	1.3	1.14/60	1.14/60	-/-	-/-	1
5. CFC-115	CF ₃ CClF ₂	0.457	3.0	1.14/-	1.30/-	-/-	-/-	1
6. Carbon-Tetrachloride	CCl ₄	3.7	1.2	1.10/120	1.06/60	1.20/-	-/-	3
7. Nitrous oxide	N ₂ O	2.4	1.5	1.12/60	1.08/20	1.12/-	1.30/-	1
8. Halon-1202	CBr ₂ F ₂	10	1.5	1.08/120	1.08/120	1.14/120	1.20/220	4
9. Halon-1211	CBrClF ₂	7.75	1.5	1.10/500	1.10/500	1.14/220	1.40/220	4
10. Halon-1301	CBrF ₃	2.5	1.4	1.16/220	1.08/120	1.20/120	1.30/-	1
11. Halon-2402	CBrF ₂ CBrF ₂	5	2.0	1.14/120	1.10/120	1.14/60	1.30/220	4
12. Methane	CH ₄	1.85	1.3	-/-	-/-	-/-	-/-	5,6
13. Methyl Chloroform	CH ₃ CCl ₃	7	1.4	1.18/60	1.18/120	1.18/120	-/-	1
14. Methyl Chloride	CH ₃ Cl	8.8	1.15	1.06/60	1.12/120	1.24/-	-/-	1
15. Methyl Bromide	CH ₃ Br	3.2	1.3	1.06/60	1.06/60	1.10/60	-/-	1
16. HCFC-22	CHClF ₂	1.76	1.4	1.10/30	1.26/60	-/-	-/-	1
17. HCFC-141b	CH ₃ CCl ₂ F	6.6	2.0	1.12/120	1.12/120	-/-	-/-	1
18. HCFC-142b	CH ₃ CClF ₂	3.1	1.2	1.20/120	1.14/120	-/-	-/-	1
19. HFC-23	CHF ₃	0.035	2.0	-/-	-/-	-/-	-/-	5,6
20. HFC-32	CH ₂ F ₂	0.55	1.4	-/-	-/-	-/-	-/-	5
21. HFC-125	CHF ₂ CF ₃	0.035	3.0	-/-	-/-	-/-	-/-	5
22. HFC-134a	CH ₂ FCF ₃	0.5	2.0	-/-	-/-	-/-	-/-	6
23. HFC-143a	CF ₃ CH ₃	1.75	2.0	-/-	-/-	-/-	-/-	5,6
24. HFC-152a	CH ₃ CHF ₂	3.2	2.0	-/-	-/-	-/-	-/-	5
25. HFC-227ea	CF ₃ CHFCF ₃	0.035	3.0	-/-	-/-	-/-	-/-	5
26. HFC-245fa	CHF ₂ CH ₂ CF ₃	1	3.0	-/-	-/-	-/-	-/-	5
27. Nitrogen Trifluoride	NF ₃	0.48	1.5	1.5/-	1.1/-	1.5/-	-/-	5

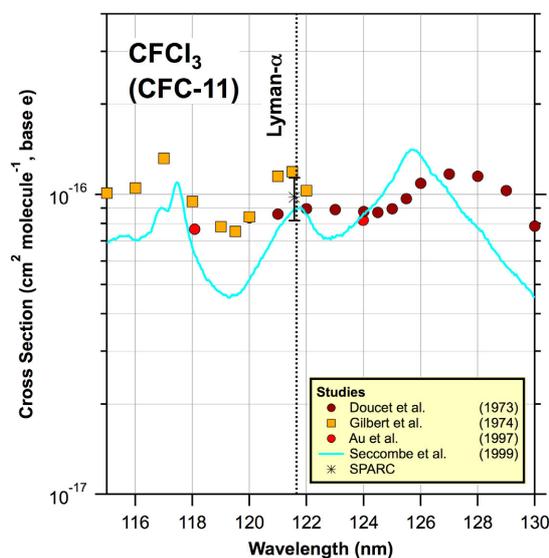
Footnotes

- * $p(298\text{ K})$ and w are 2σ (95% confidence level) values where the uncertainty at temperature T (K) is given by $p(T) = p(298\text{ K}) \exp(|w(1/T - 1/298)|)$.
 - ** Absorption cross sections are in units of $10^{-17}\text{ cm}^2\text{ molecule}^{-1}$; estimated values are given in italics
- 1 The recommended cross sections and their wavelength and temperature parameterization are taken from JPL 10-6.
 - 2 The absorption cross-section value wavelength and temperature parameterization reported in JPL10-6 contains an error; a revised set of parameters was derived here.
 - 3 The cross-section value wavelength and temperature parameterization reported in JPL10-6 has been revised to include the parameterization between 200-230 nm reported in Rontu *et al.* (2010).
 - 4 The recommended absorption cross sections at $\lambda \geq 260$ nm are based on the parameterizations given in Papanastasiou *et al.* (2013).
 - 5 Not included in JPL10-6 evaluation.
 - 6 No UV spectral data are available. Photolysis at wavelengths >169 nm expected to make a negligible contribution to the molecule's atmospheric loss.

1. CFCI₃ (CFC-11)

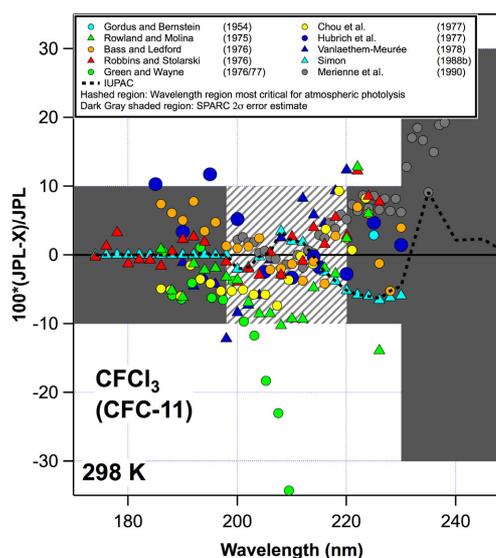
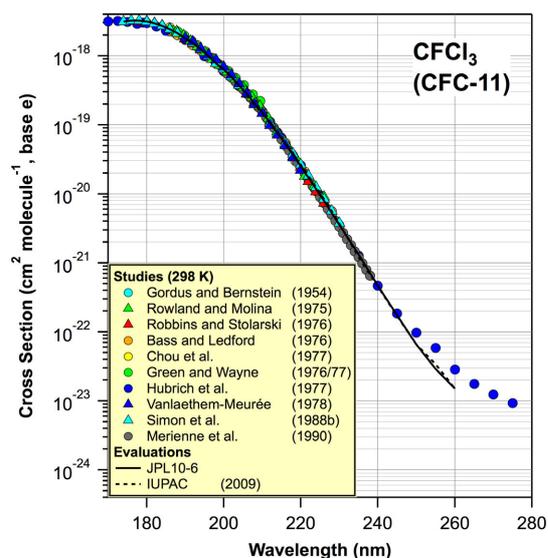
Lyman- α Cross Section

Absorption cross sections for CFCI₃ (CFC-11) have been measured in the Lyman- α wavelength region by Doucet *et al.* (1973) (120–204 nm), Gilbert *et al.* (1974) (61–122 nm), Au *et al.* (1997) (6.2–225.4 nm), and Seccombe *et al.* (1999) (50–150 nm). The reported cross sections agree to within 25%. The recommended Lyman- α cross section is an average of the results from Doucet *et al.*, Gilbert *et al.*, and Seccombe *et al.* (linearly interpolated to 121.567 nm) of $9.8 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$. The uncertainty in $\sigma(\text{Lyman-}\alpha, 298 \text{ K})$, $p(298 \text{ K})$, is estimated to be 1.20, which covers the range in available experimental data.



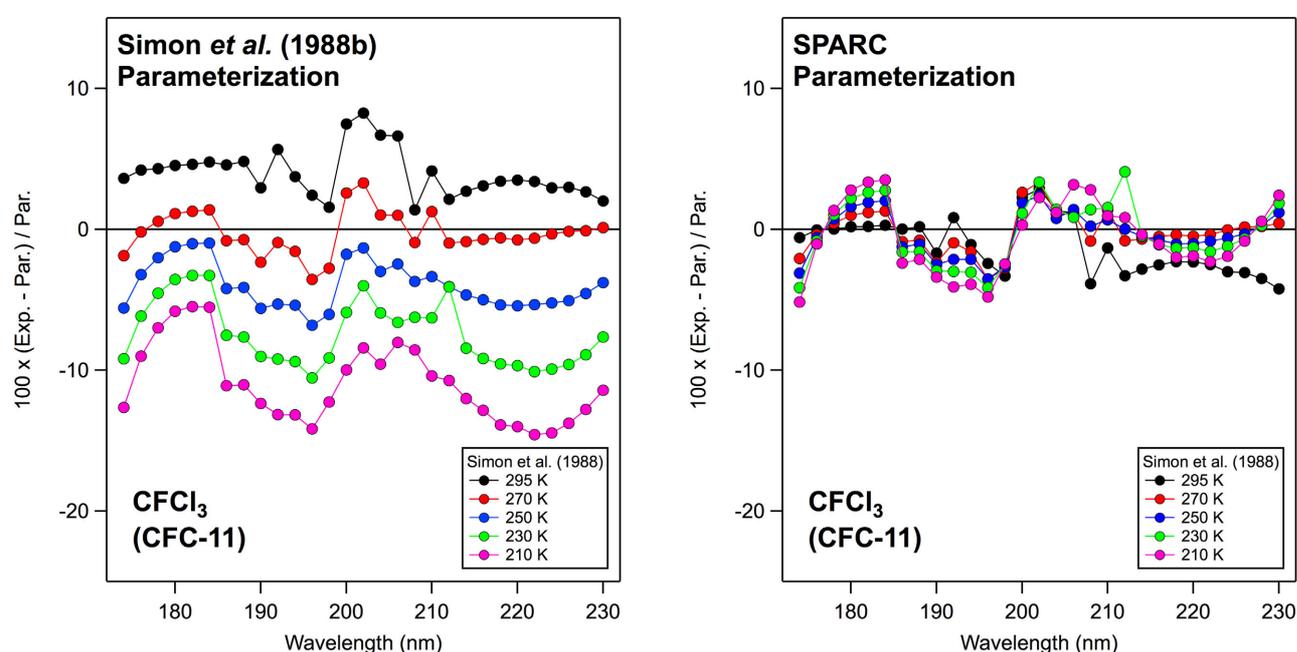
UV Absorption Spectrum

There are numerous UV absorption spectrum measurements for CFCI₃ available in the literature. The recommendation given here is the same as that of the JPL10-6 recommendation, which is based on a combination of studies as described in the note within the JPL10-6 evaluation for this molecule. The spread in the experimental data relative to the JPL10-6 recommendation is shown in the attached figure. The estimated uncertainties in the room temperature absorption cross-section data, as given in Table 3.4, encompass nearly the entire range in the available experimental data.



UV Spectrum Temperature Dependence

Several UV cross-section temperature-dependence studies are available in the literature as reviewed in JPL10-6. Mérienne *et al.* (1990) (200-238 nm; 220, 240, and 296 K) and Simon *et al.* (1988b) (174-230 nm; 225-295 K) have reported parameterizations of the wavelength and temperature dependence. JPL10-6 recommends the Simon *et al.* parameterization. However, the cross-section values derived from the Simon *et al.* parameterization do not reproduce their experimental data very well. Their parameterization systematically over-estimates the cross sections at the lower temperatures, while under-estimating those at 295 K. We have re-fit the Simon *et al.* data using the same empirical expression to derive a parameterization that fits their data at all temperatures (210 – 295 K) to better than 5% with no systematic differences observed (see figures below). This new parameterization is recommended here and is given in the table below.



Absorption cross-section parameterization for CFC-11 (CFCl_3) from the data reported by Simon *et al.* (1988b) for the wavelength range 174 to 226 nm and temperatures between 225 and 298 K

$$\text{Log}_{10}(\sigma(\lambda, T)) = \sum_i A_i \lambda^i + (T - 273) \sum_i B_i \lambda^i$$

$$A_0 = -82.55$$

$$A_1 = 0.75448$$

$$A_2 = -0.001749$$

$$A_3 = -5.493 \times 10^{-6}$$

$$A_4 = 1.7089 \times 10^{-8}$$

$$B_0 = -5.7463$$

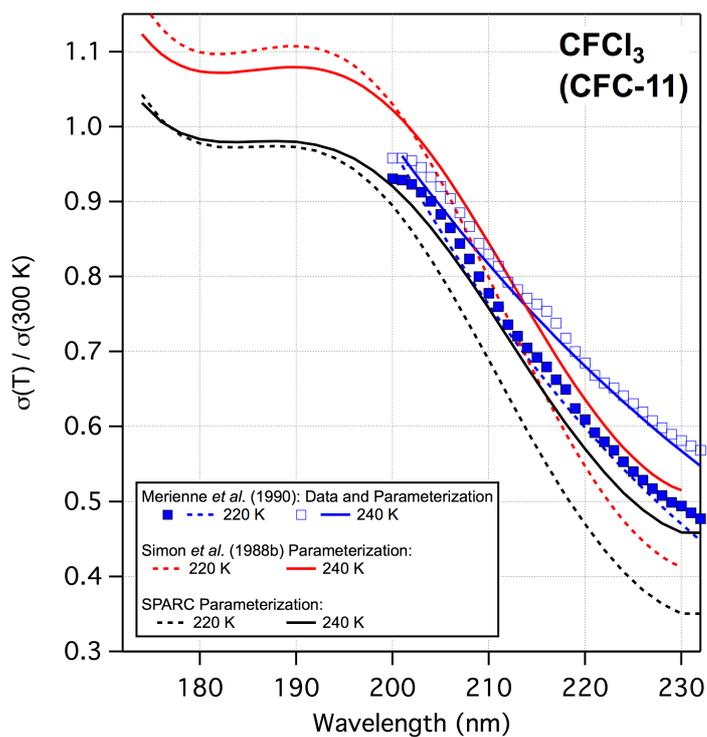
$$B_1 = 0.115997$$

$$B_2 = -0.000874014$$

$$B_3 = 2.91147 \times 10^{-6}$$

$$B_4 = -3.6148 \times 10^{-9}$$

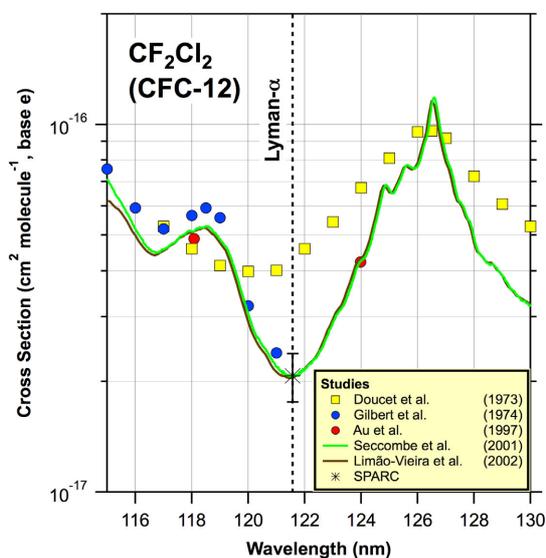
It should also be noted that the cross-section data and parameterization reported by Mérienne *et al.* for wavelengths >200 nm leads to a different temperature dependence than obtained using the Simon *et al.* parameterization or the revised parameterization given here (SPARC) as shown in the figure below. The difference with the SPARC parameterization at 200 nm is $\sim 5\%$ at 220 and 240 K, while increasing at longer wavelengths to $\sim 15\%$ at 230 nm. The uncertainty factors given in Table 3.4 were taken to cover the range of these differences.



2. CF₂Cl₂ (CFC-12)

Lyman- α Cross Section

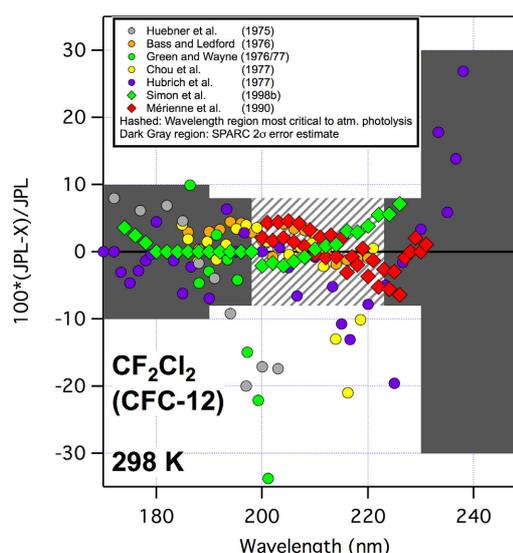
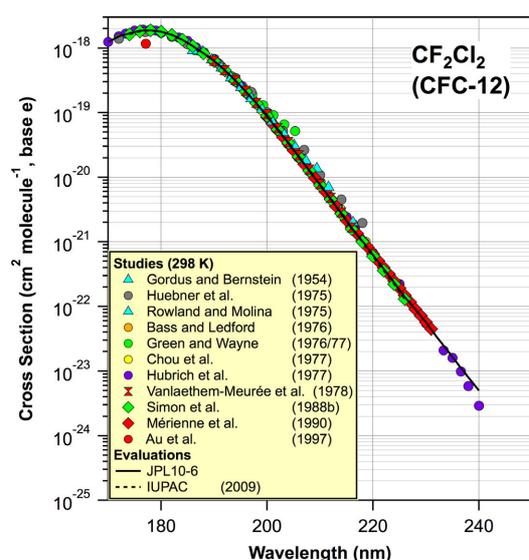
Absorption cross sections for CF₂Cl₂ (CFC-12) have been measured in the Lyman- α wavelength region at 298 K by Doucet *et al.* (1973) (117-200 nm), Gilbert *et al.* (1974) (63-121 nm), Au *et al.* (1997) (6.2-207 nm), Limão-Vieira *et al.* (2002) (113-225 nm), and Seccombe *et al.* (2001) (50-150 nm). The agreement among these studies is good, to better than 5%, except for the Doucet *et al.* study whose data between 120 and 124 nm are systematically greater and the difference at 121.567 nm is nearly a factor of 2. An average of the high-resolution data of Seccombe *et al.* and Limão-Vieira *et al.*, $2.07 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$, at Lyman- α is recommended. The uncertainty factor, $p(298 \text{ K})$, in $\sigma(\text{Lyman-}\alpha, 298 \text{ K})$ is estimated to be 1.15.



UV Absorption Spectrum

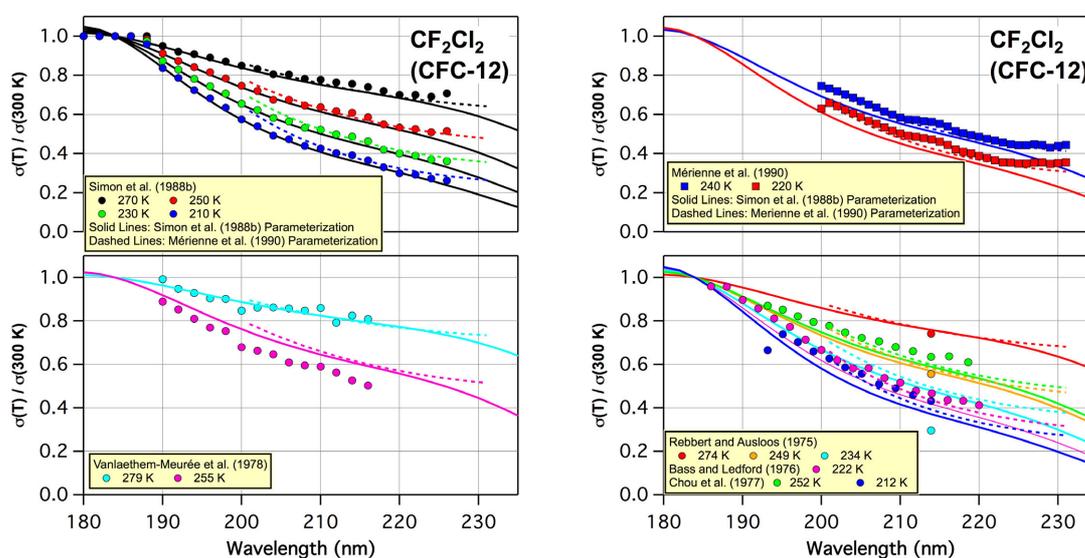
There are numerous UV absorption cross-section value studies for CF₂Cl₂. The recommendation given here is the same as that of the JPL10-6 recommendation, which is based on a combination of studies as described in the note within the JPL10-6 evaluation for this molecule. The spread in the experimental data relative to the JPL10-6 recommendation is shown in the attached figure. The estimated uncertainty factor, $p(298 \text{ K})$, in the room-temperature absorption cross-section data given in Table 3.

4 encompasses the range in the available experimental data.



UV Spectrum Temperature Dependence

Several UV cross-section temperature-dependence studies are available for CF₂Cl₂ as reviewed in JPL10-6. The absorption cross-section temperature-dependence parameterization recommended in JPL10-6 for the wavelength range 200 to 231 nm was taken from Mérienne *et al.* (1990). JPL10-6 did not report the cross-section parameterization from the study of Simon *et al.* (1988b) (174-230 nm; 225-295 K) that covers shorter wavelengths due to an error in the parameterization coefficients reported by these investigators. The Simon *et al.* data has been re-fit here and the parameterization is given in the table below and is recommended. The agreement of this parameterization with the results from other studies of the cross-section temperature dependence, as shown in the figures below, is good, to within ~5%. The uncertainty factor, w , given in Table 3.4 encompasses the range of the cross sections reported in the various studies. At 298 K, the revised parameterization of the Simon *et al.* data is in good agreement with the JPL10-6 recommended values, to better than 5% for wavelengths ≤ 230 nm.



Absorption cross-section parameterization for CFC-12 (CF₂Cl₂) from the data reported by Simon *et al.* (1988b) for the wavelength range 174 to 226 nm and temperatures between 225 and 298 K

$$\text{Log}_{10}(\sigma(\lambda, T)) = \sum_i A_i \lambda^i + (T - 273) \sum_i B_i \lambda^i$$

$$A_0 = -654.48602$$

$$A_1 = 11.3316594$$

$$A_2 = -0.07413773$$

$$A_3 = 0.00021176449$$

$$A_4 = -2.2472927 \times 10^{-7}$$

$$B_0 = 7.2196167$$

$$B_1 = -0.142178066$$

$$B_2 = 0.00104589285$$

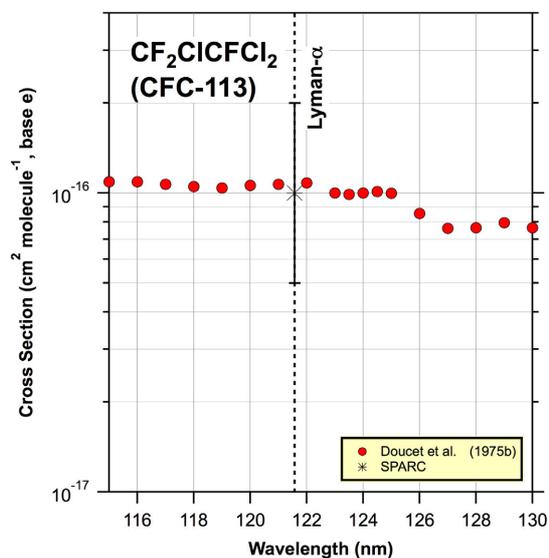
$$B_3 = -3.4086704 \times 10^{-6}$$

$$B_4 = 4.1577462 \times 10^{-9}$$

3. CF₂CICFCl₂ (CFC-113)

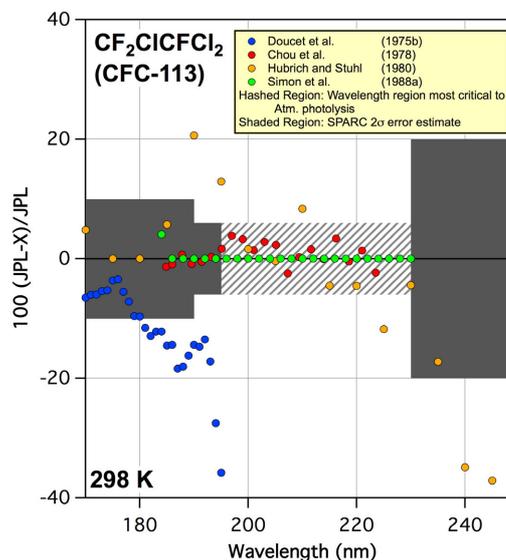
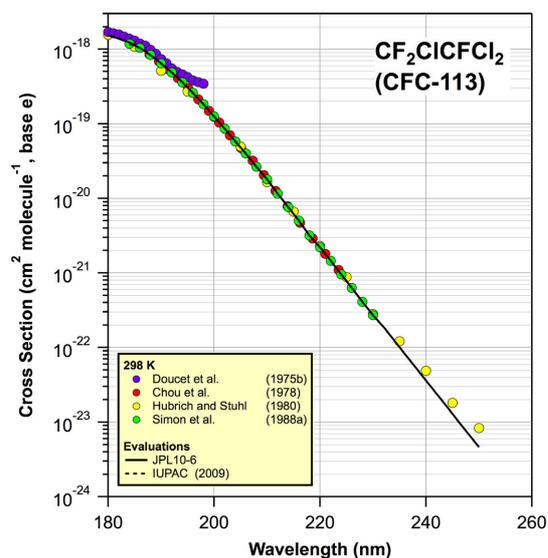
Lyman- α Cross Section

The VUV absorption spectrum of CF₂CICFCl₂ (CFC-113) was measured by Doucet *et al.* (1975b) between 110 and 198 nm. The spectrum has little structure and a σ (Lyman- α , 298 K) value of 10×10^{-17} cm² molecule⁻¹ is recommended. An uncertainty factor, p (298 K), in σ (Lyman- α , 298 K) of 2.0 is recommended, which is based primarily on the fact that there is only a single experimental determination.



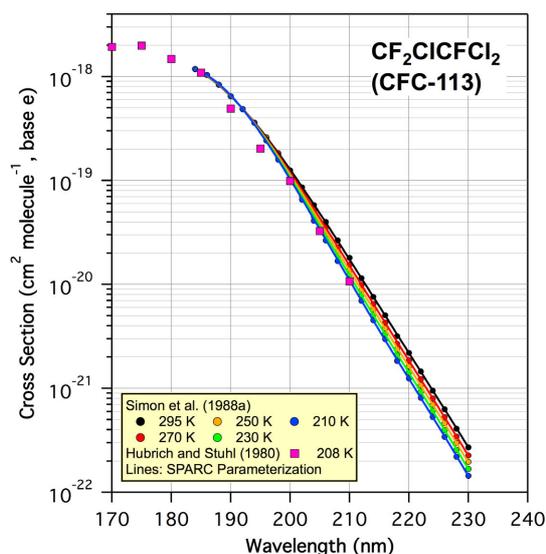
UV Absorption Spectrum

There are several studies of the CF₂CICFCl₂ UV absorption spectrum. The spread in the experimental data relative to the JPL10-6 recommendation is shown below. The data from Hubrich and Stuhl (1980) show larger scatter, while the data from Doucet *et al.* (1975b) show systematic deviations from the JPL10-6 recommendation.



UV Spectrum Temperature Dependence

The absorption cross-section temperature-dependence parameterization for $\text{CF}_2\text{ClCFCl}_2$ recommended in JPL10-6, as taken from Simon *et al.* (1988a), contains an error in the reported fit parameters. The Simon *et al.* (1988a) cross-section data were re-fit here using the formulation used in their original paper where the results are valid over the temperature range 210-300 K and wavelength range 182-230 nm. The obtained parameters are given below. The uncertainty factors given in Table 3.4 cover the range of the majority of the available data, particularly in the most critical wavelength region.



Absorption cross-section parameterization for CFC-113 ($\text{CF}_2\text{ClCFCl}_2$) from the data reported by Simon *et al.* (1988a)

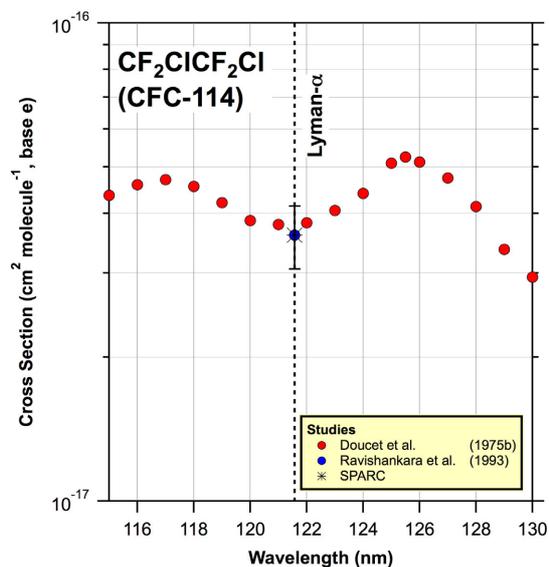
$$\log_{10} \sigma(\lambda, T) = \sum A_n \lambda^n + (T - 273) \times \sum B_n \lambda^n$$

$A_0 = -1112.111832$	$B_0 = 11.62056201$
$A_1 = 20.47564047$	$B_1 = -0.2223995208$
$A_2 = -0.1426332745$	$B_2 = 0.001590706707$
$A_3 = 0.0004393747238$	$B_3 = -5.040602321 \times 10^{-6}$
$A_4 = -5.072508872 \times 10^{-7}$	$B_4 = 5.973112715 \times 10^{-9}$

4. CF₂ClCF₂Cl (CFC-114)

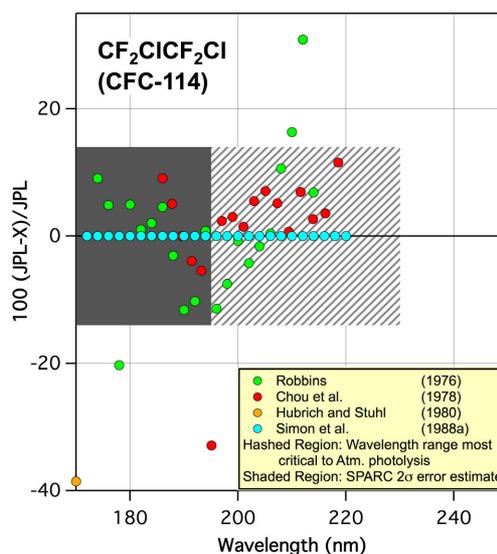
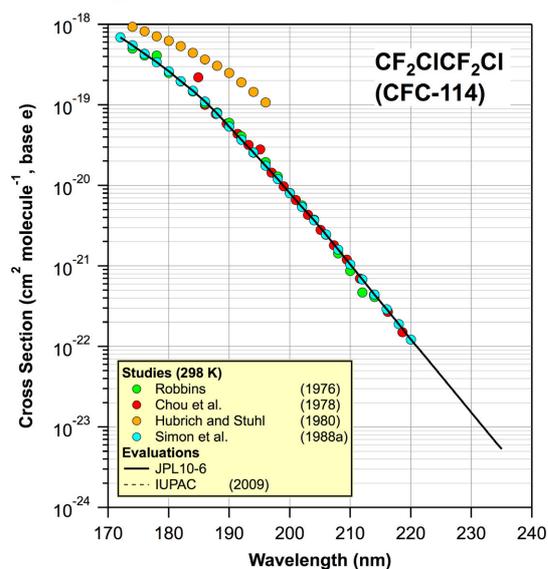
Lyman- α Cross Section

The VUV absorption spectrum of CF₂ClCF₂Cl (CFC-114) has been measured by Doucet *et al.* (1975b) (110-190 nm) and Ravishankara *et al.* (1993) (121.567 nm). The results from these studies at 121.567 nm are in good agreement, to within ~6%. The recommended σ (Lyman- α , 298 K) value is taken from Ravishankara *et al.*, 3.6×10^{-17} cm² molecule⁻¹, who measured the cross section directly at Lyman- α . An uncertainty factor, p (298 K), of 1.15 is recommended.



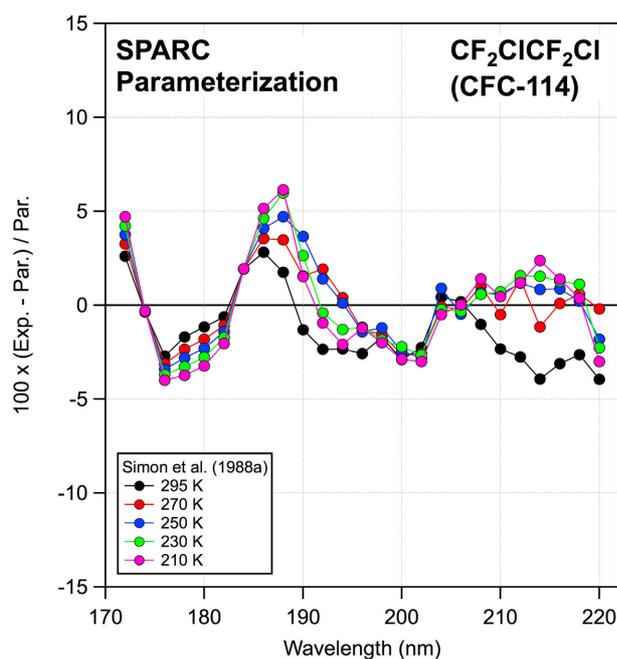
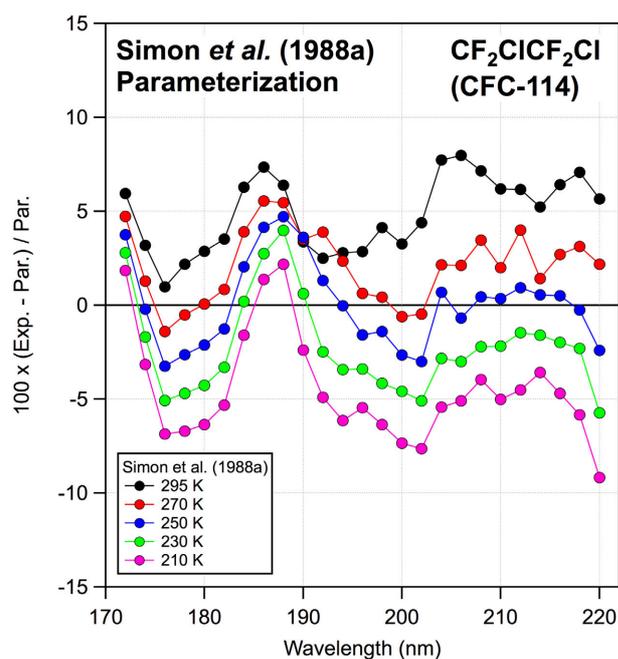
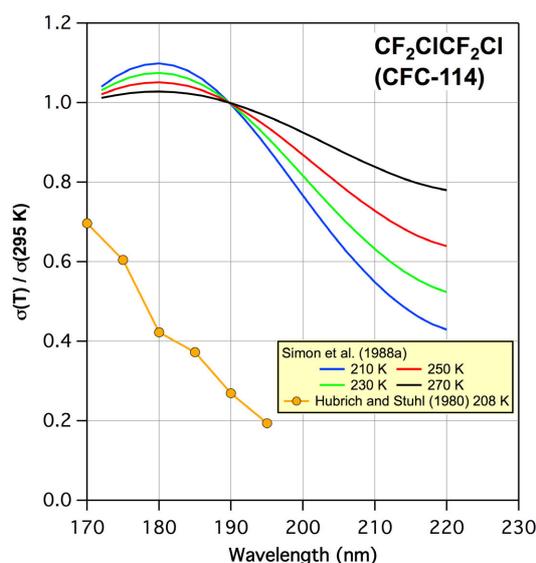
UV Absorption Spectrum

The UV absorption spectrum of CF₂ClCF₂Cl (CFC-114) has been measured in several studies. The recommendation given here is the same as that of the JPL10-6 recommendation, which is based on a combination of studies as described in the note within the JPL10-6 evaluation for this molecule. The spread in the experimental data relative to the JPL10-6 recommendation is shown in the attached figure. Uncertainty factors, p (298 K), were assigned to encompass the majority of the available data, although some of the long wavelength data of Robbins (1977) falls outside of this range.



UV Spectrum Temperature Dependence

The temperature dependence of the $\text{CF}_2\text{ClCF}_2\text{Cl}$ UV absorption spectrum was reported in Hubrich and Stuhl (1980) (160-235 nm; 208 and 296 K) and Simon *et al.* (1988a) (172-220 nm; 210-295 K), as shown in the attached figure. JPL10-6 recommended the parameterization from Simon *et al.*, although the reported fit parameters do not reproduce their experimental data very well. The Simon *et al.* data was re-fit using the same empirical formula and the parameters, which yield an improved representation of the Simon *et al.* data (see figures below) are given in the table below. This parameterization is recommended here. The uncertainty factors in Table 3.4 are based on the reported accuracy of the Simon *et al.* measurements, but also account for the fact that the only other available study is in poor agreement.



Absorption cross-section parameterization for CFC-114 ($\text{CF}_2\text{ClCF}_2\text{Cl}$) from the data reported by Simon *et al.* (1988a)

$$\log_{10} \sigma(\lambda, T) = \sum_i A_i \lambda^i + (T - 273) \sum_i B_i \lambda^i$$

$$A_0 = -184.86$$

$$A_1 = 2.98117$$

$$A_2 = -0.0190482$$

$$A_3 = 5.152 \times 10^{-5}$$

$$A_4 = -5.1086 \times 10^{-8}$$

$$B_0 = -1.9446$$

$$B_1 = 0.0437746$$

$$B_2 = -0.000365055$$

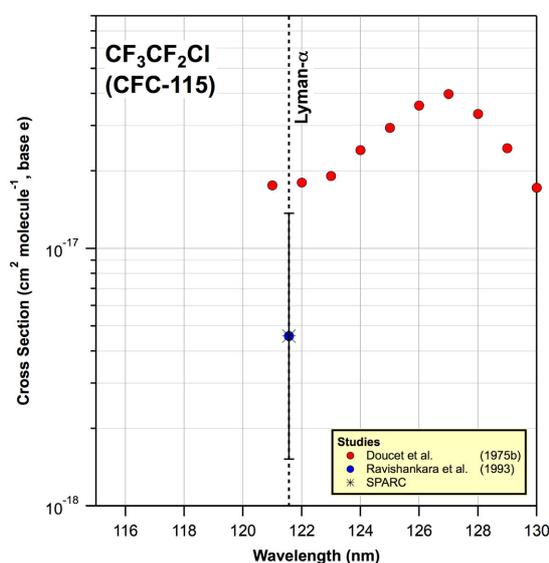
$$B_3 = 1.33636 \times 10^{-6}$$

$$B_4 = -1.81075 \times 10^{-9}$$

5. CF₃CF₂Cl (CFC-115)

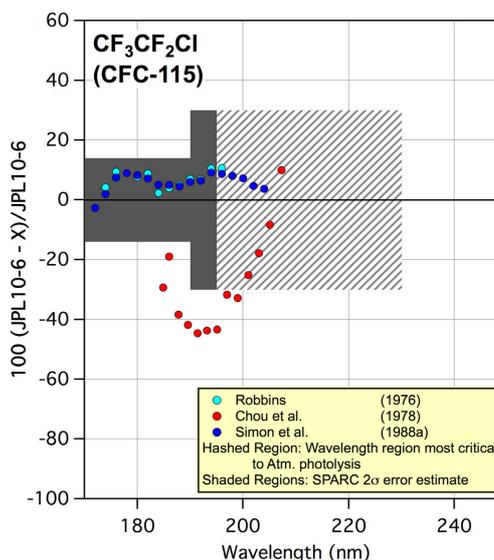
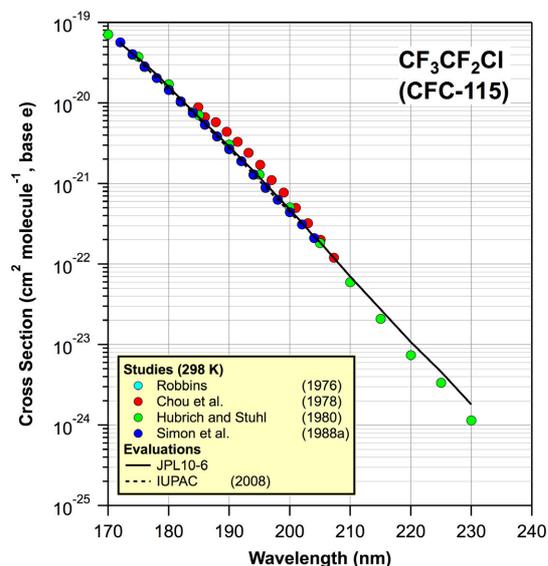
Lyman- α Cross Section

The VUV absorption spectrum of CF₃CF₂Cl (CFC-115) was measured by Doucet *et al.* (1975b) between 120 and 175 nm and at 121.567 nm by Ravishankara *et al.* (1993). The results from these two studies differ by nearly a factor of 4 and the source of the discrepancy is unknown. It is worth noting, however, that the cross-section results from these two groups for CF₂ClCF₂Cl (CFC-114) are in very good agreement. The σ (Lyman- α , 298 K) value of 4.57×10^{-18} cm² molecule⁻¹ from Ravishankara *et al.* is recommended. Due to the large discrepancy in the available data a correspondingly large uncertainty factor, p (298 K), of 3 is assigned, which encompasses the available data.



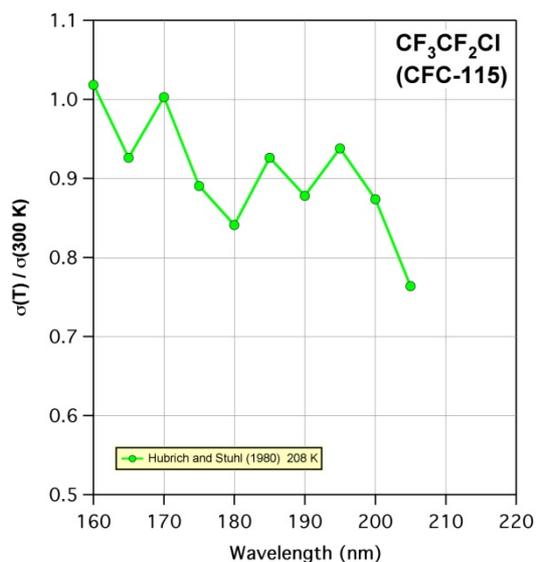
UV Absorption Spectrum

There are several studies of the CF₃CF₂Cl UV absorption spectrum as reviewed in JPL10-6. The spread in the experimental data relative to the JPL10-6 recommendation is shown in the attached figure. The uncertainty factors given in Table 3.4 were taken to cover the range of the experimental data, although some of the data from Chou *et al.* (1978) fall outside the recommended values.



UV Spectrum Temperature Dependence

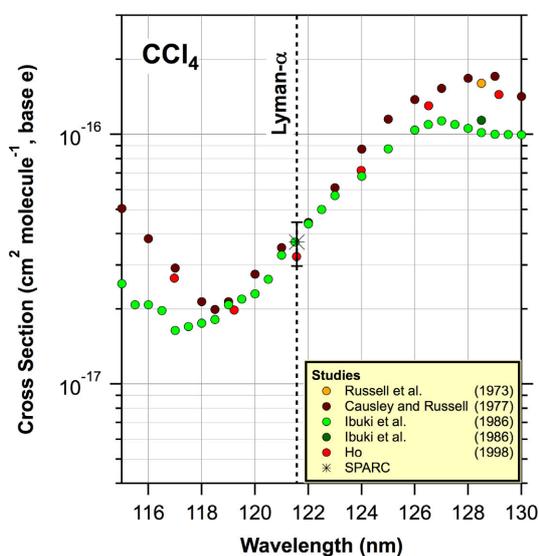
The temperature dependence of the $\text{CF}_3\text{CH}_2\text{Cl}$ UV absorption spectrum was reported in Hubrich and Stuhl (1980) (160-230 nm; 208 and 298 K) and Simon *et al.* (1988a) (172-204 nm; 210-300 K). Simon *et al.* report very weak cross-section temperature dependence, (<5% difference between 210 K and 300 K at 200 nm). The parameterization by Simon *et al.* and reproduced in JPL10-6 is recommended here as well. The uncertainty factors given in Table 3.4 primarily reflect the overall uncertainty in the absolute cross-section value with only a minor contribution due to the uncertainty in its temperature dependence.



6. CCl₄ (Carbon Tetrachloride)

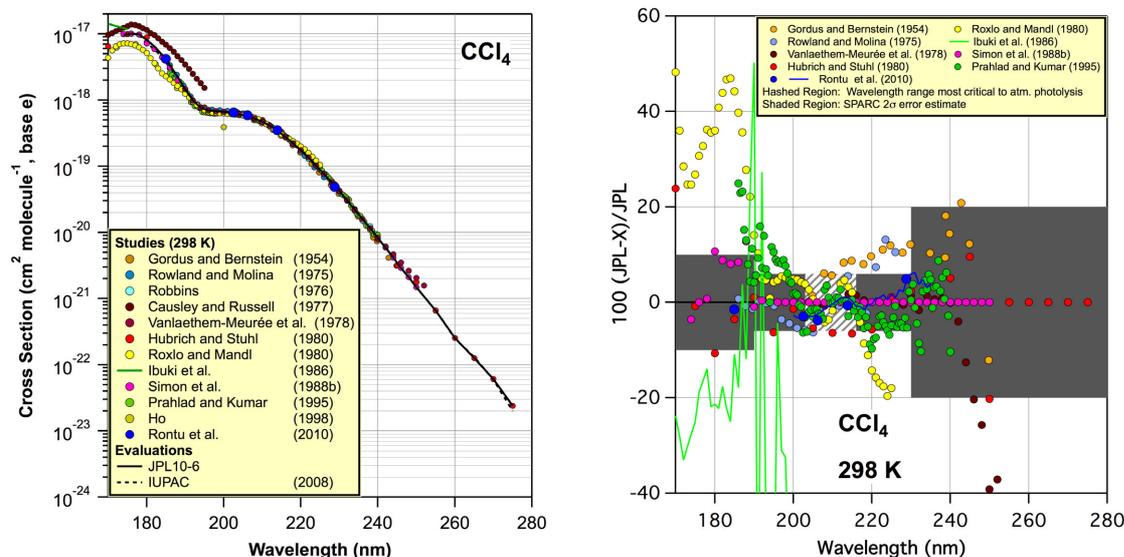
Lyman- α Cross Section

The VUV absorption spectrum of CCl₄ has been measured by Russell *et al.* (1973) (112–175 nm), Causley and Russell (1977) (111–195 nm), Ibuki *et al.* (1986) (105–210 nm), and Ho (1998) (4.9–200 nm). The agreement in $\sigma(\text{Lyman-}\alpha, 298 \text{ K})$ is reasonably good, to within $\sim 15\%$. The recommended $\sigma(\text{Lyman-}\alpha, 298 \text{ K})$ is the average of the interpolated results from Causley and Russell, Ibuki *et al.*, and Ho, $3.7 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$, with an uncertainty factor, $p(298 \text{ K})$, of 1.2.



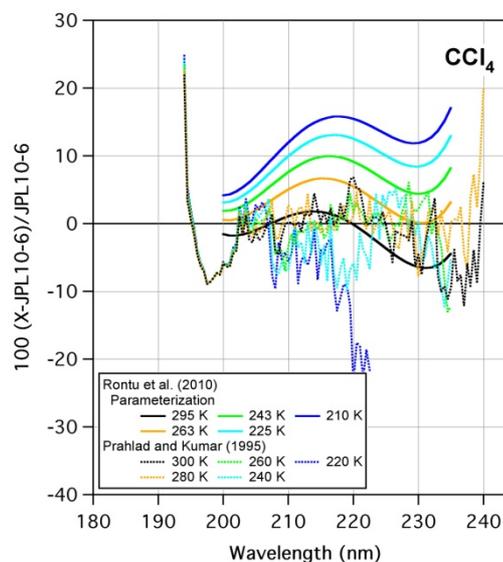
UV Absorption Spectrum

The UV absorption spectrum of CCl₄ has been reported in numerous studies. The recent study of Rontu *et al.* (2010) measured CCl₄ absorption cross sections at 183.95, 202.206, 206.200, 213.857, and 228.8 nm, using atomic line sources, and the spectrum between 200 and 235 nm using diode array spectroscopy. The results from Rontu *et al.* are in agreement with previously reported values, but are of higher precision and accuracy. The spread in the room-temperature experimental data relative to that of the JPL10-6 recommendation is shown in the attached figure. The revised cross-section parameterization reported by Rontu *et al.* and given below is recommended here. The uncertainty factor, $p(298 \text{ K})$, given in Table 3.4 is reduced from the uncertainty given in JPL10-6 primarily due to the consideration of the results from the study of Rontu *et al.*



UV Spectrum Temperature Dependence

JPL10-6 recommends the CCl₄ UV spectrum parameterization reported by Simon *et al.* (1988b) (174-250 nm; 225-295 K), which reproduces their experimental values to within $\pm 5\%$. The agreement of this parameterization with the more recent studies of Prahlad and Kumar (1995) (186-240 nm; 220-300 K) and Rontu *et al.* (2010) (200-235 nm; 210-350 K) is shown in the attached figure. The CCl₄ absorption cross-section parameterization reported in Rontu *et al.*, given below, is recommended here. The uncertainty factors, $p(298\text{ K})$ and w , reported in Table 3.4 encompass the range in the cross-section values reported in Simon *et al.* (1988b), Prahlad and Kumar (1995), and Rontu *et al.* (2010).



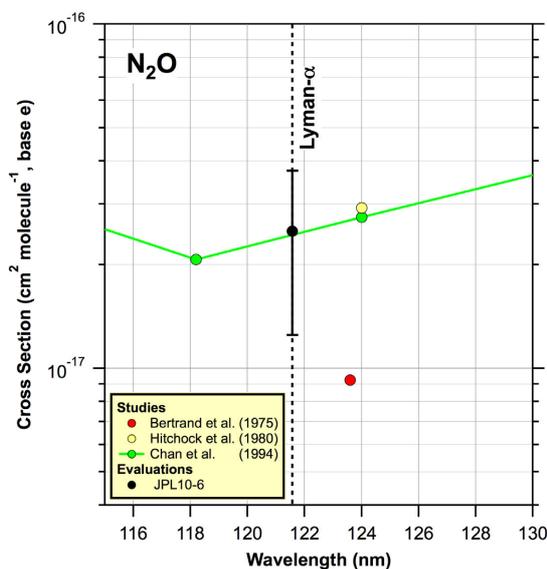
Absorption cross-section parameterization for CCl₄ as taken from Rontu *et al.* (2010).

$$\log_{10} \sigma(\lambda, T) = \sum_i A_i \lambda^i + (T - 273) \sum_i B_i \lambda^i$$

i	A_i	B_i
0	1112.736208	-1.116511649
1	-22.02146808	0.02447268904
2	0.1596666745	-0.0001954842393
3	-0.0005104078676	$6.775547148 \times 10^{-7}$
4	$6.062440506 \times 10^{-7}$	$-8.621070147 \times 10^{-10}$

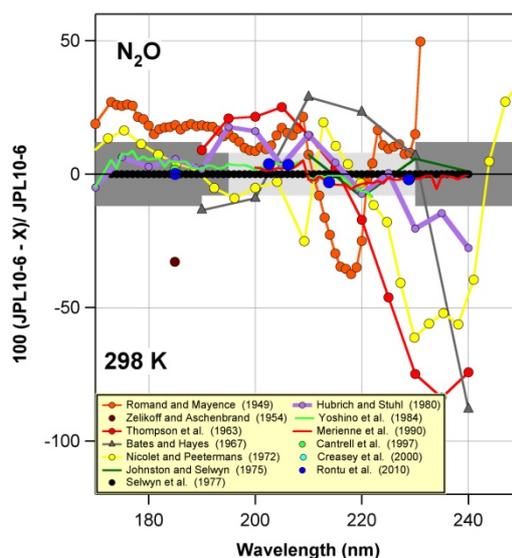
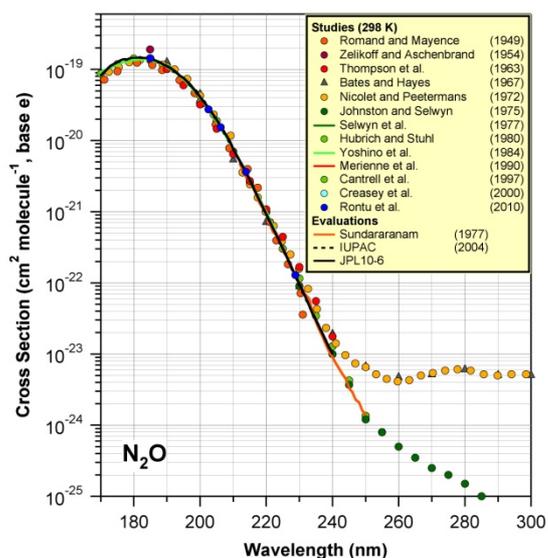
7. N₂OLyman- α Cross Section

The VUV absorption spectrum of N₂O has been measured by Bertrand *et al.* (1975) (123.6 nm), Hitchcock *et al.* (1980) (16.8-155 nm), and Chan *et al.* (1994) (6.1-168 nm). The cross-section results from Chan *et al.* and Hitchcock *et al.* are in good agreement at 124 nm, to within 6%, while the value reported by Bertrand *et al.* at 123.6 nm is less by nearly a factor of 3. The reason for the difference is unknown. A linear interpolation of the Chan *et al.* cross-section data at 118 and 124 nm yields a Lyman- α cross section of 2.4×10^{-17} cm² molecule⁻¹; this assumes no significant structure in this region of the spectrum. An uncertainty factor, $p(298 \text{ K})$, of 1.5 is recommended due primarily to the lack of direct measurements at 121.567 nm.



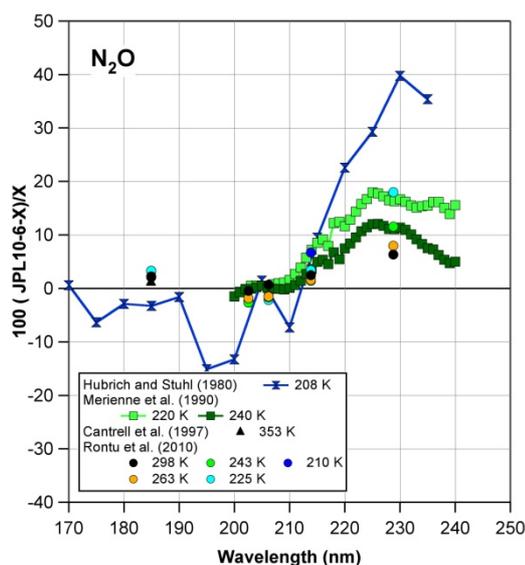
UV Absorption Spectrum

Numerous studies have reported on the UV absorption spectrum of N₂O as reviewed in JPL10-6. JPL10-6 recommends the cross-section results of Selwyn *et al.* (1977) over the most critical wavelength region. The spread in the experimental data relative to the JPL10-6 recommendation is shown in the attached figure. The cross-section results from the recent study by Rontu *et al.* (2010) (183.95, 202.206, 206.200, 213.857, and 228.8 nm) are in very good agreement with the JPL10-6 recommendation. The uncertainty factors, $p(298 \text{ K})$, are reduced from those given in JPL10-6 based primarily on the results from the Rontu *et al.* study.



UV Spectrum Temperature Dependence

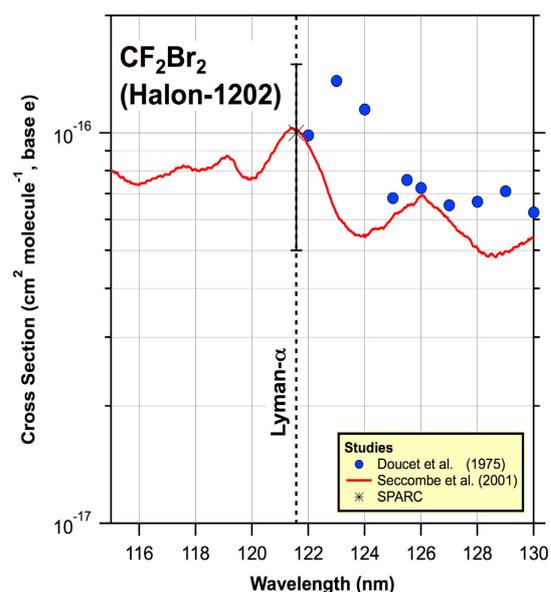
The N₂O absorption-spectrum temperature dependence has been reported in several studies, and the data are in good agreement, to within 5%, in the wavelength region most critical to atmospheric photolysis. JPL10-6 recommends the temperature-dependence parameterization reported by Selwyn *et al.* (1977), which reproduces their data to better than 5% at wavelengths <230 nm. Their parameterization is recommended here as well. The recent study by Rontu *et al.* (2010) (210–350 K) is in excellent agreement, to within 3%, with the JPL10-6 recommendation at 183.95, 202.206, 206.200, and 213.857 nm. There is a systematic difference in the cross-section temperature dependence at 228.8 nm between the Mérienne *et al.* (1990) and Rontu *et al.* data and that of JPL10-6, where the difference is ~18% at 210 K. The uncertainty factor, w , given in Table 3.4 was based primarily on the data of Selwyn *et al.* (1977), Mérienne *et al.* (1990), and Rontu *et al.* (2010).



8. CF₂Br₂ (Halon-1202)

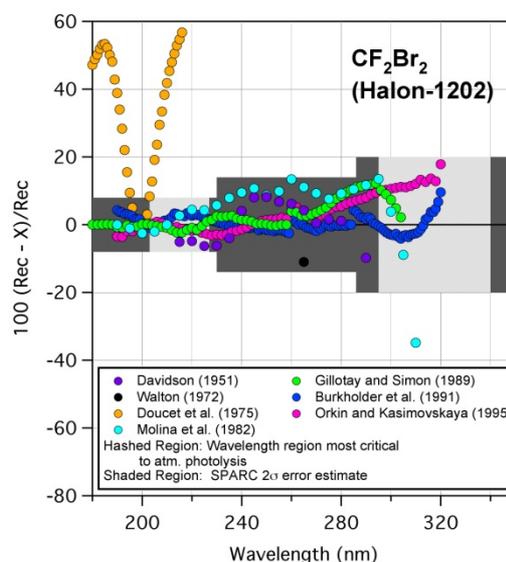
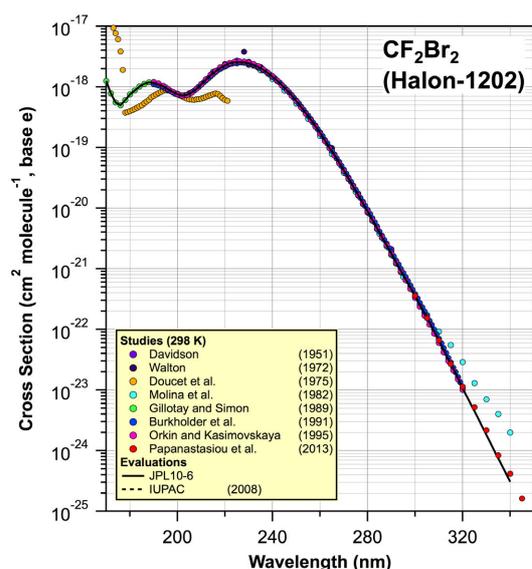
Lyman- α Cross Section

The VUV absorption spectrum of CF₂Br₂ (Halon-1202) has been measured by Doucet *et al.* (1975a) (60-220 nm) and Seccombe *et al.* (2001) (55-175 nm). The reported spectra show some systematic discrepancies in the wavelength dependence, although the two studies are in reasonable agreement at 121.567 nm. The high-resolution σ (Lyman- α , 298 K) measurement of Seccombe *et al.*, 10×10^{-17} cm² molecule⁻¹, is recommended with an uncertainty factor, p (298 K), of 1.5.



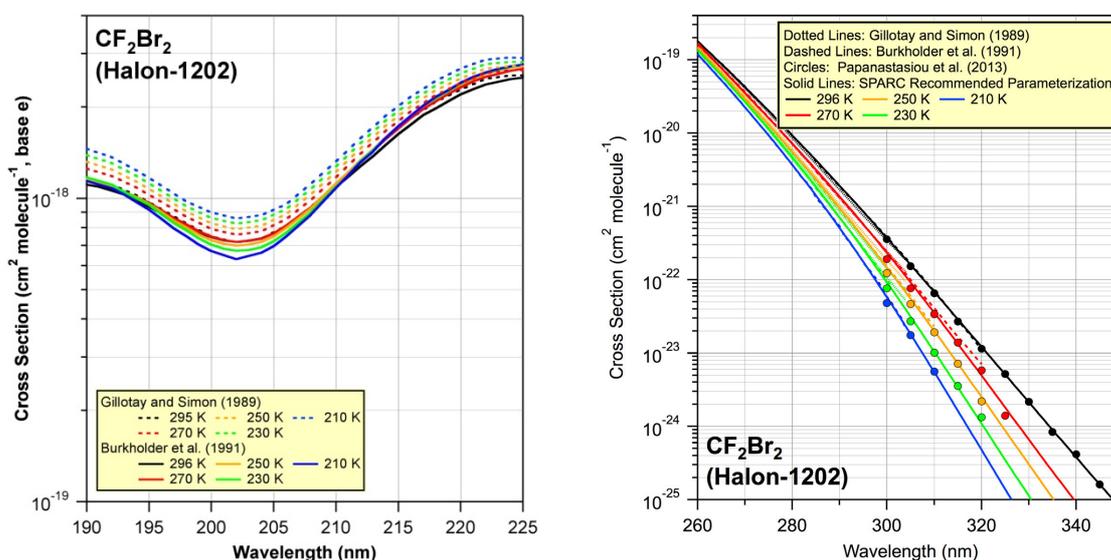
UV Absorption Spectrum

Several groups have reported the CF₂Br₂ UV absorption spectrum as summarized in JPL10-6. More recently Papanastasiou *et al.* (2013) (300-325 nm; 210-296 K) have reported absorption cross-section data in the long-wavelength region that were corrected for Rayleigh scattering. The recommended absorption cross sections given here are the JPL10-6 recommendation for wavelengths <260 nm and the parameterization from Papanastasiou *et al.* for wavelengths \geq 260 nm (see below). The spread in the experimental data relative to the recommendation is shown in the attached figure. The recommended uncertainty factors, p (298 K), given in Table 3.4 encompass the range of the majority of the available experimental data.



UV Spectrum Temperature Dependence

The CF₂Br₂ UV absorption-spectrum temperature dependence has been reported in Gillotay and Simon (170-304 nm; 210-295 K), Burkholder *et al.* (190-320 nm; 210-296 K), and more recently in Papanastasiou *et al.* (2013) (300-350 nm; 210-296 K). JPL10-6 provides the cross-section parameterizations reported in Gillotay and Simon and Burkholder *et al.*, but does not make a recommendation. In the short-wavelength region the agreement in the cross-section values is within ~20% at 210 K, while the data from the Gillotay and Simon and Burkholder *et al.* studies show different trends with temperature. For the short-wavelength region, the Burkholder *et al.* parameterization is recommended here. The Papanastasiou *et al.* study has extended the wavelength range in previous studies to cover the wavelength region critical to atmospheric photolysis, while also resolving the discrepancies in the previous data sets. Their work also extended the temperature range and provided a parameterization of the cross-section value wavelength and temperature dependence at wavelengths ≥260 nm, which is given below and recommended here. The uncertainty factors given in Table 3.4 encompass the range in the reported cross-section values.



Absorption cross-section parameterization for CF₂Br₂ (Halon-1202) for wavelengths ≥260 nm and temperatures between 210 and 298 K as taken from Papanastasiou *et al.* (2013)

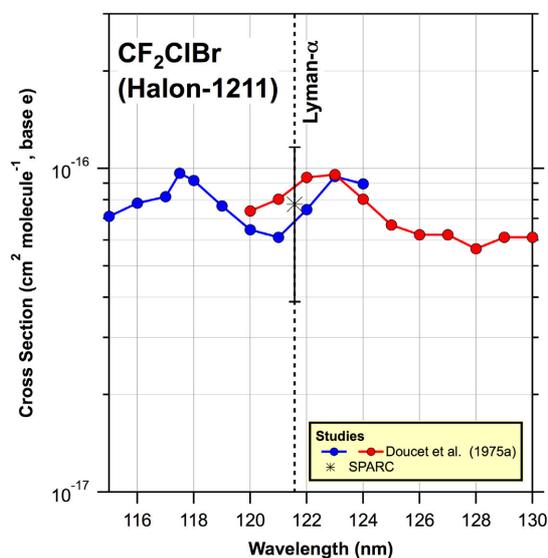
$$\ln(\sigma(\lambda, T)) = \sum_i A_i (\lambda - \bar{\lambda})^i \times \left[1 + (296 - T) \sum_i B_i (\lambda - \bar{\lambda})^i \right]$$

$\bar{\lambda} = 287.861$		
i	A_i	B_i
0	-47.4178	0.0003173
1	-0.1567273	1.2323×10^{-5}
2	-2.624376×10^{-4}	2.68×10^{-8}
3	-6.78412×10^{-6}	-5.28×10^{-9}
4	1.261478×10^{-7}	6.99×10^{-11}

9. CF₂ClBr (Halon-1211)

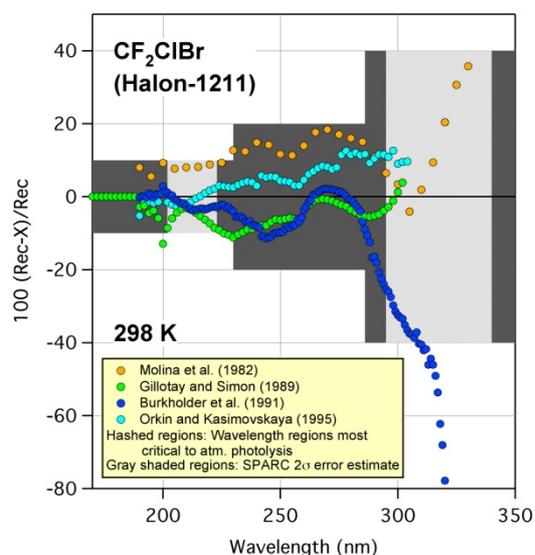
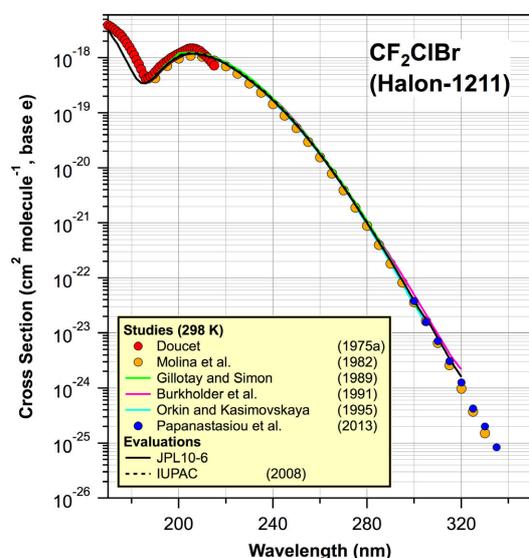
Lyman- α Cross Section

The VUV absorption spectrum of CF₂ClBr (Halon-1211) has been measured by Doucet *et al.* (1975a) (60-220 nm). A σ (Lyman- α , 298 K) value of 7.75×10^{-17} cm² molecule⁻¹ is obtained from the two reported spectrum measurements by these authors. An uncertainty factor, p (298 K), of 1.5 is assigned primarily due to the fact that there is only a single study available.



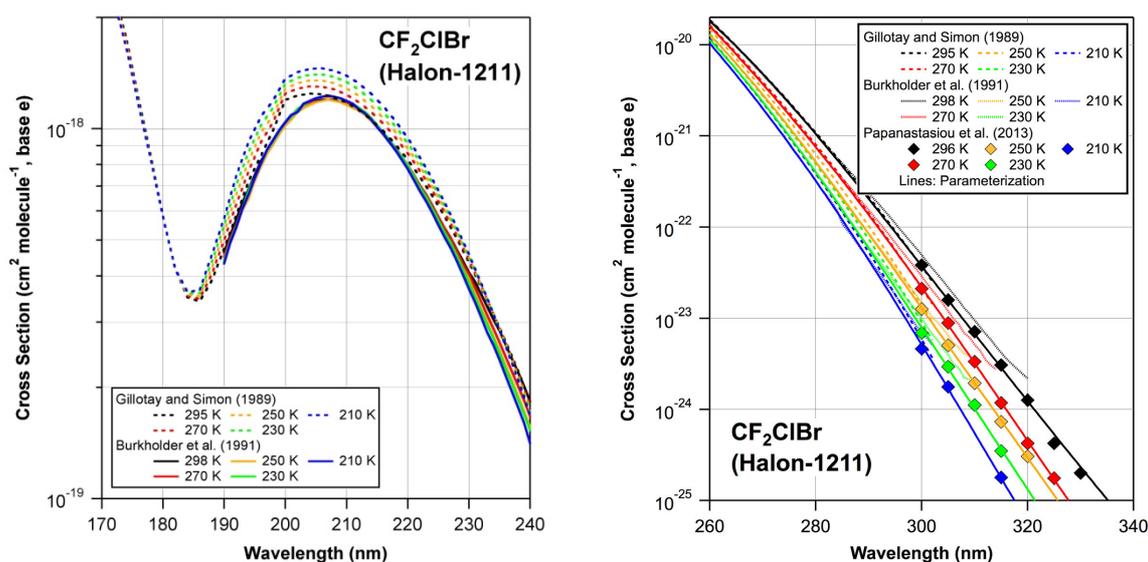
UV Absorption Spectrum

The UV absorption spectrum of CF₂ClBr (Halon-1211) has been reported in several studies as reviewed by JPL10-6. More recently Papanastasiou *et al.* (2013) reported CF₂ClBr absorption cross sections between 300 and 350 nm that included corrections for Rayleigh scattering. The cross sections recommended here are a combination of the JPL10-6 recommendation for wavelengths <260 nm and the parameterization reported in Papanastasiou *et al.*, given below, for wavelengths \geq 260 nm. The spread in the experimental data relative to this recommendation is shown in the attached figure. The uncertainty factors, p (298 K), cover the range in the available experimental data, except in the long wavelength region where the uncertainties are reduced based primarily on the results of Papanastasiou *et al.*



UV Spectrum Temperature Dependence

The temperature dependence of the CF₂ClBr UV absorption spectrum was reported in Gillotay and Simon (1989) (169-302 nm; 210-295 K), Burkholder *et al.* (1991) (190-320 nm; 210-296 K), and Papanastasiou *et al.* (2013) (300-335 nm; 210-296 K). JPL10-6 reports the parameterizations given by Gillotay and Simon and Burkholder *et al.*, but does not make a recommendation. A summary of the available data is given in the attached figures. The recommendation given here for the cross-section temperature dependence in the short-wavelength region is taken from Burkholder *et al.* (1991) (190-320 nm; 210-296 K). In the long-wavelength region, $\lambda \geq 260$ nm, the cross-section parameterization recommendation is taken from Papanastasiou *et al.*, which was derived from their data and that of Gillotay and Simon (1989) (169-302 nm; 210-295 K) and Burkholder *et al.* (1991) (190-320 nm; 210-296 K). The uncertainty factors given in Table 3.4 are significantly reduced from those reported in JPL10-6 due primarily to the consideration of the Papanastasiou *et al.* study. The uncertainty factors for the short-wavelength region cover the range of the available experimental data. For the long-wavelength region the uncertainty factors are greater due primarily to the limited amount of accurate experimental data available, but are substantially reduced from the uncertainty factor reported in JPL10-6.



Absorption cross-section parameterization for CF₂ClBr (Halon-1211) for wavelengths ≥ 260 nm and temperatures between 210 and 298 K as taken from Papanastasiou *et al.* (2013)

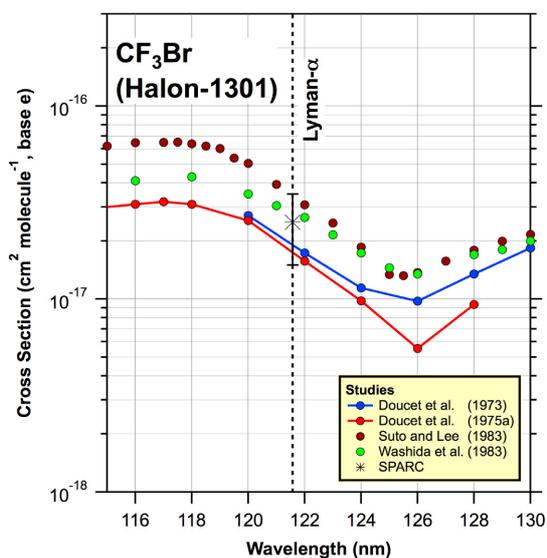
$$\ln(\sigma(\lambda, T)) = \sum_i A_i (\lambda - \bar{\lambda})^i \times \left[1 + (296 - T) \sum_i B_i (\lambda - \bar{\lambda})^i \right]$$

$\bar{\lambda} = 280.376$		
i	A_i	B_i
0	-48.3578	0.0002989
1	-0.1547325	8.5306×10^{-6}
2	-4.966942×10^{-4}	4.26×10^{-8}
3	1.56338×10^{-6}	-1.84×10^{-9}
4	3.664034×10^{-8}	1.284×10^{-11}

10. CF₃Br (Halon-1301)

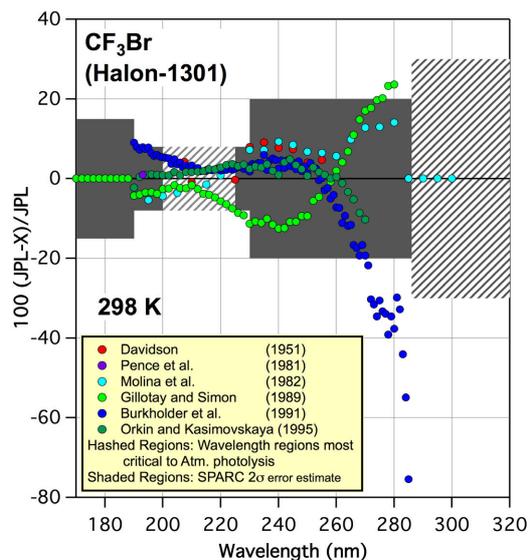
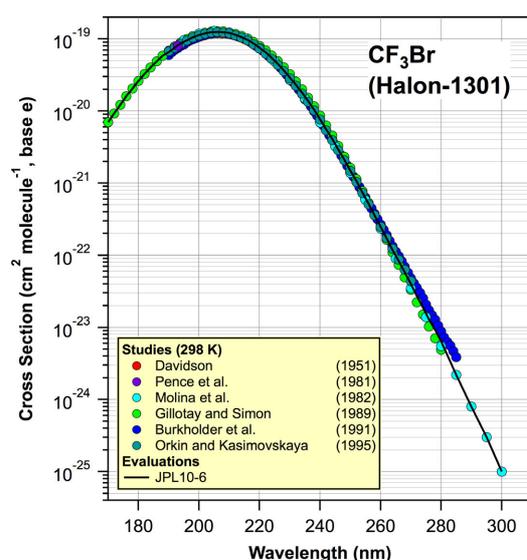
Lyman- α Cross Section

The VUV absorption spectrum of CF₃Br (Halon-1301) has been measured by Doucet *et al.* (1973) (120-206 nm), Doucet *et al.* (1975a) (60-128 nm), Suto and Lee (1983) (106-152 nm), and Washida *et al.* (1983) (116-130 nm). In the region of Lyman- α , the Doucet *et al.* results are lower by ~40% than the Suto and Lee and Washida *et al.* results. An average of the four studies, linearly interpolated to 121.567 nm, yields the recommended σ (Lyman- α , 298 K) value of 2.5×10^{-17} cm² molecule⁻¹. An uncertainty factor, p (298 K), of 1.4 encompasses the available data.



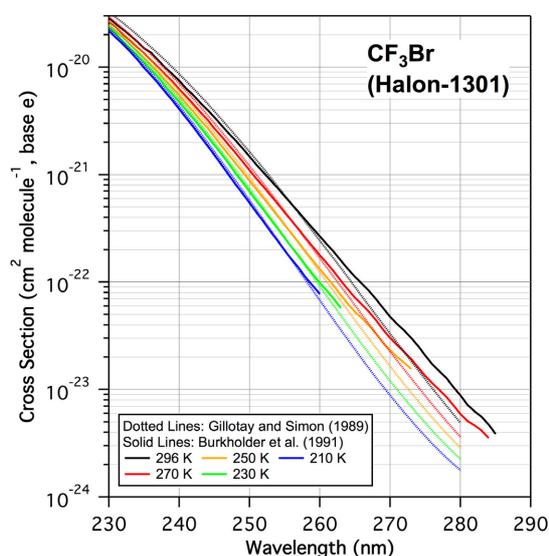
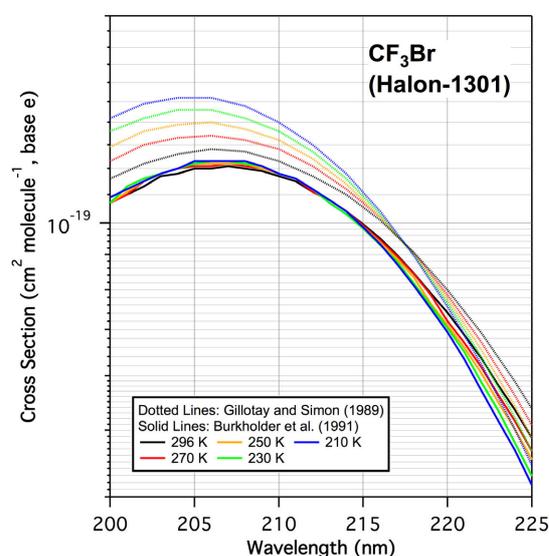
UV Absorption Spectrum

The UV absorption spectrum of CF₃Br has been reported in several studies as reviewed in JPL10-6. The spread in the experimental data relative to the JPL10-6 recommendation at 298 K (which is also recommended here) is shown in the attached figure. The cross-section data in the most critical short-wavelength region agrees to better than 10%. The uncertainty factors in Table 3.4 were assigned to cover the range of experimental data. There are limited cross-section data available in the long-wavelength region (no experimental data for wavelengths >300 nm) and the data that are available are in relatively poor agreement. JPL10-6 recommends the data of Molina *et al.* (1982) for wavelengths >280 nm. The uncertainty factors given in Table 3.4 reflect a high level of uncertainty in the cross-section data for wavelengths >280 nm.



UV Spectrum Temperature Dependence

No recommendation was given in JPL10-6 for the spectrum temperature dependence, although the cross-section parameterizations reported in Gillotay and Simon (1989) (178-280 nm, 210-300 K) and Burkholder *et al.* (1991) (190-285 nm, 210-296 K) were provided. The cross-section temperature dependences in the short-wavelength region from these studies are in relatively poor agreement, e.g., differences of ~20% at 205 nm and 210 K. Differences in the absolute cross-section values and their temperature dependence in the longer-wavelength region, >260 nm, exist between the data sets as well, e.g., the difference at 270 nm and 250 K is 30%. Note, however, that neither study reports cross-section temperature-dependent data in the long-wavelength actinic region. The parameterization from Burkholder *et al.* (1991) is recommended here. The uncertainty factors given in Table 3.4 cover the range of the reported values in the various wavelength regions.



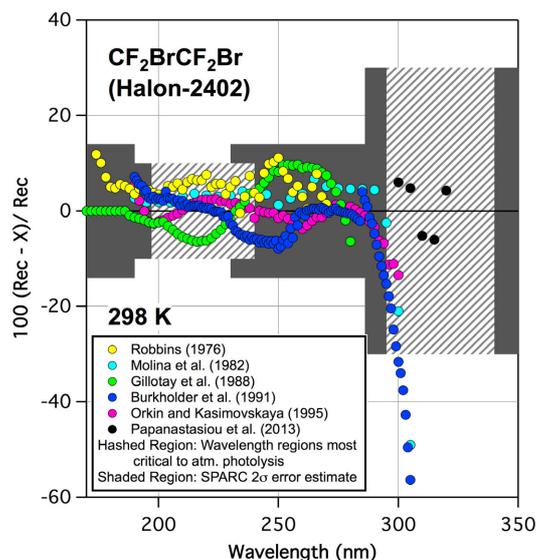
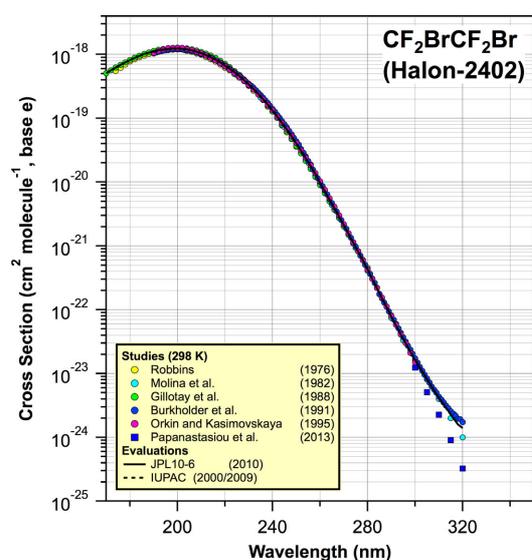
11. CF₂BrCF₂Br (Halon-2402)

Lyman- α Cross Section

There are no VUV spectrum measurements available for CF₂BrCF₂Br (Halon-2402). σ (Lyman- α , 298 K) is expected to be greater than that for CF₃Br (Halon-1301) and less than that for CF₂Br₂ (Halon-1202). A σ (Lyman- α , 298 K) value of 5×10^{-17} cm² molecule⁻¹ is estimated with an uncertainty factor, p (298 K), of 2.

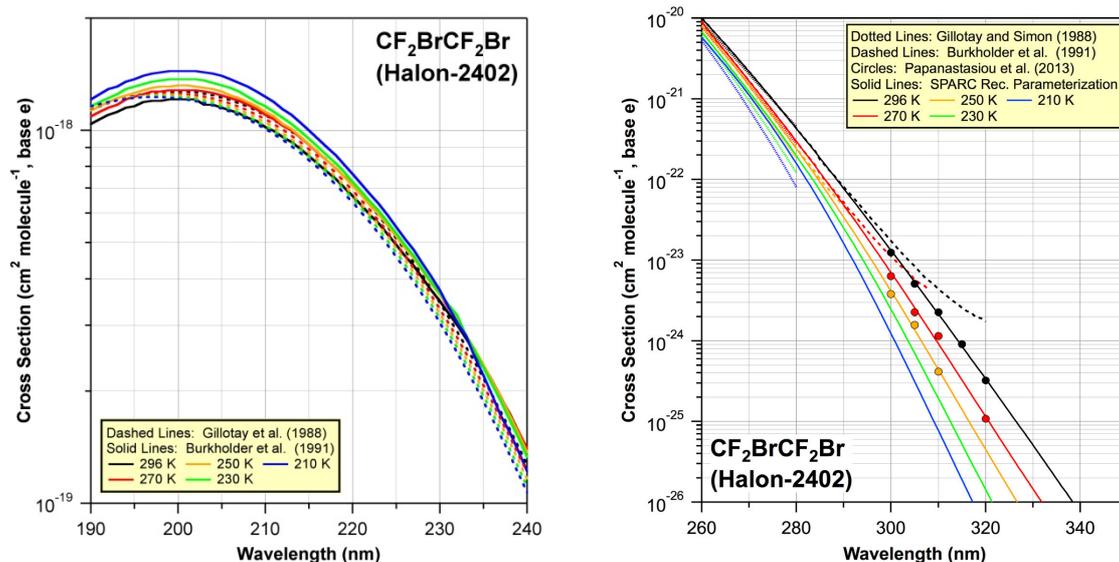
UV Absorption Spectrum

There are several studies of the CF₂BrCF₂Br UV absorption spectrum available as summarized in JPL10-6. More recently Papanastasiou *et al.* (2013) (300-325 nm; 250, 270, and 296 K) have reported cross-section data in the long-wavelength region, which has been corrected for Rayleigh scattering. The recommendation given here is taken from JPL10-6 for wavelengths <260 nm and from Papanastasiou *et al.* for wavelengths \geq 260 nm. The spread in the experimental data relative to the recommendation is shown in the attached figure. The uncertainty factors given in Table 3.4 are significantly lower than reported in JPL10-6 and cover the range of the available experimental data, except in the long-wavelength region where the superseded data from Burkholder *et al.* (1991) fall outside the given uncertainty range.



UV Spectrum Temperature Dependence

The temperature dependence of the CF₂BrCF₂Br UV absorption spectrum has been reported in Gillotay *et al.* (1988) (180-280 nm; 210-295 K), Burkholder *et al.* (1991) (190-320 nm; 210-296 K), and most recently in Papanastasiou *et al.* (2013). In the short-wavelength region, the cross-section data agree to better than 20%, although the reported trends in the cross sections with temperature differ somewhat. JPL10-6 reports the cross-section parameterizations from the Gillotay *et al.* and Burkholder *et al.* studies, but does not make a recommendation. For wavelengths <260 nm, the parameterization given by Gillotay *et al.* is recommended here. In the long-wavelength region, the cross-section parameterization reported in Papanastasiou *et al.*, given below, is recommended.



Absorption cross-section parameterization for CF₂BrCF₂Br (Halon-2402) for wavelengths ≥ 260 nm and temperatures between 210 and 298 K as taken from Papanastasiou *et al.* (2013)

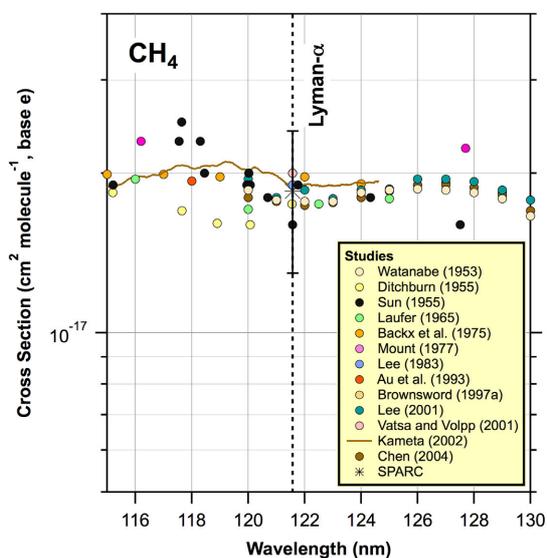
$$\ln(\sigma(\lambda, T)) = \sum_i A_i (\lambda - \bar{\lambda})^i \times \left[1 + (296 - T) \sum_i B_i (\lambda - \bar{\lambda})^i \right]$$

$\bar{\lambda} = 274.64$		
i	A_i	B_i
0	-48.3611	0.0001877
1	-0.1595	7.252×10^{-6}
2	-1.026×10^{-4}	2.917×10^{-7}
3	-1.334×10^{-5}	-1.725×10^{-9}
4	1.458×10^{-7}	-2.675×10^{-11}

12. CH₄ (Methane)

Lyman- α Cross Section

The VUV absorption spectrum of CH₄ (methane) has been extensively studied at and around the Lyman- α wavelength including work by Watanabe *et al.* (1953) (120-144 nm), Ditchburn (1955) (27-151 nm), Sun and Weissler (1955) (37-131 nm), Laufer and McNesby (1965) (113-143 nm), Backx *et al.* (1975) (13.8-144 nm), Mount *et al.* (1977) (137-160 nm), Lee and Chiang (1983) Lee *et al.* (2001) (120-153 nm), Au *et al.* (1993) (5.6-165 nm), Brownsword *et al.* (1997a) (121.6 nm), Vatsa and Volpp (2001) (121.567 nm), Kameta *et al.* (2002) (52-125 nm), and Chen and Wu (2004) (120-142 nm). The measured or interpolated values are in reasonable agreement at 121.567 nm, to within 20%. Based on these studies, a $\sigma(\text{Lyman-}\alpha, 298 \text{ K})$ of $1.85 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ is recommended with an uncertainty factor, $p(298 \text{ K})$, of 1.3.



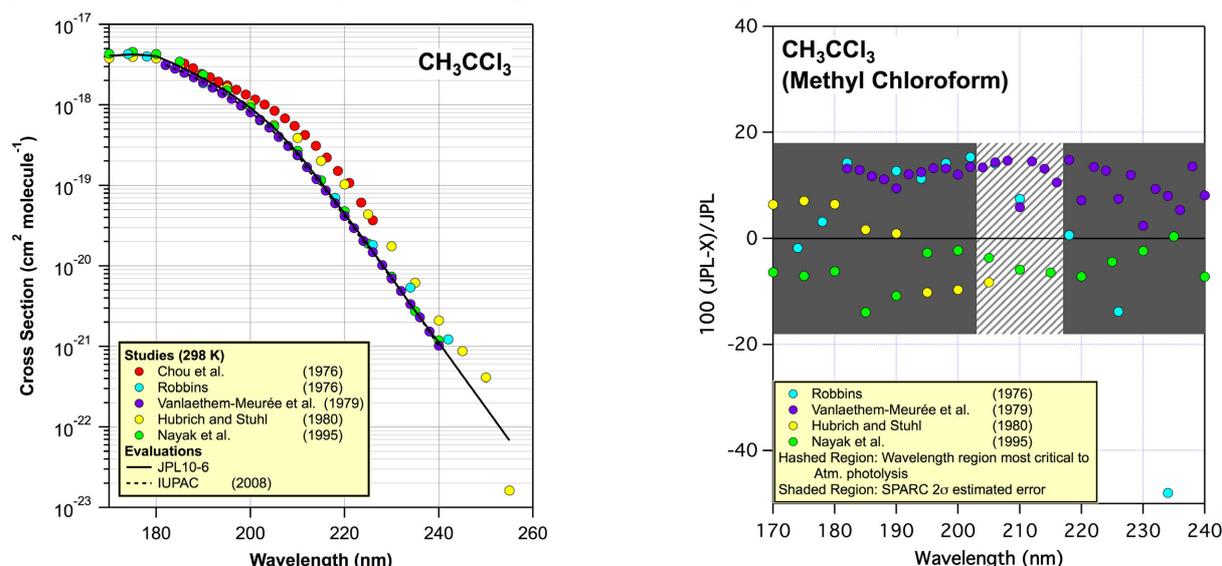
13. CH₃CCl₃ (Methyl Chloroform)

Lyman- α Cross Section

There are no Lyman- α cross-section data available for CH₃CCl₃ (Methyl chloroform). It is expected that $\sigma(\text{Lyman-}\alpha, 298 \text{ K})$ for CH₃CCl₃ would be significantly greater than that for CH₃CF₂Cl (HFC-142b) and slightly greater than that for CH₃CFCl₂ (HCFC-141b). A cross section of $7 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ is estimated; the cross section is not expected to exceed $10 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$. The uncertainty in $\sigma(\text{Lyman-}\alpha, 298 \text{ K})$, $p(298 \text{ K})$, is estimated to be 1.4.

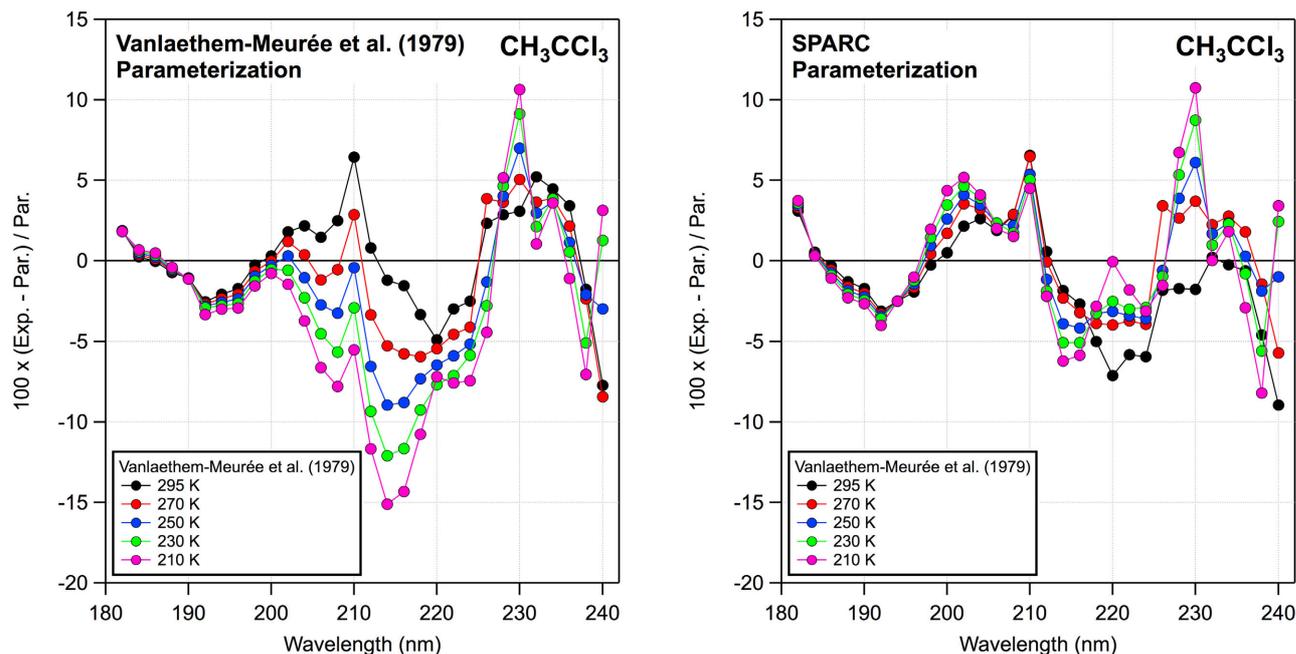
UV Absorption Spectrum

The UV absorption spectrum of CH₃CCl₃ has been measured in a number of studies. The recommendation given here is the same as that of the JPL10-6 recommendation, which is based on a combination of studies as described in the note within the JPL10-6 evaluation for this molecule. The absorption cross sections are in reasonable agreement, to within 15%, in the most critical wavelength region. The spread in the experimental data relative to the JPL10-6 recommendation is shown in the attached figure. The uncertainty factor, $p(298 \text{ K})$, given in Table 3.4 encompasses the range of available experimental data.



UV Spectrum Temperature Dependence

The temperature dependence of the CH₃CCl₃ UV absorption spectrum has been reported in Vanlaethem-Meurée *et al.* (1979) (210-295 K) and Nayak *et al.* (1995) (223-333 K). The spectrum parameterization reported by Vanlaethem-Meurée *et al.* does not reproduce their experimental data very well. Their data was re-fit using the same empirical formula to obtain an improved fit (see figures below). The fit parameters are given in the table below and are recommended here. The data of Nayak *et al.* and the new parameterization of the Vanlaethem-Meurée *et al.* data are shown in the attached figure. Both studies show a systematic decrease in the absorption cross section at wavelengths >200 nm, although the magnitude of the temperature dependence differs. The uncertainty factors given in Table 3.4 cover the range in the available experimental data.



Absorption cross-section parameterization for CH_3CCl_3 from the data reported by Vanlaethem-Meurée *et al.* (1979)

$$\log_{10} \sigma(\lambda, T) = \sum A_n \lambda^n + (T - 273) \times \sum B_n \lambda^n$$

$$A_0 = 164.15$$

$$A_1 = -3.866$$

$$A_2 = 0.030461$$

$$A_3 = -0.000104583$$

$$A_4 = 1.30734 \times 10^{-7}$$

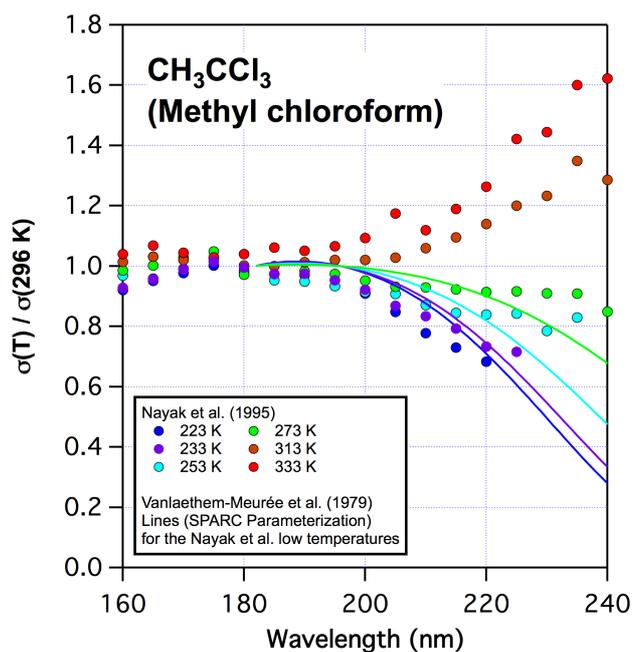
$$B_0 = 0.65591$$

$$B_1 = -0.0131953$$

$$B_2 = 0.000101047$$

$$B_3 = -3.4977 \times 10^{-7}$$

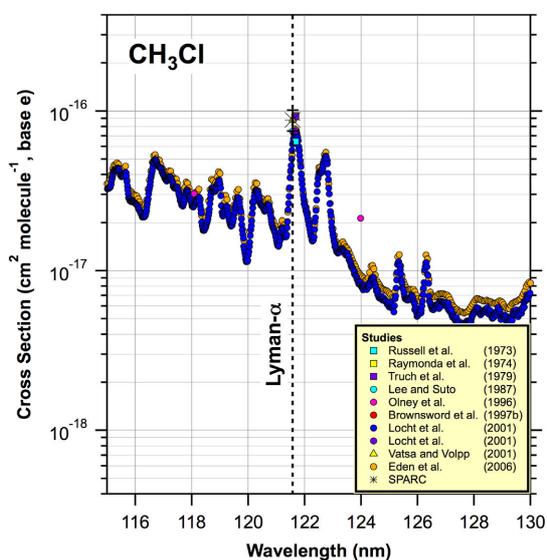
$$B_4 = 4.6223 \times 10^{-10}$$



14. CH₃Cl (Methyl Chloride)

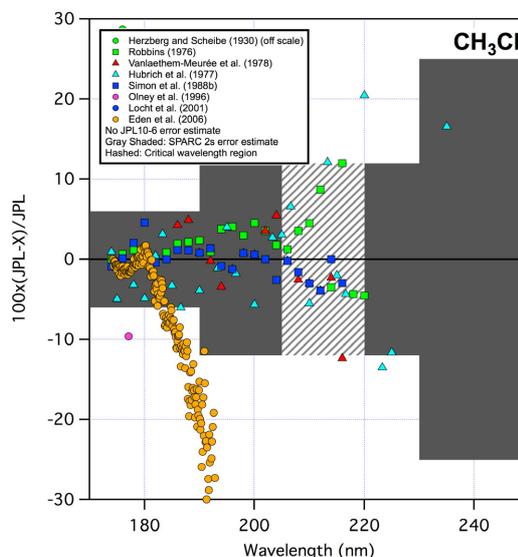
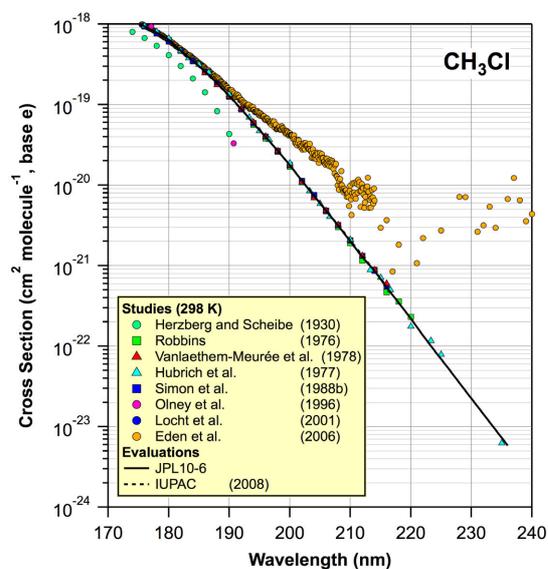
Lyman- α Cross Section

The VUV absorption spectrum of CH₃Cl (Methyl Chloride) has been reported in a number of studies; Russell *et al.* (1973) (107-141 nm), Raymonda *et al.* (1974) (107-141 nm), Truch *et al.* (1979) (107-141 nm), Lee and Suto (1987) (121.567 nm), Olney *et al.* (1996) (3-207 nm), Brownsword *et al.* (1997b) (121.6 nm), Locht *et al.* (2001) (77-207 nm), Vatsa and Volpp (2001) (121.567 nm), and Eden *et al.* (2006) (115-317 nm). The VUV spectrum in the Lyman- α vicinity contains strong diffuse band structure with a maximum nearly coincident with Lyman- α . There is reasonable agreement, to within 30%, in the reported absorption cross sections. The recommended $\sigma(\text{Lyman-}\alpha, 298 \text{ K})$ is $8.8 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ with an uncertainty factor, $p(298 \text{ K})$, of 1.15, which encompasses the available data.



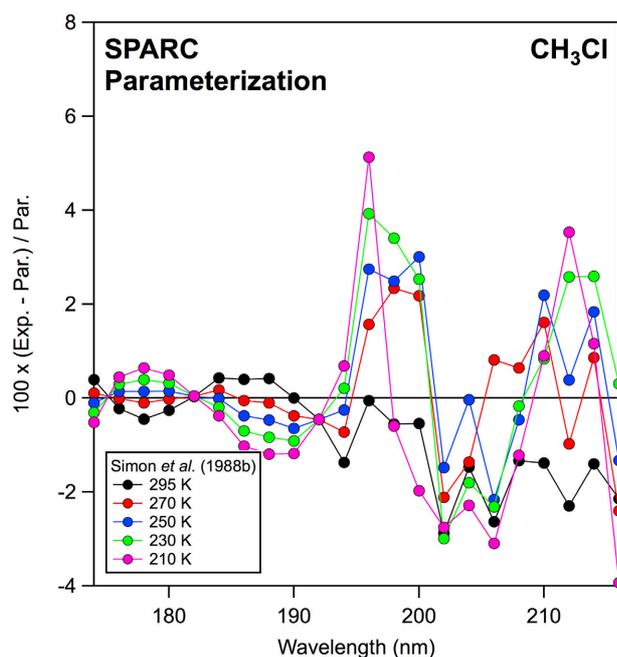
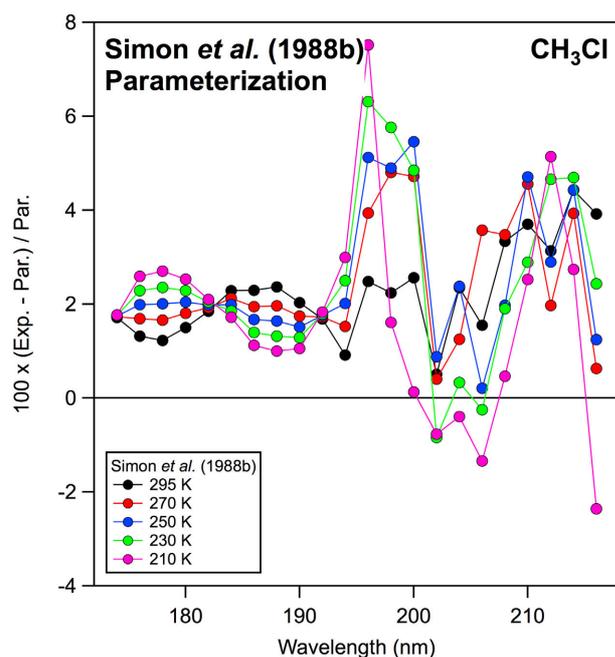
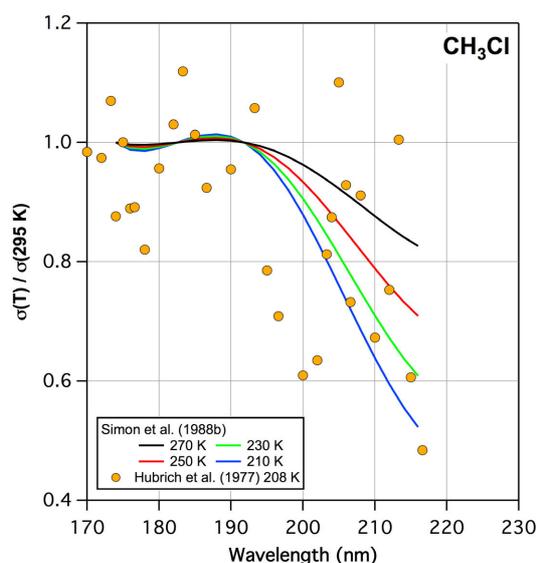
UV Absorption Spectrum

The UV absorption spectrum of CH₃Cl has been measured in several studies. The recommendation given here is the same as that of the JPL10-6 recommendation, which is based on a combination of studies as described in the note within the JPL10-6 evaluation for this molecule. The spread in the experimental data relative to the JPL10-6 recommendation is shown in the attached figure. The agreement is good, to better than 10%, except for the early work of Herzberg and Scheibe (1930) and that of Eden *et al.* (2006). The uncertainty factors, $p(298 \text{ K})$, given in Table 3.4 encompass the range of experimental data in the various wavelength regions.



UV Spectrum Temperature Dependence

Hubrich *et al.* (1977) (158-235 nm; 208 and 296 K) and Simon *et al.* (1988b) (174-216 nm; 210-295 K) have reported the temperature dependence of the CH₃Cl UV absorption spectrum. It is assumed that the Simon *et al.* study supersedes the earlier work of Vanlaethem *et al.* from the same laboratory. The results from these studies are shown in the attached figure. JPL10-6 recommends the parameterization given in Simon *et al.* (1988b), which shows a slight systematic deviation from the experimental data. Their data were re-fit using the same empirical formula to obtain an improved fit (see figures below). The revised fit is recommended here and the parameters are given in the table below. The uncertainty factors given in Table 3.4 were taken to represent the reported accuracy of the Simon *et al.* measurements as well as the limited database available for the cross-section temperature dependence.



Absorption cross-section parameterization for CH₃Cl from the data reported by Simon *et al.* (1988b)

$$\log_{10} \sigma(\lambda, T) = \sum A_n \lambda^n + (T - 273) \times \sum B_n \lambda^n$$

$$A_0 = -305.715$$

$$B_0 = -7.86957$$

$$A_1 = 5.22714$$

$$B_1 = 0.162746$$

$$A_2 = -0.0345787$$

$$B_2 = -0.00125729$$

$$A_3 = 9.9067 \times 10^{-5}$$

$$B_3 = 4.29877 \times 10^{-6}$$

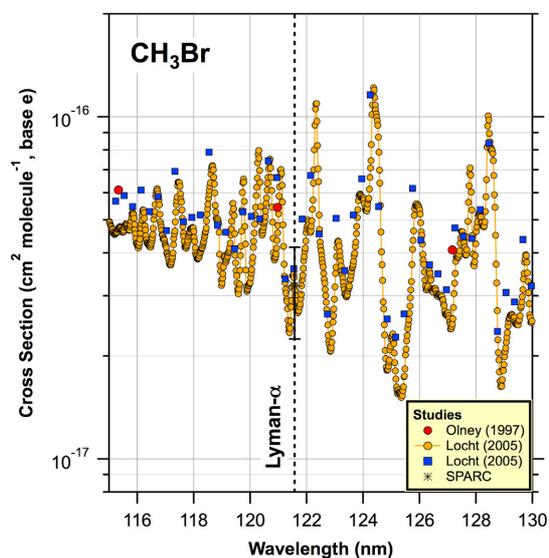
$$A_4 = -1.05544 \times 10^{-7}$$

$$B_4 = -5.486 \times 10^{-9}$$

15. CH₃Br (Methyl Bromide)

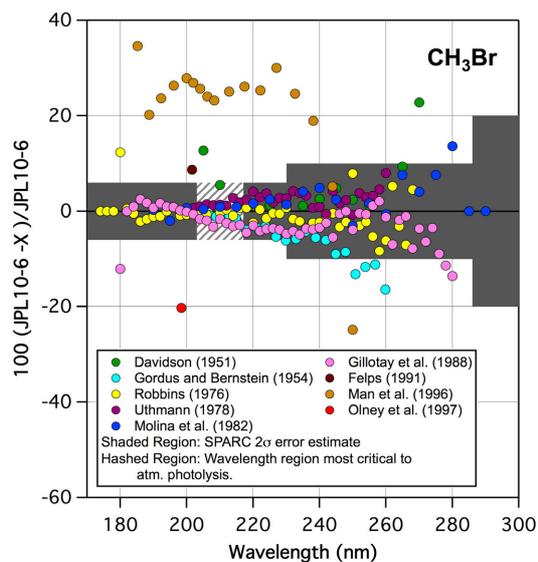
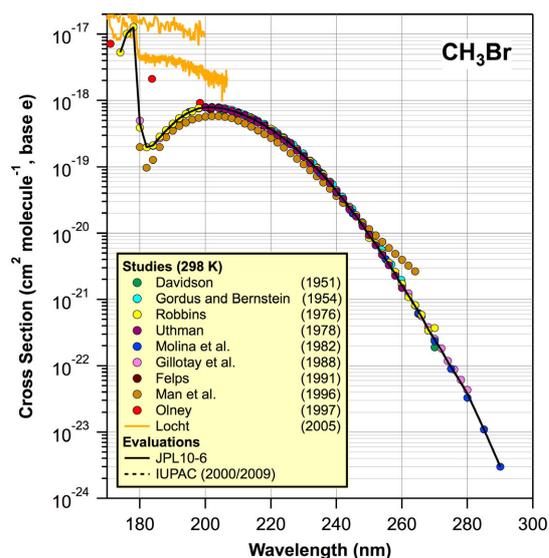
Lyman- α Cross Section

The VUV absorption spectrum of CH₃Br (Methyl Bromide) has been measured by Olney *et al.* (1997) (2.8-199 nm) and Locht *et al.* (2005) (50-207 nm). A σ (Lyman- α , 298 K) value of 3.2×10^{-17} cm² molecule⁻¹ from the Locht *et al.* study is recommended with an uncertainty factor, p (298 K), of 1.3, which covers the range in the experimental data.



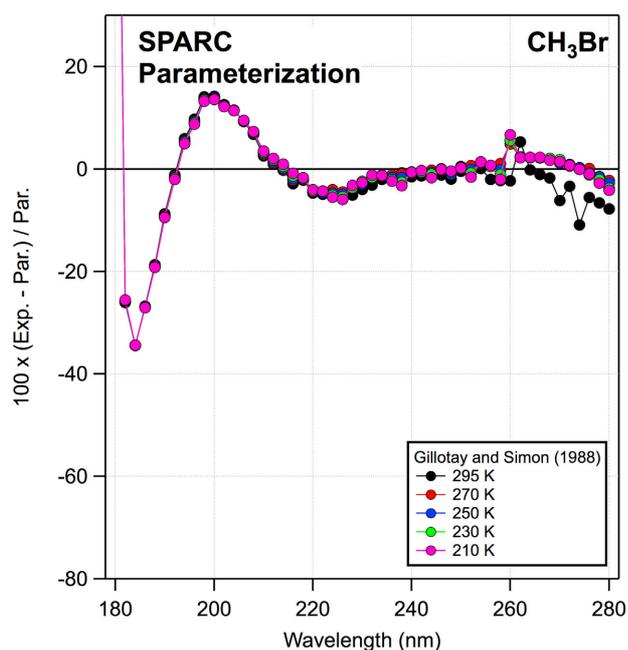
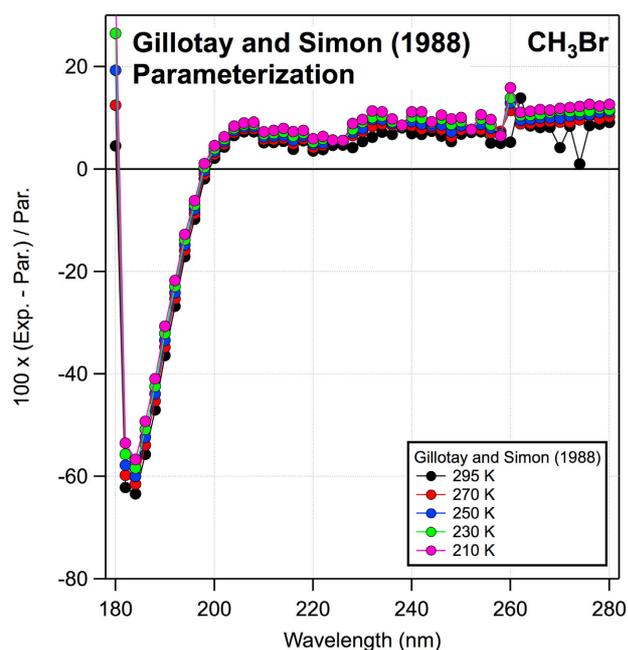
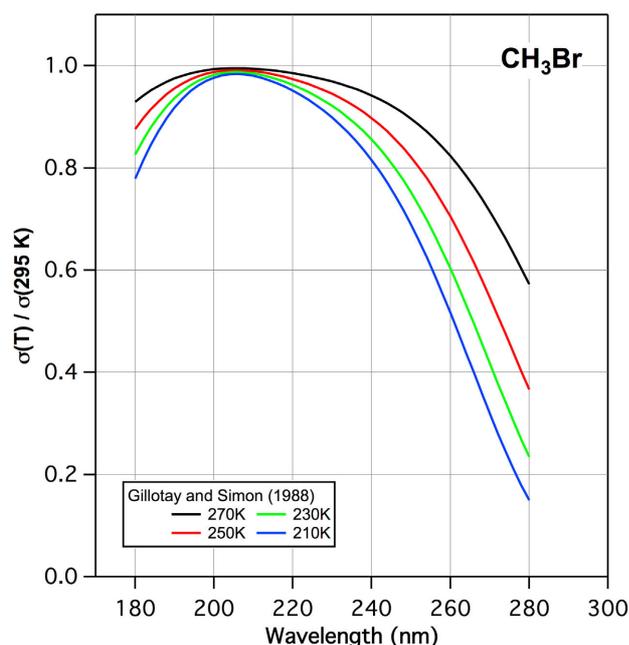
UV Absorption Spectrum

There are a number of studies that have reported on the CH₃Br UV absorption spectrum that are reviewed in JPL10-6. The recommendation given here is the same as that of the JPL10-6 recommendation, which is based on a combination of studies as described in the note within the JPL10-6 evaluation for this molecule. The majority of the cross-section data are in good agreement, to better than 5%, in the most critical wavelength region. The spread in the experimental data relative to the JPL10-6 recommendation is shown in the attached figure. The recommended uncertainty factors cover the range in experimental data with a few exceptions.



UV Spectrum Temperature Dependence

Gillotay and Simon (1988) is the only study to report on the temperature dependence of the CH₃Br UV absorption spectrum. The cross-section data relative to their room temperature spectrum is shown in the attached figure. Gillotay and Simon also reported a spectrum parameterization. However, the parameterization does not reproduce the experimental data very well. A re-fit of the their data using the same empirical formula improves the overall fit to the experimental data, but still contains systematic deviations from the experimental data (see figures below). The re-fit parameterization is given in the table below, although it is clear the empirical formula is not able to fit the experimental data, particularly at the shorter wavelengths. The uncertainty factors given in Table 3.4 are based on the reported accuracy of the Gillotay and Simon study and the fact that there is only a single study available.



Absorption cross-section parameterization for CH₃Br from the data reported by Gillotay and Simon (1988)

$$\log_{10} \sigma(\lambda, T) = \sum A_n \lambda^n + (T - 273) \times \sum B_n \lambda^n$$

$$A_0 = 7.997$$

$$A_1 = -0.889724$$

$$A_2 = 0.00838084$$

$$A_3 = -3.03191 \times 10^{-5}$$

$$A_4 = 3.69427 \times 10^{-8}$$

$$B_0 = 0.457415$$

$$B_1 = -0.00882996$$

$$B_2 = 6.40235 \times 10^{-5}$$

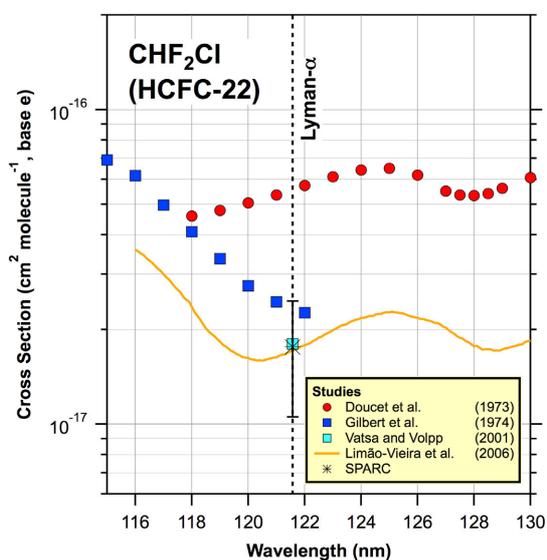
$$B_3 = -2.06827 \times 10^{-7}$$

$$B_4 = 2.51393 \times 10^{-10}$$

16. CHF₂Cl (HCFC-22)

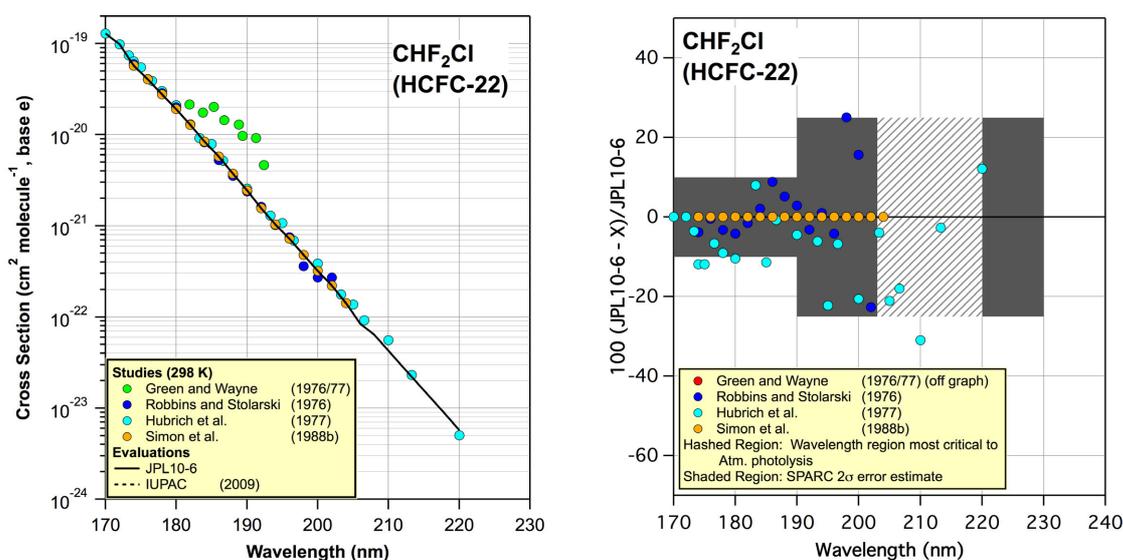
Lyman- α Cross Section

Absorption cross sections for CHF₂Cl (HCFC-22) have been measured in the Lyman- α wavelength region by Doucet *et al.* (1973) (120-200 nm), Gilbert *et al.* (1974) (60-160 nm), and Limão-Vieira *et al.* (2006) (116-225 nm) and at 121.567 nm by Vatsa and Volpp (2001). The results of Doucet *et al.* are significantly greater than the other three studies, a factor of ~ 3 at 121.567 nm, while the Gilbert *et al.* results are $\sim 25\%$ greater than the more recent work of Vatsa and Volpp and Limão-Vieira *et al.* An average of the cross sections reported by Limão-Vieira *et al.* and Vatsa and Volpp, $\sim 1.76 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$, is recommended. The recommended uncertainty factor, $p(298 \text{ K})$, of 1.4 encompasses the data of Gilbert *et al.*



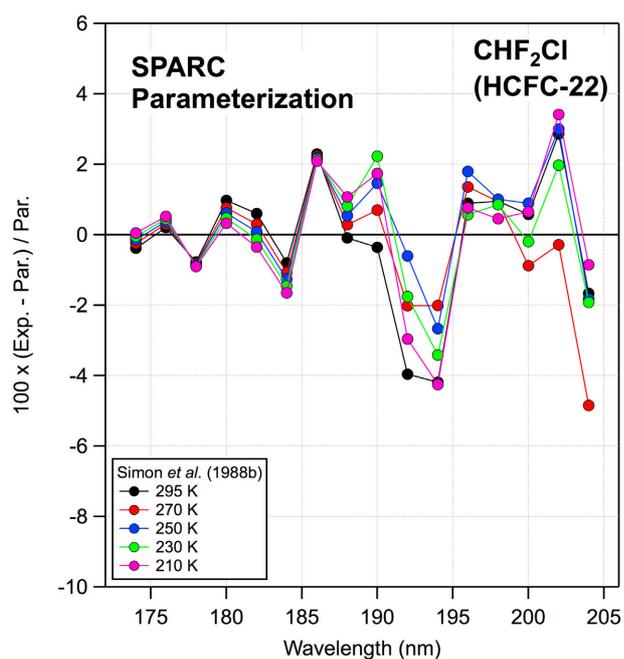
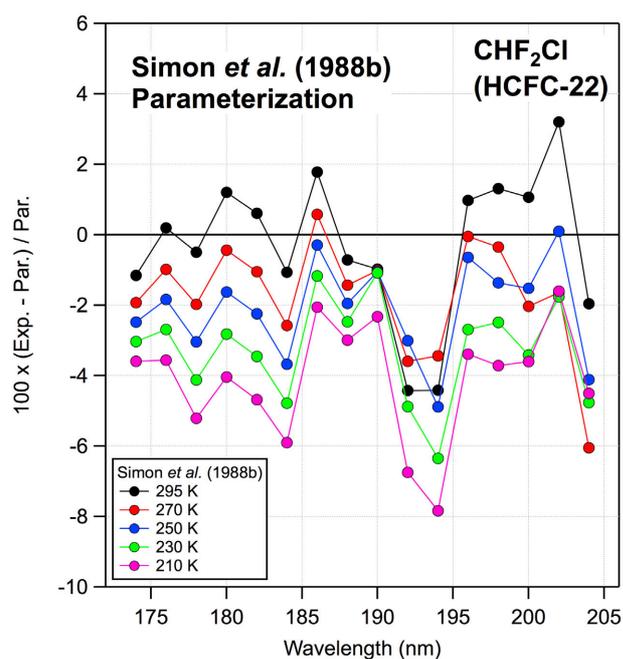
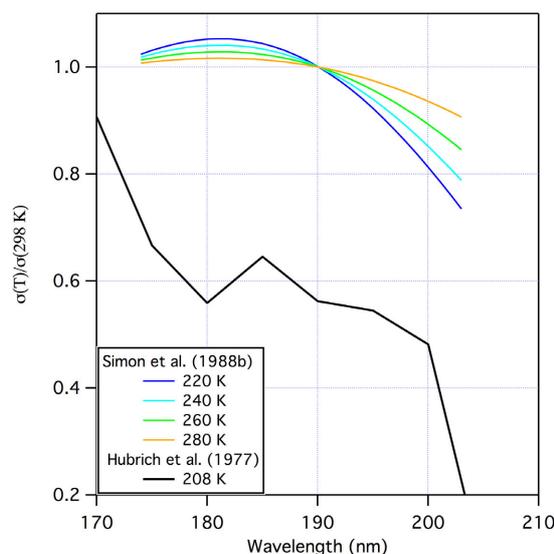
UV Absorption Spectrum

The UV absorption spectrum of CHF₂Cl (HCFC-22) has been measured in several studies. The recommendation given here is the same as that of the JPL10-6 recommendation, which is based on a combination of studies as described in the note within the JPL10-6 evaluation for this molecule. The spread in the experimental data relative to the JPL10-6 recommendation is shown in the attached figure. In the most critical wavelength region the experimental data are limited to the studies of Hubrich *et al.* (1977) and the long-wavelength limit of the Simon *et al.* (1988b) study. The uncertainty factor, $p(298 \text{ K})$, given in Table 3.4 reflects the range in the available cross-section data.



UV Spectrum Temperature Dependence

The temperature dependence of the CHF₂Cl UV absorption spectrum has been measured by Simon *et al.* (1988b) (174-204 nm; 225-295 K) and Hubrich *et al.* (1977) (158-220 nm; 208 and 295 K). A summary of the available data is shown in the attached figure. JPL10-6 recommends the cross-section parameterization reported by Simon *et al.*, however, the parameterization contains an error. The Simon *et al.* data were re-fit using the same formula to obtain a better fit to the experimental data (see figures below). The revised fit is recommended here and the parameters are given in the table below. The recommended uncertainty factor, w , given in Table 3.4 reflects the uncertainty in the Simon *et al.* data.



Absorption cross-section parameterization for CHF₂Cl (HCFC-22) from the data reported by Simon *et al.* (1988b)

$$\log_{10} \sigma(\lambda, T) = \sum A_n \lambda^n + (T - 273) \times \sum B_n \lambda^n$$

$$A_0 = -369.398$$

$$A_1 = 7.09844$$

$$A_2 = -0.0527699$$

$$A_3 = 0.0001715165$$

$$A_4 = -2.0822 \times 10^{-7}$$

$$B_0 = -6.5412$$

$$B_1 = 0.138288$$

$$B_2 = -0.00109207$$

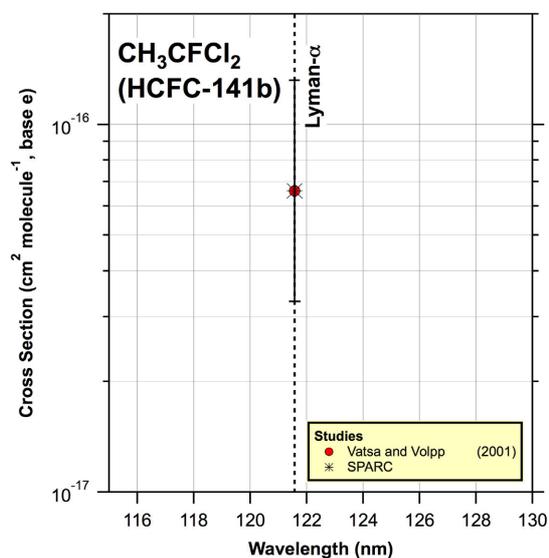
$$B_3 = 3.8164 \times 10^{-6}$$

$$B_4 = -4.9772 \times 10^{-9}$$

17. CH₃CFCl₂ (HCFC-141b)

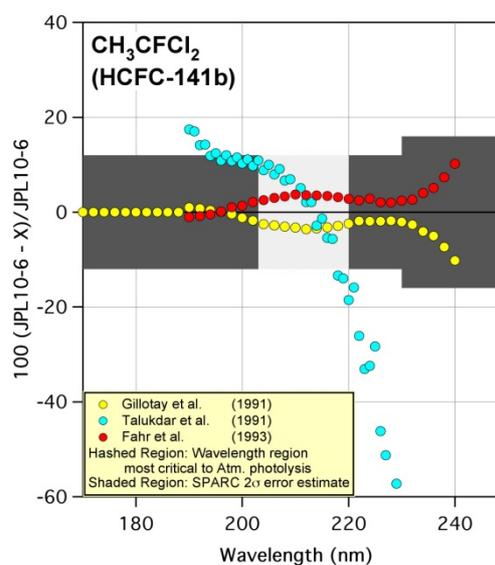
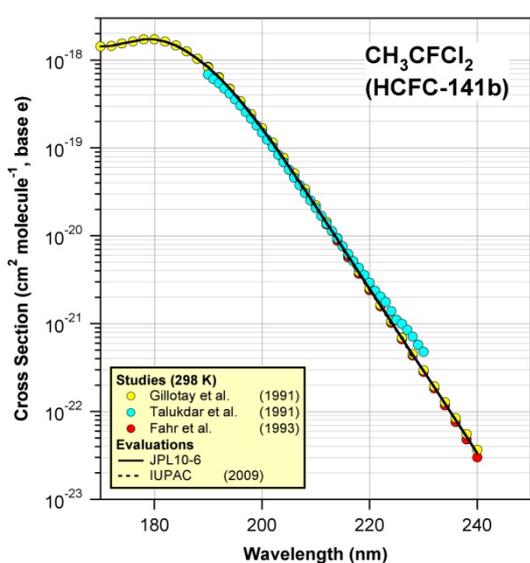
Lyman- α Cross Section

Vatsa and Volpp (2001) measured the 121.567 nm cross section of CH₃CFCl₂ (HCFC-141b) to be $6.6 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$. This is the only reported VUV spectrum data available for this molecule. An uncertainty factor, $p(298 \text{ K})$, of 2 is assigned due primarily to the limited available data.



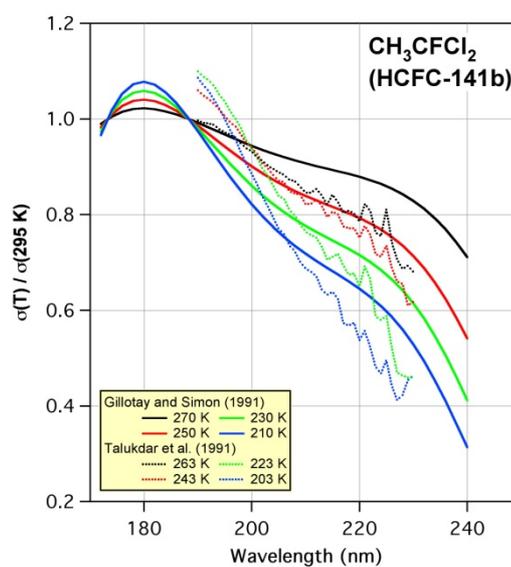
UV Absorption Spectrum

The UV absorption spectrum of CH₃CFCl₂ (HCFC-141b) has been measured in several studies. The recommendation given here is the same as that of the JPL10-6 recommendation, which is based on a combination of studies as described in the note within the JPL10-6 evaluation for this molecule. The spread in the experimental data relative to the JPL10-6 recommendation is shown in the attached figure. The uncertainty factors, $p(298 \text{ K})$, were assigned to include the majority of the available cross-section data, particularly in the wavelength range most critical to atmospheric photolysis.



UV Spectrum Temperature Dependence

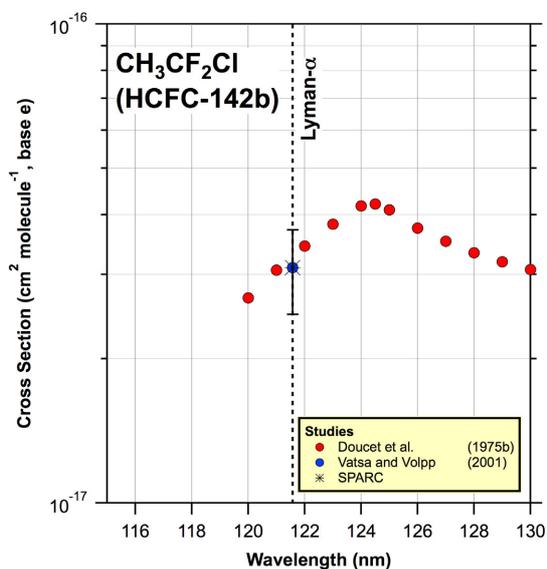
There are two studies of the CH_3CFCl_2 UV-absorption spectrum temperature dependence; the data are shown in the attached figure. The reported temperature dependence agrees to within $\sim 10\%$ in the wavelength range most critical to atmospheric photolysis. JPL10-6 recommends the Gillotay and Simon (1991) temperature-dependence parameterization, which is also recommended here. The uncertainty factors given in Table 3.4 encompass the range in the reported experimental data.



18. CH₃CF₂Cl (HCFC-142b)

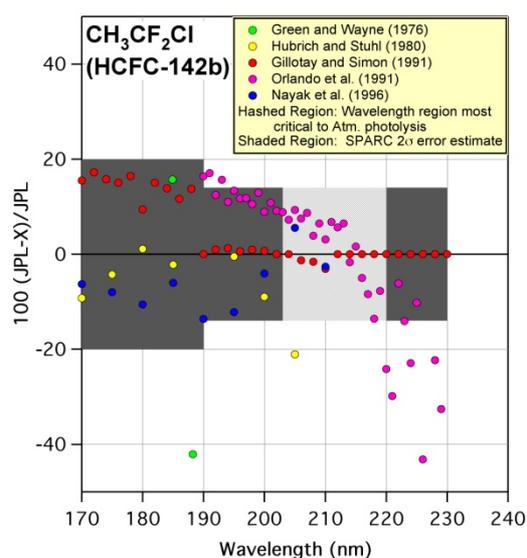
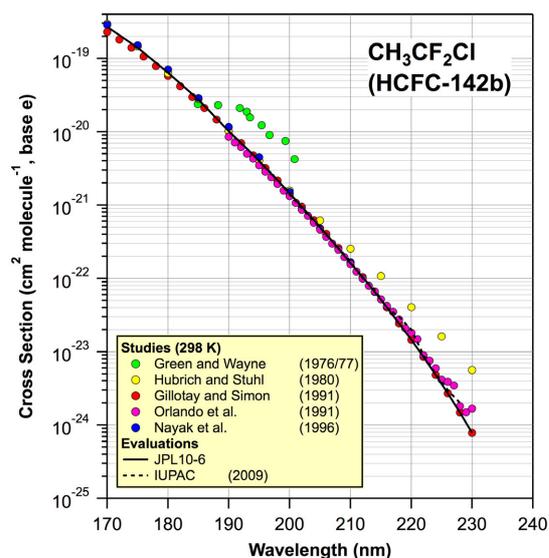
Lyman- α Cross Section

The VUV absorption spectrum of CH₃CF₂Cl (HCFC-142b) has been measured by Doucet *et al.* (1975b) (120-180 nm) and Vatsa and Volpp (2001) (121.567 nm). The results are in good agreement at 121.567 nm, to within 10%. The recommended $\sigma(\text{Lyman-}\alpha, 298 \text{ K})$ of $3.1 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ is taken from Vatsa and Volpp. An uncertainty factor, $p(298 \text{ K})$, of 1.2, which encompasses the Doucet *et al.* value, is assigned.



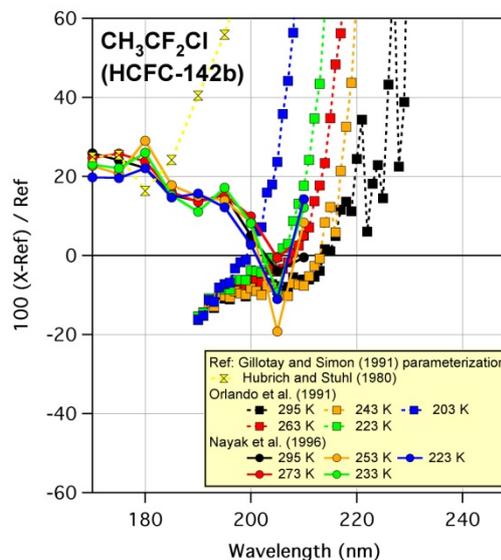
UV Absorption Spectrum

There are several studies of the CH₃CF₂Cl UV absorption spectrum that are reviewed in JPL10-6. The recommendation given here is the same as that of the JPL10-6 recommendation, which is based on a combination of studies as described in the note within the JPL10-6 evaluation for this molecule. The spread in the experimental data relative to the JPL10-6 recommendation is shown in the attached figure. The uncertainty factors given in Table 3.4 were taken to cover the range of the experimental data, although the long-wavelength data from Orlando *et al.* (1991) fall outside the recommended range.



UV Spectrum Temperature Dependence

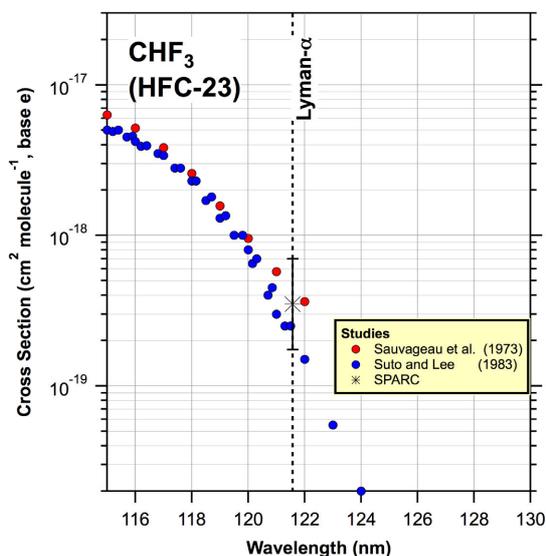
There are several studies of the temperature dependence of the $\text{CH}_3\text{CF}_2\text{Cl}$ UV absorption spectrum as reviewed in JPL10-6. JPL10-6 does not provide a recommendation for the cross-section temperature dependence, although the parameterizations from Gillotay and Simon (1991), Orlando *et al.* (1991), and Nayak *et al.* (1996) are reported. The results from Nayak *et al.* and Gillotay and Simon differ significantly at shorter wavelengths, but are in reasonable agreement in the critical wavelength region, 205-220 nm, while the data from Orlando *et al.* and Hubrich and Stuhl (1980) are systematically different. The results from Nayak *et al.* are recommended here. The uncertainty factors given in Table 3.4 reflect the level of agreement between the Nayak *et al.* and Gillotay and Simon studies.



19. CHF₃ (HFC-23)

Lyman- α Cross Section

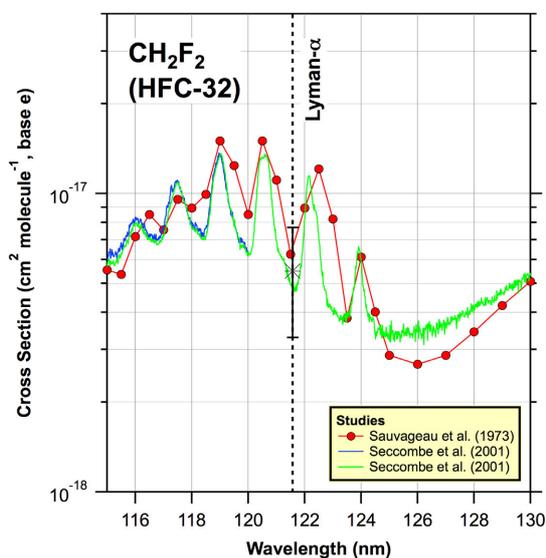
The VUV absorption spectrum of CHF₃ (HFC-23) has been measured by Sauvageau *et al.* (1973) (62-122 nm) and Suto and Lee (1983) (106-124 nm). The two studies differ by ~50% at 121.567 nm. The spectrum is consistent with a blue shift of the absorption spectrum with increased methane fluorination; $\sigma(\text{Lyman-}\alpha, 298 \text{ K})$ for CHF₃ is more than an order of magnitude lower than that of CH₂F₂ (HFC-32). The recommended $\sigma(\text{Lyman-}\alpha, 298 \text{ K})$ is an average of the results from these two studies, $0.035 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$, where the Sauvageau *et al.* data were linearly interpolated to 121.567 nm. An uncertainty factor, $p(298 \text{ K})$, of 2 is assigned, which encompasses the results from both studies.



20. CH₂F₂ (HFC-32)

Lyman- α Cross Section

The VUV absorption spectrum of CH₂F₂ (HFC-32) has been measured by Sauvageau *et al.* (1973) (60-142 nm; reported in 0.1 to 0.5 nm intervals) and Seccombe *et al.* (2001) (60-152 nm; ~0.015 nm intervals). The Lyman- α absorption cross sections reported in these studies agree, to within ~30%, with an average cross section of $0.55 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$. An uncertainty factor, $p(298 \text{ K})$, of 1.4 is recommended, which covers the range of experimental data.



21. CHF₂CF₃ (HFC-125)

Lyman- α Cross Section

There currently are no VUV absorption spectrum data for CHF₂CF₃ (HFC-125) available in the literature. The estimated σ (Lyman- α , 298 K) for CHF₂CF₃ given here is based on the assumption that it is the same as that of CHF₃ (HFC-23), $0.035 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$. An uncertainty factor, p (298 K), of 3.0 is assigned primarily due to the lack of experimental data.

22. CH₂FCF₃ (HFC-134a)

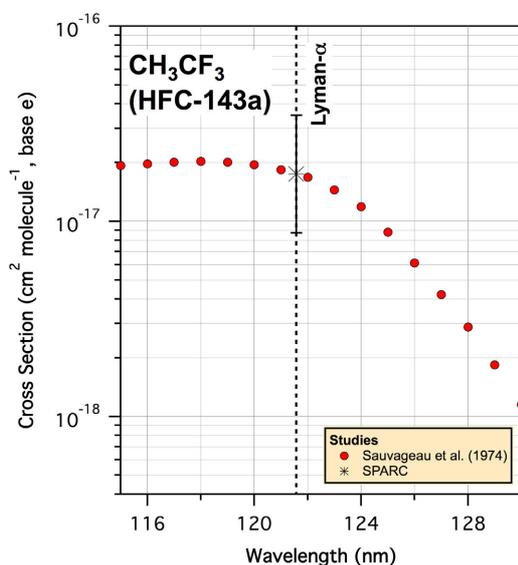
Lyman- α Cross Section

There are no σ (Lyman- α , 298 K) data available for CH₂FCF₃ (HFC-134a). σ (Lyman- α , 298 K) for CH₂FCF₃ is expected to be less than that of CH₃CF₃ (HFC-143a) and comparable to that of CH₂F₂ (HFC-32). An estimated cross-section value of $0.5 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ is recommended. An uncertainty factor, p (298 K), of 2.0 is assigned based primarily on the lack of experimental data.

23. CH₃CF₃ (HFC-143a)

Lyman- α Cross Section

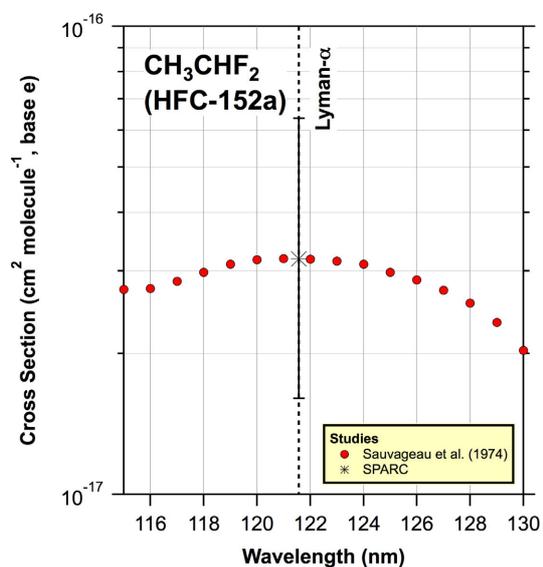
The VUV absorption spectrum of CH₃CF₃ (HFC-143a) has been measured by Sauvageau *et al.* (1974) (61-132 nm). The σ (Lyman- α , 298 K) value obtained by linear interpolation of the Sauvageau *et al.* data is recommended, $1.75 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$. An uncertainty factor, p (298 K), of 2 is recommended based primarily on the fact that there is only a single measurement of the CH₃CF₃ VUV spectrum.



24. CH₃CHF₂ (HFC-152a)

Lyman- α Cross Section

The VUV absorption spectrum of CH₃CHF₂ (HFC-152a) was measured by Sauvageau *et al.* (1974) between 60 and 134 nm at 298 K. The cross section at Lyman- α , 3.2×10^{-17} cm² molecule⁻¹, is consistent with the cross-section value trends observed in HFCs. An uncertainty factor, $p(298\text{ K})$, of 2.0 is assigned based primarily on the limited data available.



25. CF₃CHF₂ (HFC-227ea)

Lyman- α Cross Section

There currently are no VUV absorption spectrum data for CF₃CHF₂ (HFC-227ea) available in the literature. The estimated $\sigma(\text{Lyman-}\alpha, 298\text{ K})$ for CF₃CHF₂ is based on the assumption that it is the same as that of CHF₃ (HFC-23), 0.035×10^{-17} cm² molecule⁻¹. An uncertainty factor, $p(298\text{ K})$, of 3.0 is assigned primarily due to the lack of experimental data.

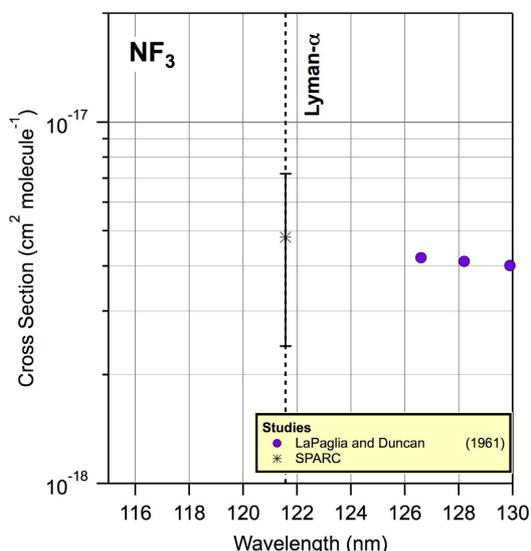
26. CHF₂CH₂CF₃ (HFC-245fa)

Lyman- α Cross Section

There are currently no VUV absorption spectrum data for CHF₂CH₂CF₃ (HFC-245fa) available in the literature. The estimated $\sigma(\text{Lyman-}\alpha, 298\text{ K})$ of 1×10^{-17} cm² molecule⁻¹ for CHF₂CH₂CF₃ is based on the assumption that it would be greater than that for CH₂FCF₃ (HFC-134a), but less than that for CH₃CHF₂ (HFC-152a). An uncertainty factor, $p(298\text{ K})$, of 3.0 is assigned primarily due to the lack of experimental data.

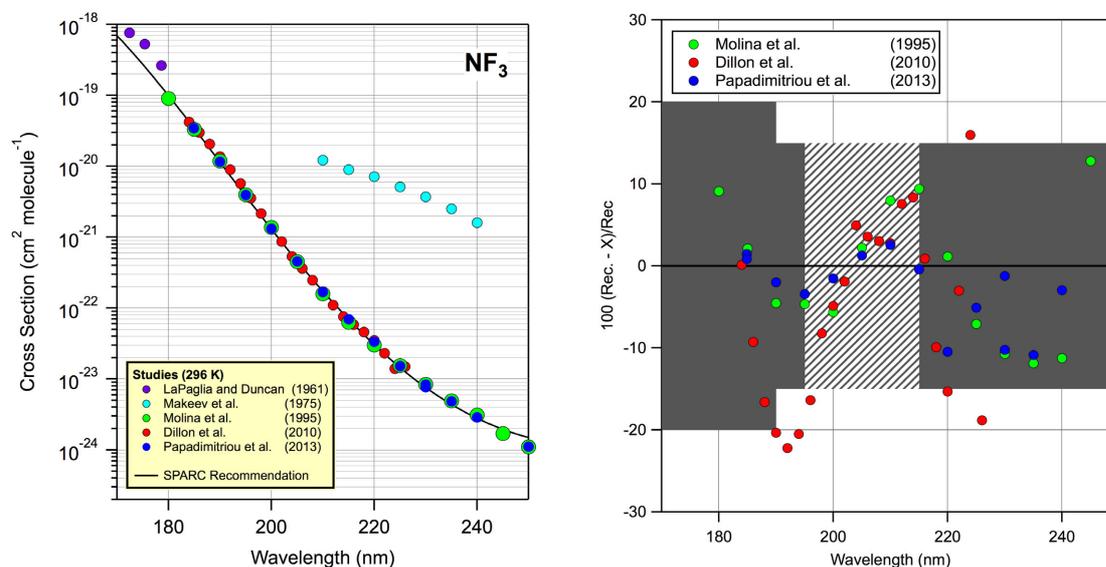
27. NF₃Lyman- α Cross Section

Absorption cross sections for NF₃ have been measured in the 126.6–178.6 nm wavelength region by La Paglia and Duncan (1961) and at 147 nm by Inel (1993). The absorption cross-section value reported by Inel is approximately a factor of 2 greater than that reported by La Paglia and Duncan. The recommended Lyman- α cross section of $4.8 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ was obtained from an extrapolation of the La Paglia and Duncan data. The uncertainty in $\sigma(\text{Lyman-}\alpha, 298 \text{ K})$, p(298 K), is estimated to be 1.5 to account for the fact that there is no published data at Lyman- α .



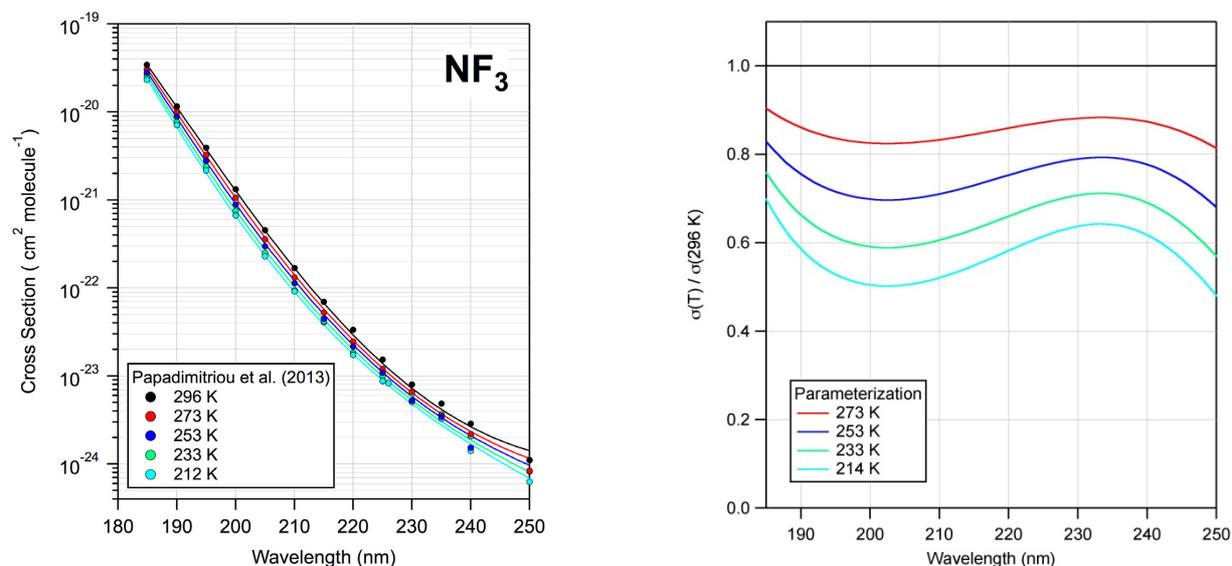
UV Absorption Spectrum

There are several UV absorption spectrum measurements for NF₃ available in the literature as shown in the figures below. JPL10-6 did not include an evaluation or recommendation for the UV absorption spectrum of NF₃. The data from Makeev *et al.* (1975) appear to have substantial errors and were not considered in the present recommendation. The room temperature spectra reported by Molina *et al.* (1995), Dillon *et al.* (2010), and Papadimitriou *et al.* (2013) are in good agreement over the common wavelength region. A parameterization of the spectrum reported by Papadimitriou *et al.* is recommended for use in model calculations. The parameterization reproduces the Molina *et al.* and Dillon *et al.* datasets to better than ~10% at all wavelengths, see figure below. The estimated uncertainties in the room temperature absorption cross-section data, as given in Table 3.4, encompass the range in the available experimental data. It is noted that the cross-section data from the study of La Paglia and Duncan (1961) at wavelengths <180 nm are systematically greater than an extrapolation of the recommended parameterization.



UV Spectrum Temperature Dependence

There is a single study available of the NF_3 UV absorption spectrum temperature dependence. Papadimitriou *et al.* (2013) measured the NF_3 spectrum at discrete wavelengths between 184.9 and 270 nm at 296, 273, 253, 233, and 212 K. The cross-section data are shown in the figures below along with the results from an empirical wavelength and temperature-dependent parameterization (solid lines). The formula and parameterization coefficients are given in the table below.



Absorption cross-section parameterization for NF_3 taken from Papadimitriou *et al.* (2013), which is valid between 184.9 and 250 nm and over the temperature range 212 to 296 K.

$$\log_{10} \sigma(\lambda, T) = \sum_i A_i \lambda^i + (296 - T) \sum_i B_i \lambda^i$$

i	A_i	B_i
0	-218.67	0.9261
1	4.03743	-0.0130187
2	-0.0295605	6.096×10^{-5}
3	9.596×10^{-5}	-9.75×10^{-8}
4	-1.3171×10^{-7}	9.76×10^{-12}
5	4.929×10^{-11}	—

References

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