

CHAPTER 3 – SUPPLEMENT 5

Evaluation of Atmospheric Loss Processes: 2-D Modeling Supplement

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This supplement provides a summary of the gas-phase atmospheric loss processes and uncertainties obtained from the steady-state 2-D model simulations for year 2000 conditions that are presented in Chapter 3. A summary is provided for each molecule where the left-hand panels contain model results obtained using the JPL10-6 kinetic and photochemical recommendations and uncertainties (where available) and the right-hand panels contain results obtained using the recommendations given in the SPARC Lifetimes report. For each molecule, the baseline global lifetime and range in lifetime computed using the parameters and uncertainties, taken from Table 3.7 in Chapter 3, also are provided.

The top pair of panels present the global annually averaged model calculated total first-order loss coefficients as a function of altitude (Z), $k'(Z)$, for molecule X as well as the contributions from the individual loss process (reactive and photolytic)

$$k'(Z) = \left(k_{\text{OH}}(T)[\text{OH}]_Z + k_{\text{O}}(T)[\text{O}(\text{^1D})]_Z + k_{\text{Cl}}(T)[\text{Cl}]_Z \right) + \int \sigma(\lambda, T) \Phi F(\lambda, Z, \chi) d\lambda$$

where k_{OH} , k_{O} , and k_{Cl} , are the temperature-dependent bimolecular rate coefficients, $[\text{OH}]_Z$, $[\text{O}(\text{^1D})]_Z$, and $[\text{Cl}]_Z$ are the atmospheric concentration profiles of OH, O(¹D), and Cl, $\sigma(\lambda, T)$ is the absorption cross section of molecule X as a function of wavelength (λ) and temperature (T), Φ is the photolysis quantum yield (taken to be unity for all molecules in this assessment), and $F(\lambda, Z, \chi)$ is the solar flux that is a function of wavelength, altitude, and solar zenith angle (χ). The photolytic loss term has been further sub-divided into contributions from Lyman- α , (121.567 nm) and the wavelength ranges 169-190, 190-230, 230-286, and >286 nm in the graphs to more clearly identify the most critical wavelength ranges for each molecule. The local lifetime, $1/k'(Z)$, in years is given on the top axes. Overall the first-order losses from the JPL10-6 and SPARC recommendations are generally similar. One key difference is that Lyman- α cross sections were not included in JPL10-6 (N₂O is the exception), but were evaluated in the present SPARC recommendations and included in the SPARC model calculations.

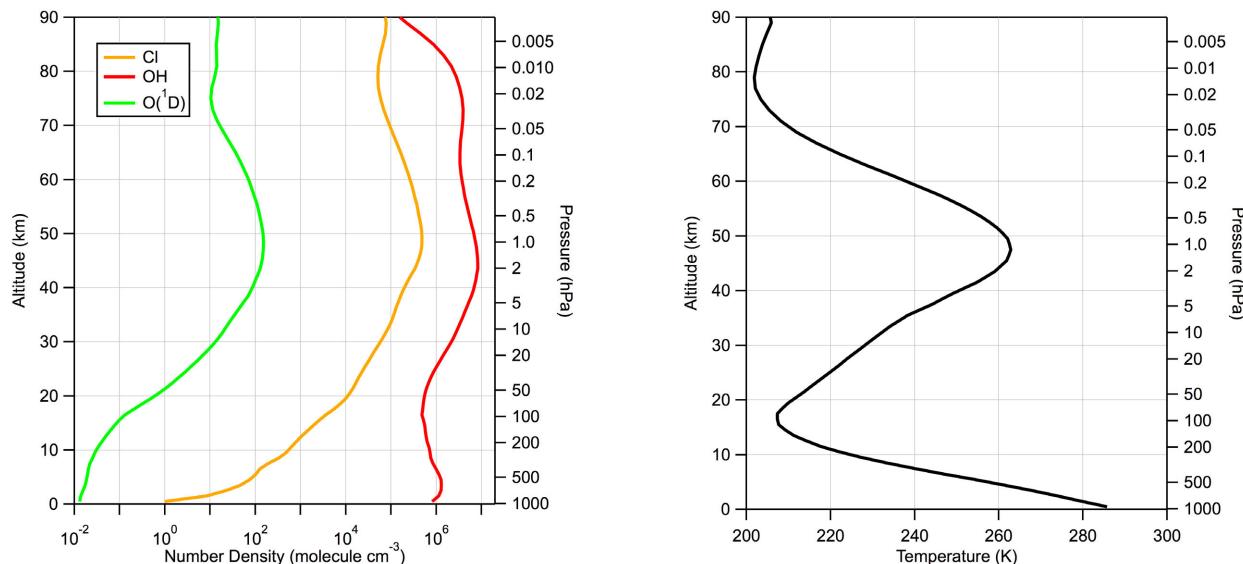
The middle pair of panels show the contributions of the uncertainty in the individual loss processes, as a function of altitude, to the total overall 2σ uncertainty in $k'(Z)$ from the baseline and slow/fast model calculations. The uncertainties are generally significantly reduced in the SPARC recommendations, as discussed in Chapter 3. In particular, uncertainties in the absorption cross-section data and its temperature dependence are quantitatively defined in the SPARC evaluation. For CFC-113, CFC-114, CFC-115, HCFCs, HFCs, N₂O, CH₃Cl, NF₃, and CH₄ Lyman- α photolysis is the primary loss process in the mesosphere, altitudes above ~60 km.

The bottom pair of panels show the molecular loss rate (in units of molecule cm⁻³ s⁻¹), along with the molecules mixing ratio vertical profile. The solid (black) lines depict the baseline simulation, with the 2σ slow and 2σ fast uncertainty simulations shown by the dotted (green) and dashed (red) curves, respectively. The slow/fast limiting calculated loss rates include the ozone feedback effect, as the loss rates were allowed to interact with the model constituents, as discussed in Chapter 3. Including the ozone feedback, however, in general, has a small effect on the calculated globally averaged lifetimes, <5%.

The differences between the JPL10-6 and SPARC based calculations due primarily to differences in the estimated uncertainties in the model input parameters are readily apparent, with the overall uncertainty generally smaller when the SPARC recommendations are used for most, but not all,

molecules. One aspect of the molecular loss rate profiles is that for most of the molecules the 2σ slow and 2σ fast profiles tend to “cross-over” in the stratosphere, i.e., in the troposphere-lower stratosphere the molecular loss rates in the slow simulation are less than those of the fast simulation, with the opposite occurring in the upper stratosphere and above. The “cross-over” is due to the fact that the changes in the model input parameters alters the vertical concentration profiles, as shown in the mixing ratio figures, i.e., the 2σ slow calculation shifts the profile to higher altitude, while the 2σ fast calculation shifts the profile toward lower altitude. Cross-over behavior was not observed for molecules that have relatively weak losses such that the concentration profiles change very little between the slow and fast uncertainty simulations (e.g. CFC-115, HFC-134a, HFC-143a, HFC-23, HFC-125, and HFC-227ea).

The globally annually averaged vertical profiles for the Cl atom, OH radical, and O(1D) atom number densities from the 2-D model (see Chapter 3 text for details) as well as the temperature profile are given in the figures below.



Section 3.6 in Chapter 3 discusses the lifetime sensitivity to uncertainties in the O₂ and O₃ absorption cross sections. These cross sections are used in the APL radiative transfer code to compute the incident solar flux and O₂ photolysis for use in the 2-D model. The baseline O₂ and O₃ cross sections are given in the table and figure below.

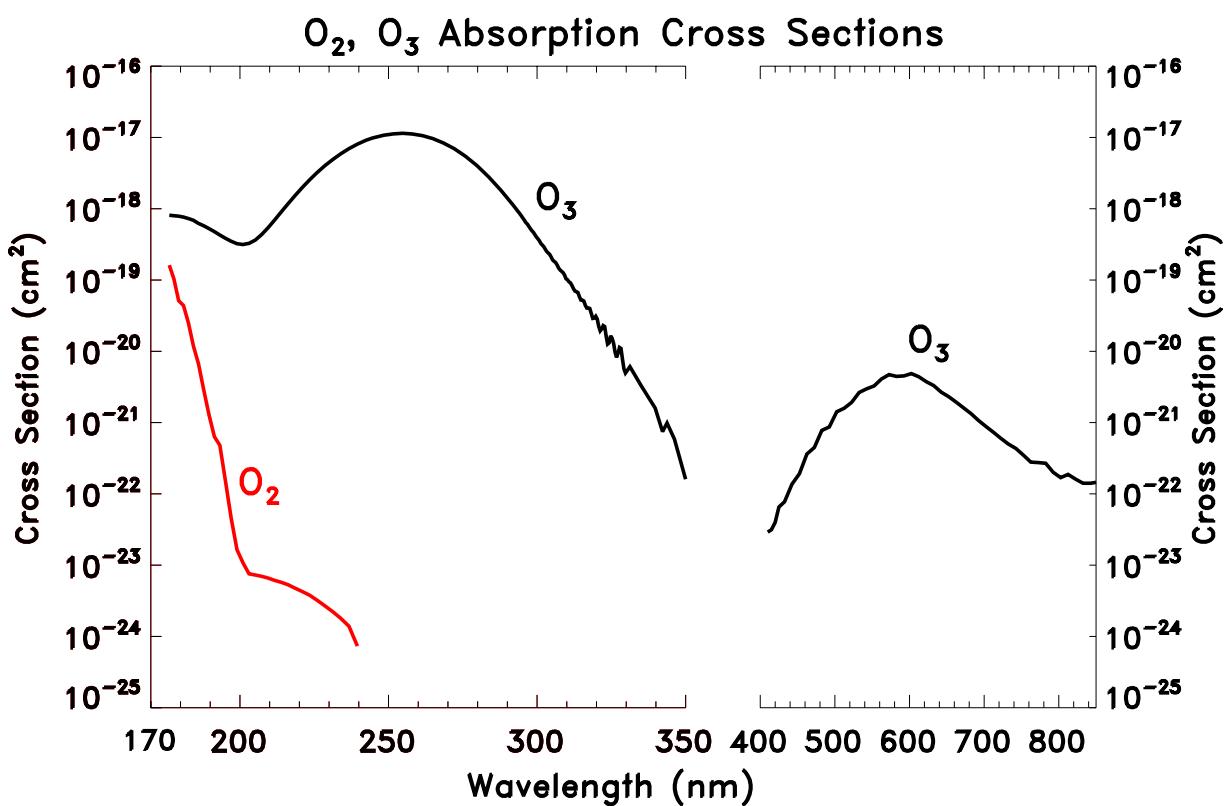
Wavelength ranges and O₂ and O₃ absorption cross sections (298 K) used in the APL radiative transfer code (see text for details).

Bin	Wavelength Range (nm)	O ₂ cross section 10 ⁻²⁴ cm ²	O ₃ cross section 10 ⁻²⁰ cm ²
1	175.439 - 176.991	161800	81.10
2	176.991 - 178.571	103100	79.90
3	178.571 - 180.180	51370	78.60
4	180.180 - 181.818	43840	76.30
5	181.818 - 183.486	25040	72.90
6	183.486 - 185.185	11860	68.80
7	185.185 - 186.916	6642	62.17
8	186.916 - 188.679	2880	57.67
9	188.679 - 190.476	1289	52.62
10	190.476 - 192.308	635.1	47.70
11	192.308 - 194.175	480.4	42.78
12	194.175 - 196.078	151.3	38.53
13	196.078 - 198.020	45.34	34.94
14	198.020 - 200.000	16.46	32.31
15	200.000 - 202.020	10.81	31.48
16	202.020 - 204.082	7.557	32.70
17	204.082 - 206.186	7.277	36.26
18	206.186 - 208.333	6.984	43.26
19	208.333 - 210.526	6.602	53.94
20	210.526 - 212.766	6.125	69.22
21	212.766 - 215.054	5.745	90.40
22	215.054 - 217.391	5.304	118.0
23	217.391 - 219.780	4.749	153.6
24	219.780 - 222.222	4.268	199.0
25	222.222 - 224.719	3.784	255.0
26	224.719 - 227.273	3.214	322.4
27	227.273 - 229.885	2.687	401.6
28	229.885 - 232.558	2.223	490.4
29	232.558 - 235.294	1.795	589.6
30	235.294 - 238.095	1.388	697.0
31	238.095 - 240.964	0.7318	807.1
32	240.964 - 243.902		914.4
33	243.902 - 245.018		978.4
34	245.018 - 246.914		1016
35	246.914 - 250.000		1076
36	250.000 - 253.165		1122
37	253.165 - 256.410		1144
38	256.410 - 259.740		1119
39	259.740 - 263.158		1059
40	263.158 - 266.667		963.3
41	266.667 - 270.270		836.4
42	270.270 - 273.973		696.3
43	273.973 - 277.778		545.4
44	277.778 - 281.690		404.1
45	281.690 - 285.714		279.7
46	285.714 - 289.855		182.4
47	289.855 - 294.118		111.9
48	294.118 - 295.000		81.13
49	295.000 - 295.500		73.59
50	295.500 - 296.000		68.71

Bin	Wavelength Range (nm)	O ₂ cross section 10 ⁻²⁴ cm ²	O ₃ cross section 10 ⁻²⁰ cm ²
51	296.000 - 296.500		63.76
52	296.500 - 297.000		60.80
53	297.000 - 297.500		56.51
54	297.500 - 298.000		52.46
55	298.000 - 298.500		49.24
56	298.500 - 299.000		46.83
57	299.000 - 299.500		43.39
58	299.500 - 300.000		40.23
59	300.000 - 300.500		38.03
60	300.500 - 301.000		35.69
61	301.000 - 301.500		32.72
62	301.500 - 302.000		30.95
63	302.000 - 302.500		29.38
64	302.500 - 303.000		27.10
65	303.000 - 303.500		25.10
66	303.500 - 304.000		23.95
67	304.000 - 304.500		22.87
68	304.500 - 305.000		20.98
69	305.000 - 305.500		19.14
70	305.500 - 306.000		18.26
71	306.000 - 306.500		17.57
72	306.500 - 307.000		16.30
73	307.000 - 307.500		14.74
74	307.500 - 308.000		13.82
75	308.000 - 308.500		13.25
76	308.500 - 309.000		12.68
77	309.000 - 309.500		11.71
78	309.500 - 310.000		10.42
79	310.000 - 310.500		10.06
80	310.500 - 311.000		9.424
81	311.000 - 311.500		9.104
82	311.500 - 312.000		8.351
83	312.000 - 312.500		7.566
84	312.500 - 313.000		6.994
85	313.000 - 313.500		6.860
86	313.500 - 314.000		6.674
87	314.000 - 314.500		5.832
88	314.500 - 315.000		5.235
89	315.000 - 315.500		5.209
90	315.500 - 316.000		5.073
91	316.000 - 316.500		4.403
92	316.500 - 317.000		4.039
93	317.000 - 317.500		4.048
94	317.500 - 318.000		3.987
95	318.000 - 318.500		3.392
96	318.500 - 319.000		2.897
97	319.000 - 319.500		2.926
98	319.500 - 320.000		3.101
99	320.000 - 320.500		2.827
100	320.500 - 321.000		2.241
101	321.000 - 321.500		1.934
102	321.500 - 322.000		2.058
103	322.000 - 322.500		2.295
104	322.500 - 323.000		2.222
105	323.000 - 323.500		1.624

Bin	Wavelength Range (nm)	O ₂ cross section 10 ⁻²⁴ cm ²	O ₃ cross section 10 ⁻²⁰ cm ²
106	323.500 - 324.000		1.263
107	324.000 - 324.500		1.317
108	324.500 - 325.000		1.649
109	325.000 - 325.500		1.520
110	325.500 - 326.000		1.293
111	326.000 - 326.500		0.974
112	326.500 - 327.000		0.821
113	327.000 - 327.500		0.941
114	327.500 - 328.000		1.131
115	328.000 - 328.500		1.094
116	328.500 - 329.000		0.765
117	329.000 - 329.500		0.5641
118	329.500 - 330.000		0.4959
119	330.000 - 332.500		0.6085
120	332.500 - 337.500		0.3309
121	337.500 - 341.981		0.1599
122	341.981 - 342.500		0.07461
123	342.500 - 345.000		0.09854
124	345.000 - 347.500		0.05837
125	347.500 - 352.500		0.01599
126	352.500 - 357.500		0.0000
127	357.500 - 362.500		0.0000
128	362.500 - 367.500		0.0000
129	367.500 - 372.500		0.0000
130	372.500 - 377.500		0.0000
131	377.500 - 382.500		0.0000
132	382.500 - 387.500		0.0000
133	387.500 - 392.500		0.0000
134	392.500 - 397.500		0.0000
135	397.500 - 402.500		0.0000
136	402.500 - 407.500		0.0000
137	407.500 - 412.500		0.002910
138	412.500 - 417.500		0.003140
139	417.500 - 422.500		0.003990
140	422.500 - 427.500		0.006540
141	427.500 - 437.500		0.007745
142	437.500 - 447.500		0.01370
143	447.500 - 457.500		0.01915
144	457.500 - 467.500		0.03625
145	467.500 - 477.500		0.04475
146	477.500 - 487.500		0.0777
147	487.500 - 497.500		0.08685
148	497.500 - 507.500		0.0868
149	507.500 - 517.500		0.1420
150	517.500 - 527.500		0.1590
151	527.500 - 537.500		0.1925
152	537.500 - 547.500		0.2645
153	547.500 - 557.500		0.2975
154	557.500 - 567.500		0.3265
155	567.500 - 577.500		0.4095
156	577.500 - 587.500		0.4710
157	587.500 - 597.500		0.4450
158	597.500 - 607.500		0.4515
159	607.500 - 617.500		0.4865
160	617.500 - 627.500		0.4390

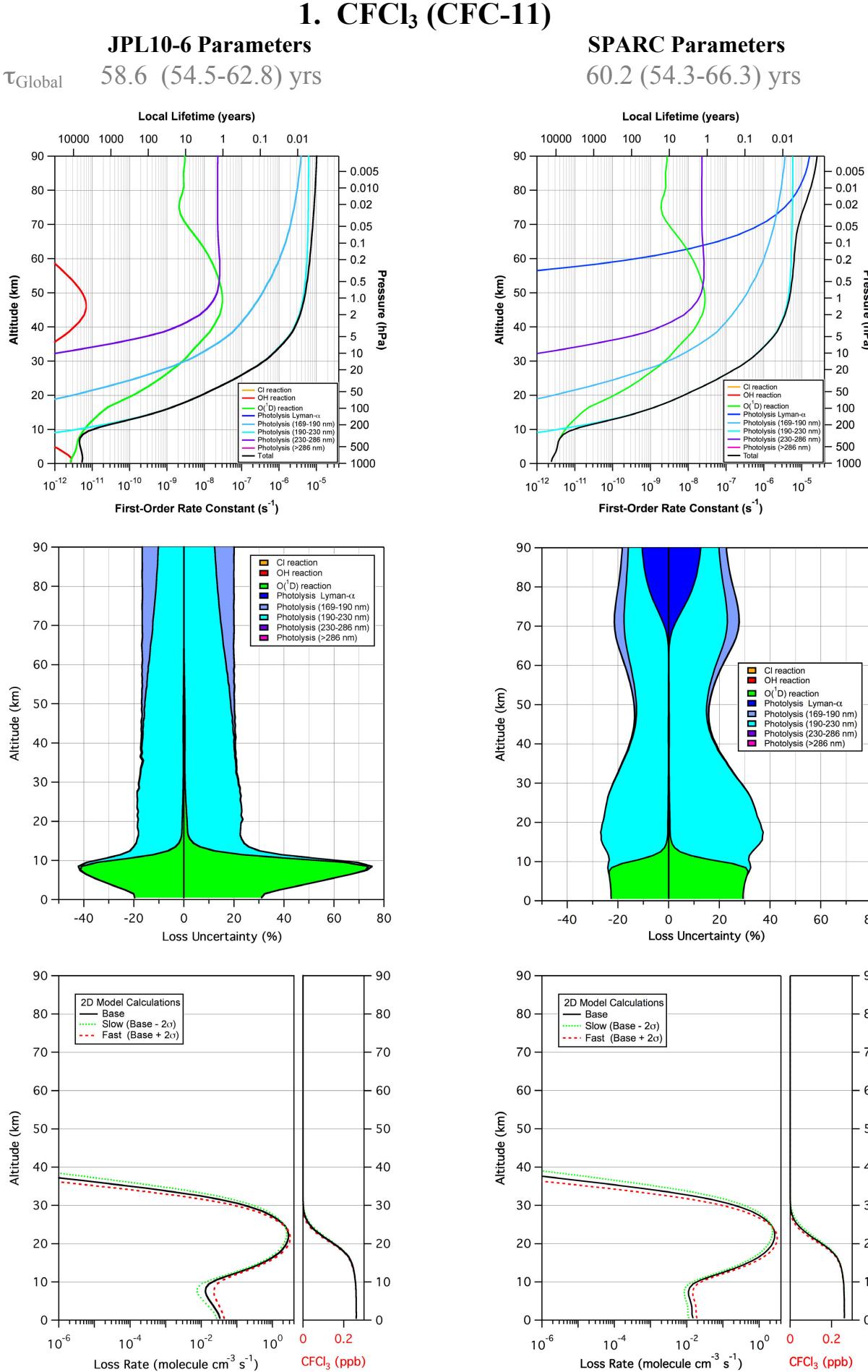
Bin	Wavelength Range (nm)	O_2 cross section 10^{-24} cm^2	O_3 cross section 10^{-20} cm^2
161	627.500 - 637.500		0.3750
162	637.500 - 647.500		0.3300
163	647.500 - 657.500		0.2675
164	657.500 - 667.500		0.2310
165	667.500 - 677.500		0.1935
166	677.500 - 687.500		0.1605
167	687.500 - 697.500		0.1335
168	697.500 - 707.500		0.1070
169	707.500 - 717.500		0.0730
170	717.500 - 727.500		0.0600
171	727.500 - 737.500		0.0500
172	737.500 - 747.500		0.0433
173	747.500 - 757.500		0.0350
174	757.500 - 767.500		0.0279
175	767.500 - 777.500		0.0275
176	777.500 - 787.500		0.0269
177	787.500 - 797.500		0.0201
178	797.500 - 807.500		0.0169
179	807.500 - 817.500		0.0187
180	817.500 - 827.500		0.0161
181	827.500 - 837.500		0.0141
182	837.500 - 847.500		0.0141
183	847.500 - 852.500		0.0145



Gas-Phase Loss Processes

Estimated Uncertainties

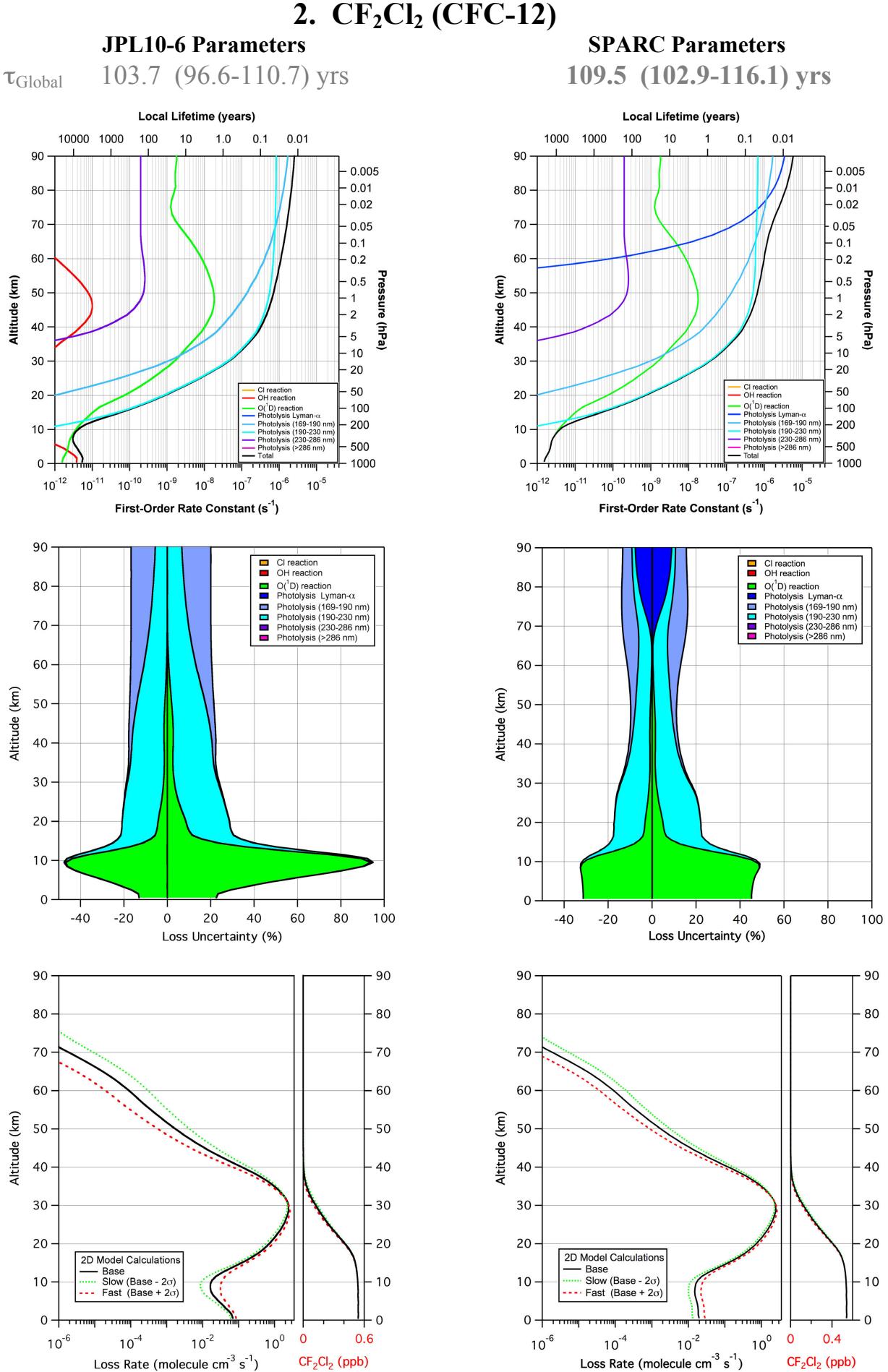
Molecular Loss Rates, Uncertainties, and Profiles



Gas-Phase Loss Processes

Estimated Uncertainties

Molecular Loss Rates, Uncertainties, and Profiles



Gas-Phase Loss Processes

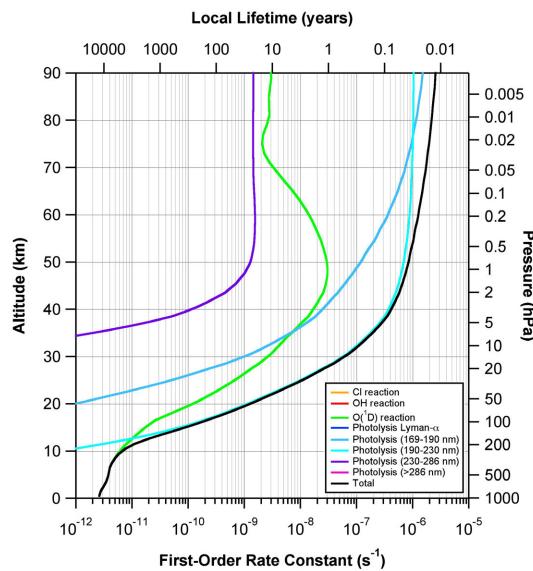
Estimated Uncertainties

Molecular Loss Rates, Uncertainties, and Profiles

3. CF₂ClCFCl₂ (CFC-113)

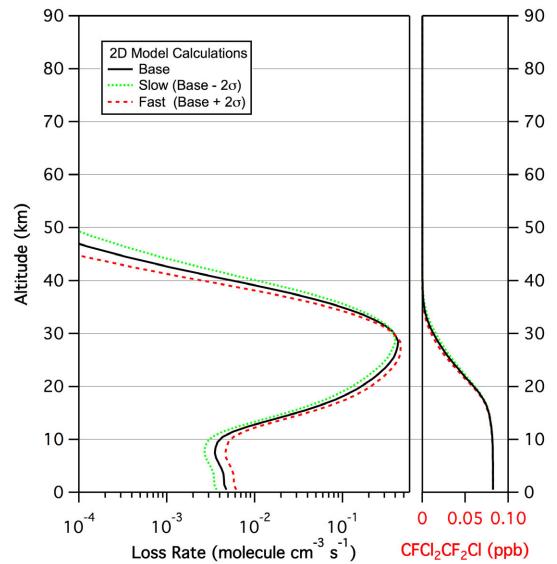
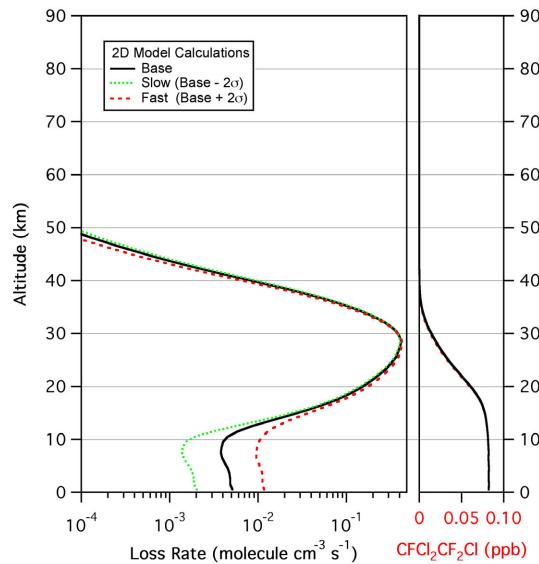
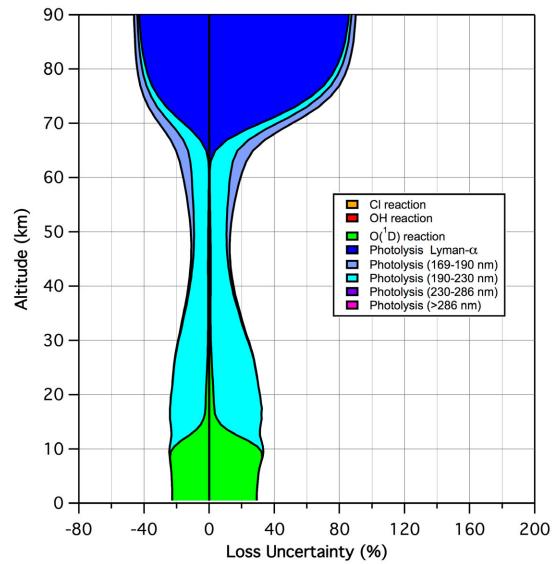
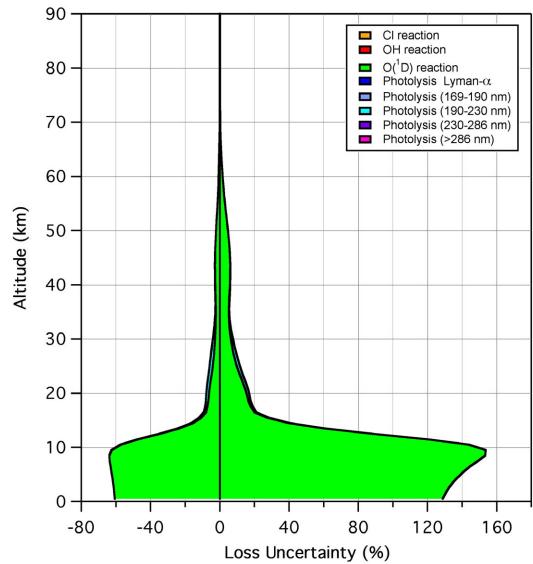
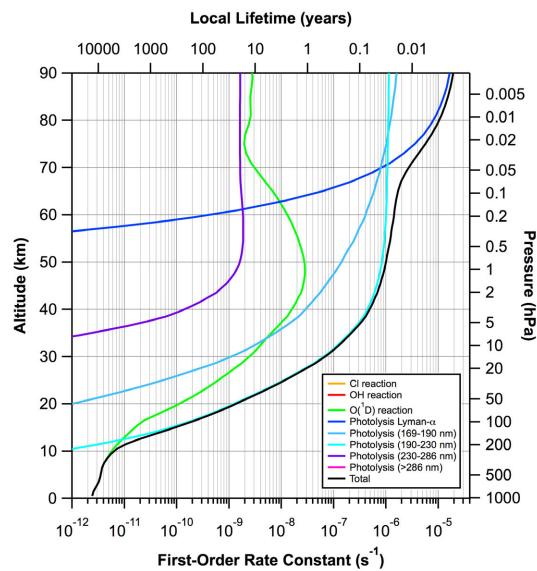
JPL10-6 Parameters

τ_{Global} 95.4 (90.4-98.4) yrs



SPARC Parameters

93.6 (86.6-100.7) yrs



4. $\text{CF}_2\text{ClCF}_2\text{Cl}$ (CFC-114)

JPL10-6 Parameters

τ_{Global} 204.2 (186.1-217.8) yrs

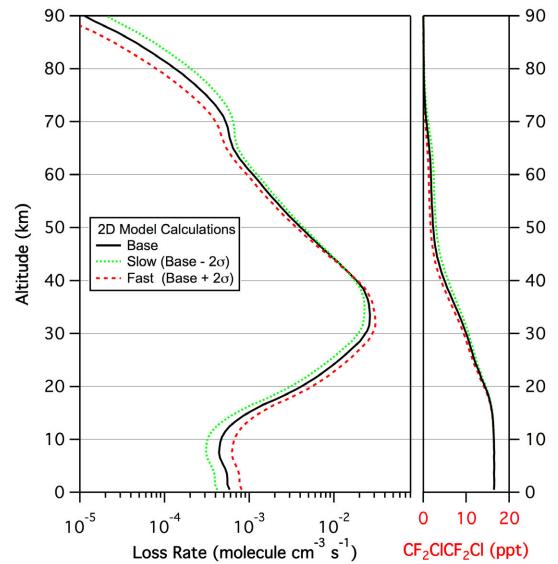
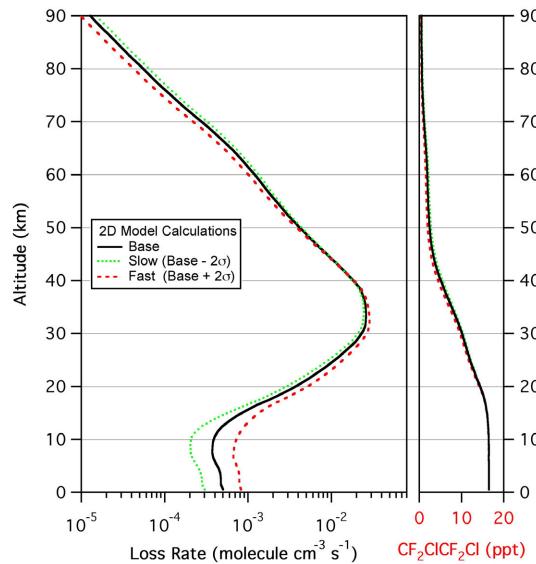
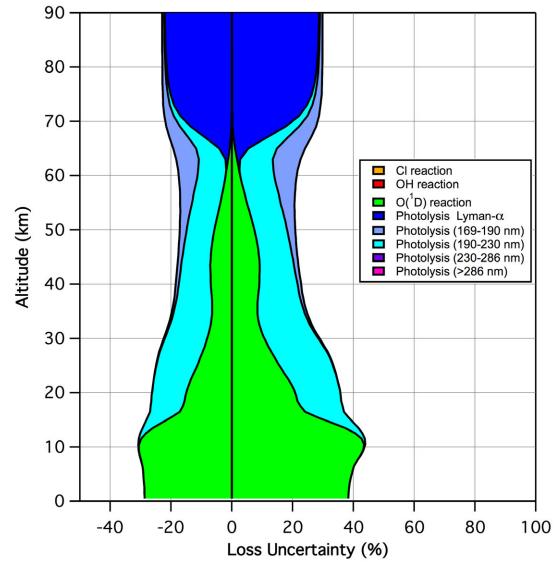
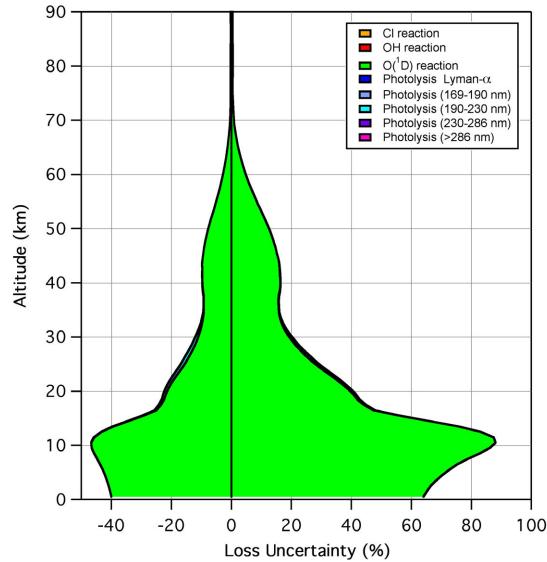
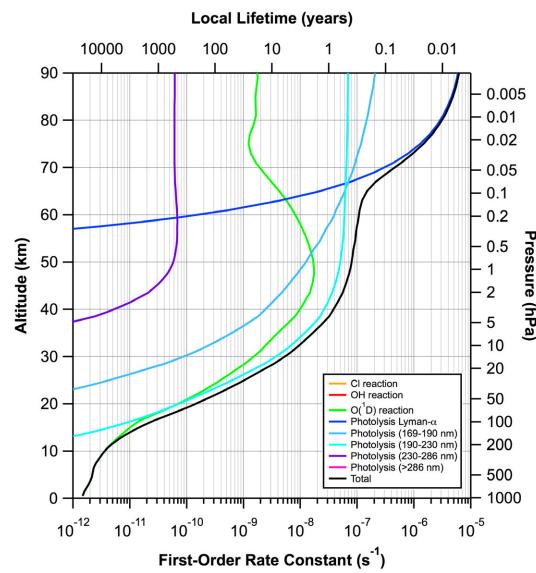
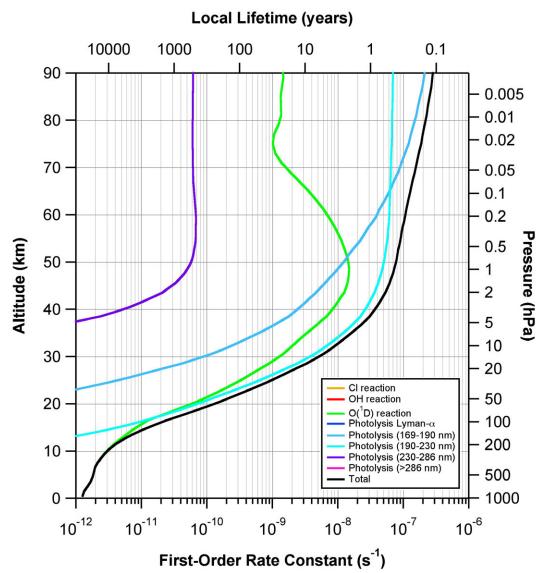
SPARC Parameters

199.7 (178.3-223.9) yrs

Gas-Phase Loss Processes

Estimated Uncertainties

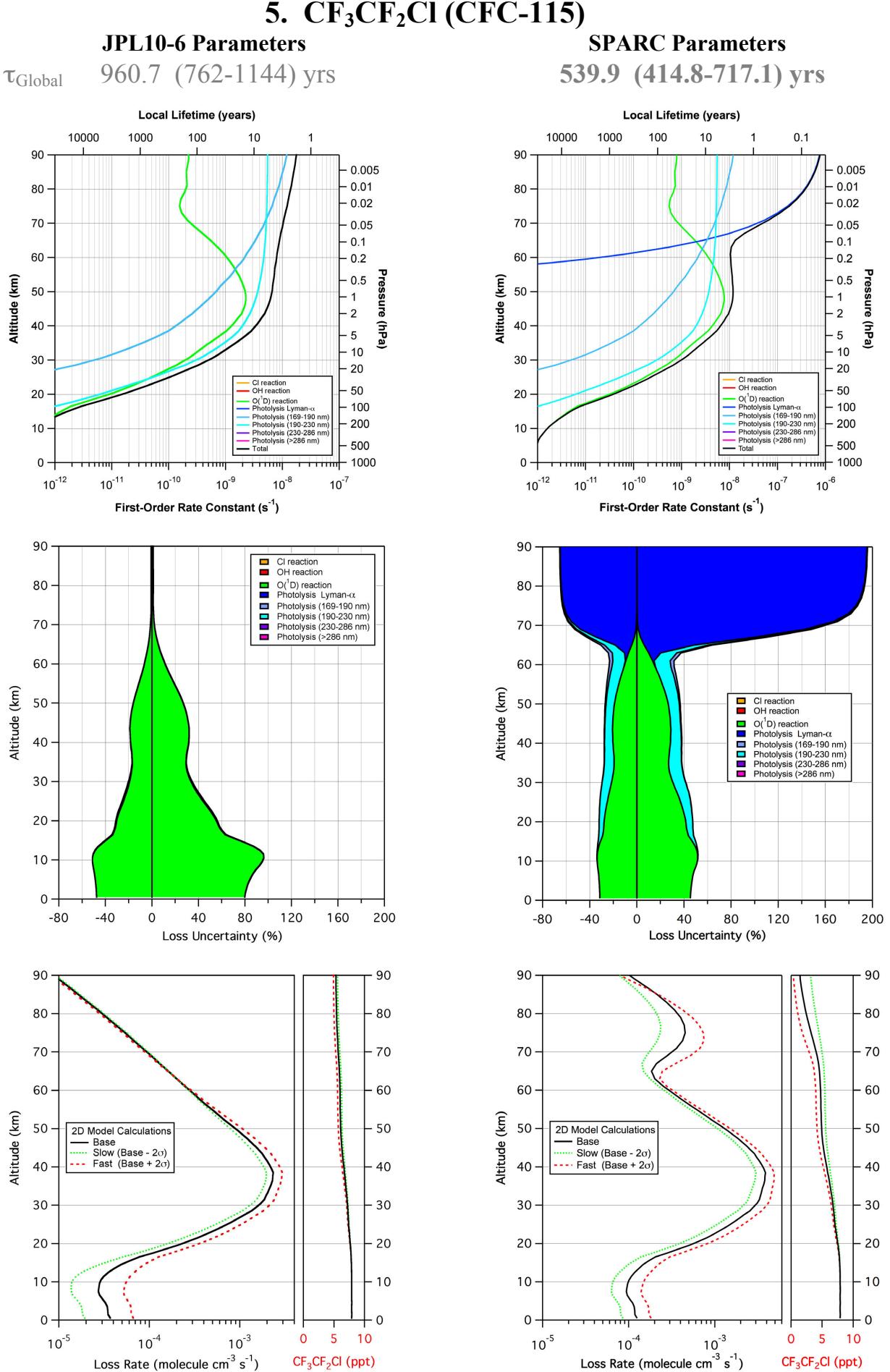
Molecular Loss Rates, Uncertainties, and Profiles



Gas-Phase Loss Processes

Estimated Uncertainties

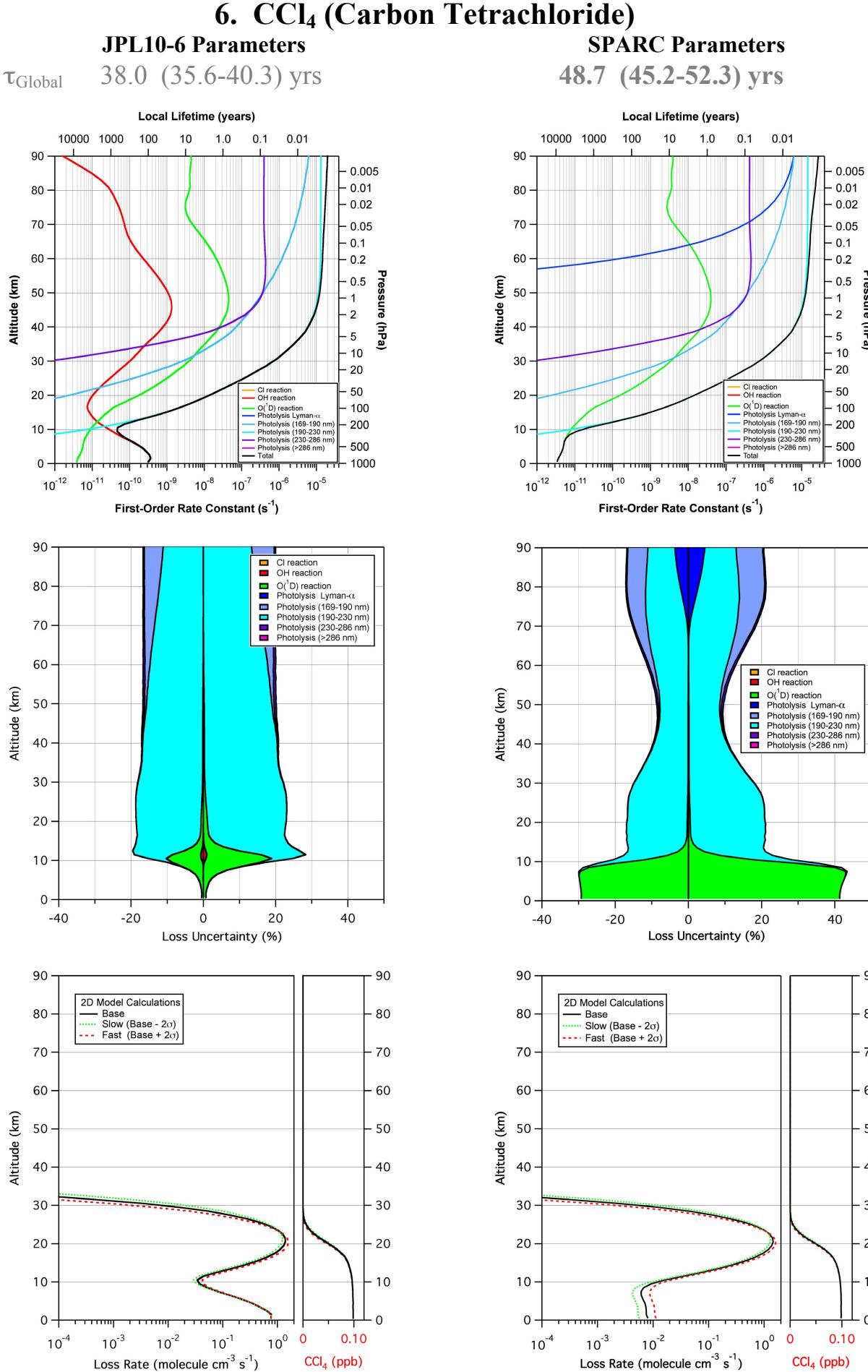
Molecular Loss Rates, Uncertainties, and Profiles

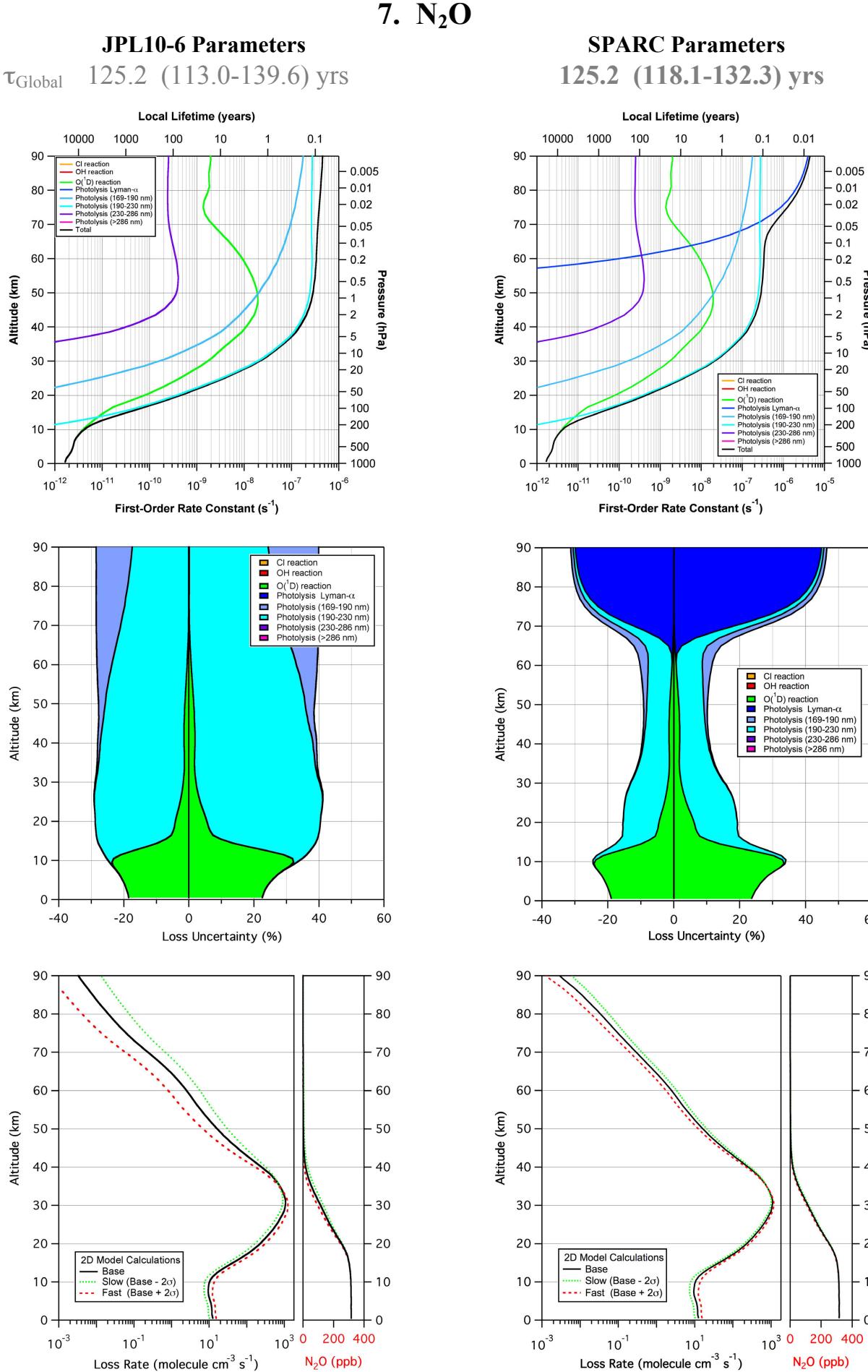


Gas-Phase Loss Processes

Estimated Uncertainties

Molecular Loss Rates, Uncertainties, and Profiles

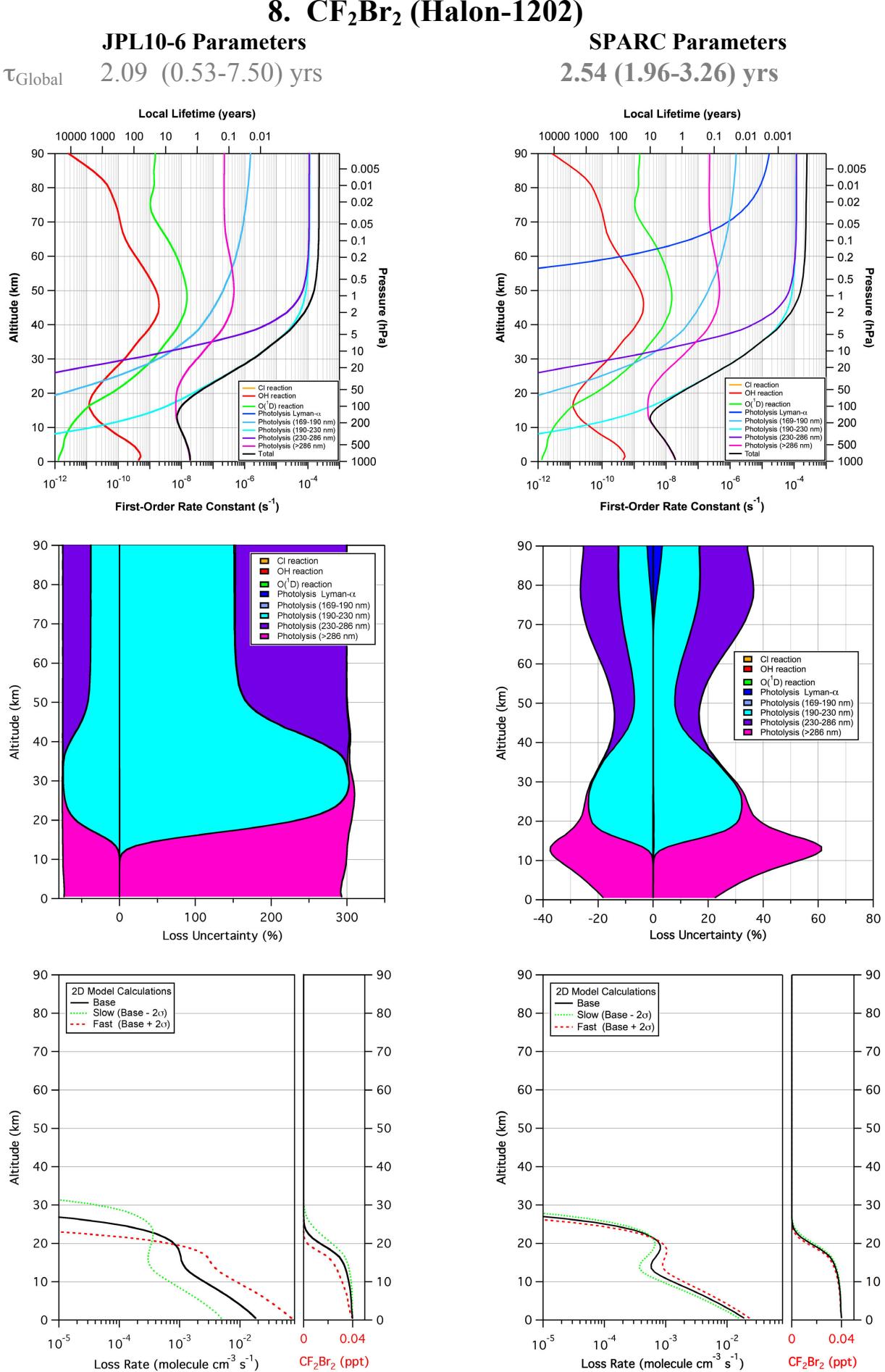


Gas-Phase Loss Processes**Estimated Uncertainties****Molecular Loss Rates,
Uncertainties, and Profiles**

Gas-Phase Loss Processes

Estimated Uncertainties

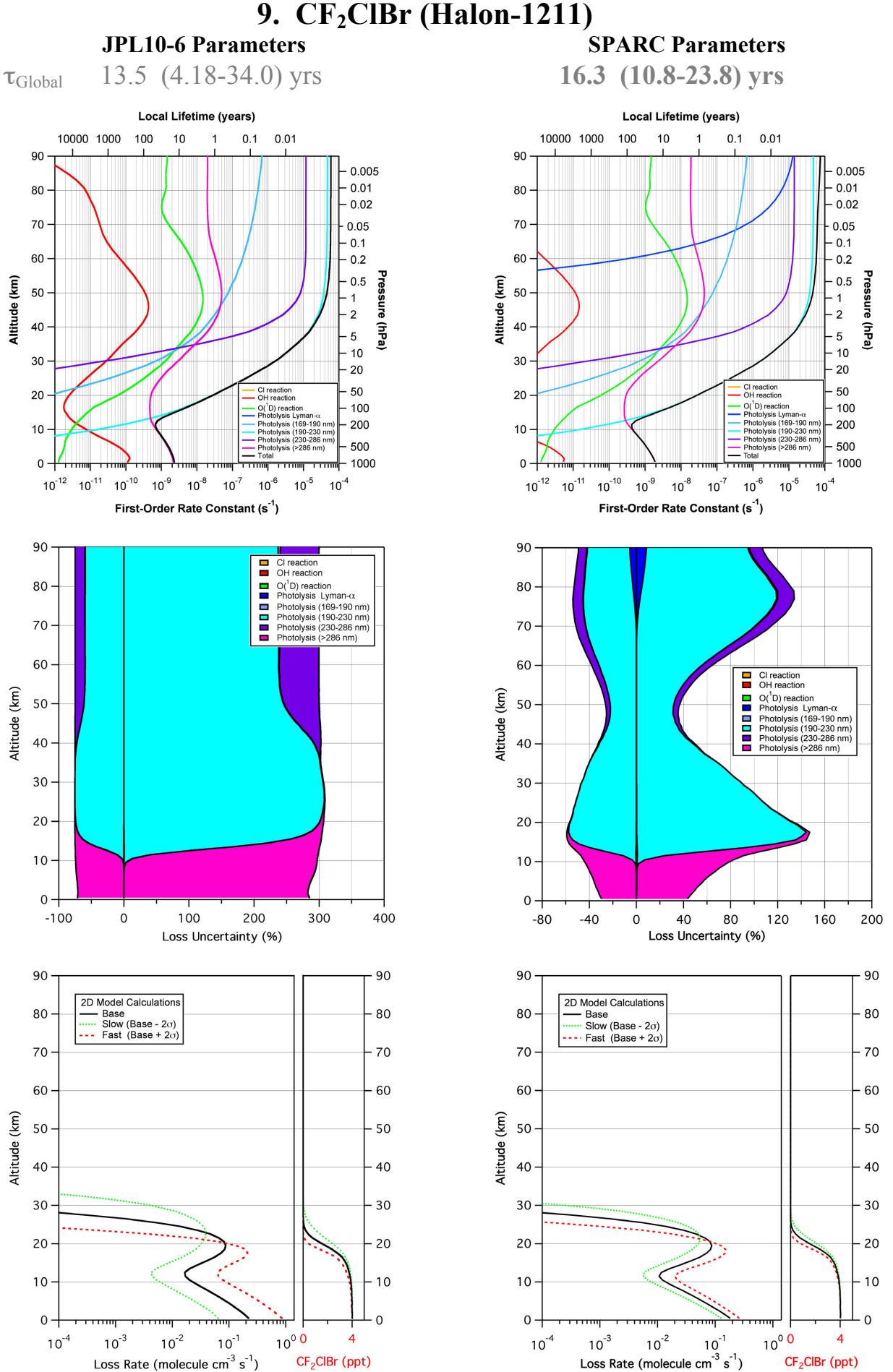
Molecular Loss Rates, Uncertainties, and Profiles



Gas-Phase Loss Processes

Estimated Uncertainties

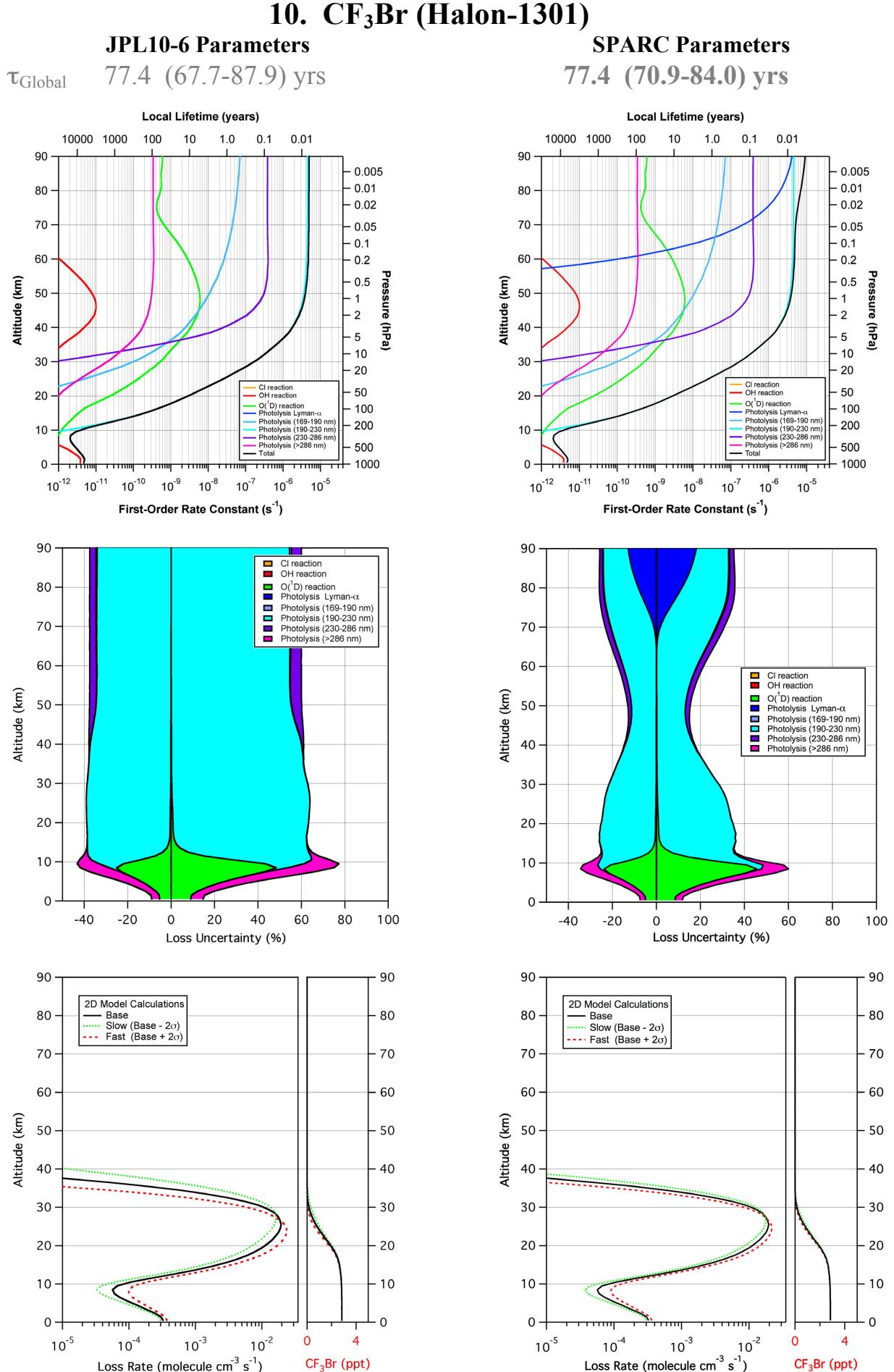
Molecular Loss Rates, Uncertainties, and Profiles



Gas-Phase Loss Processes

Estimated Uncertainties

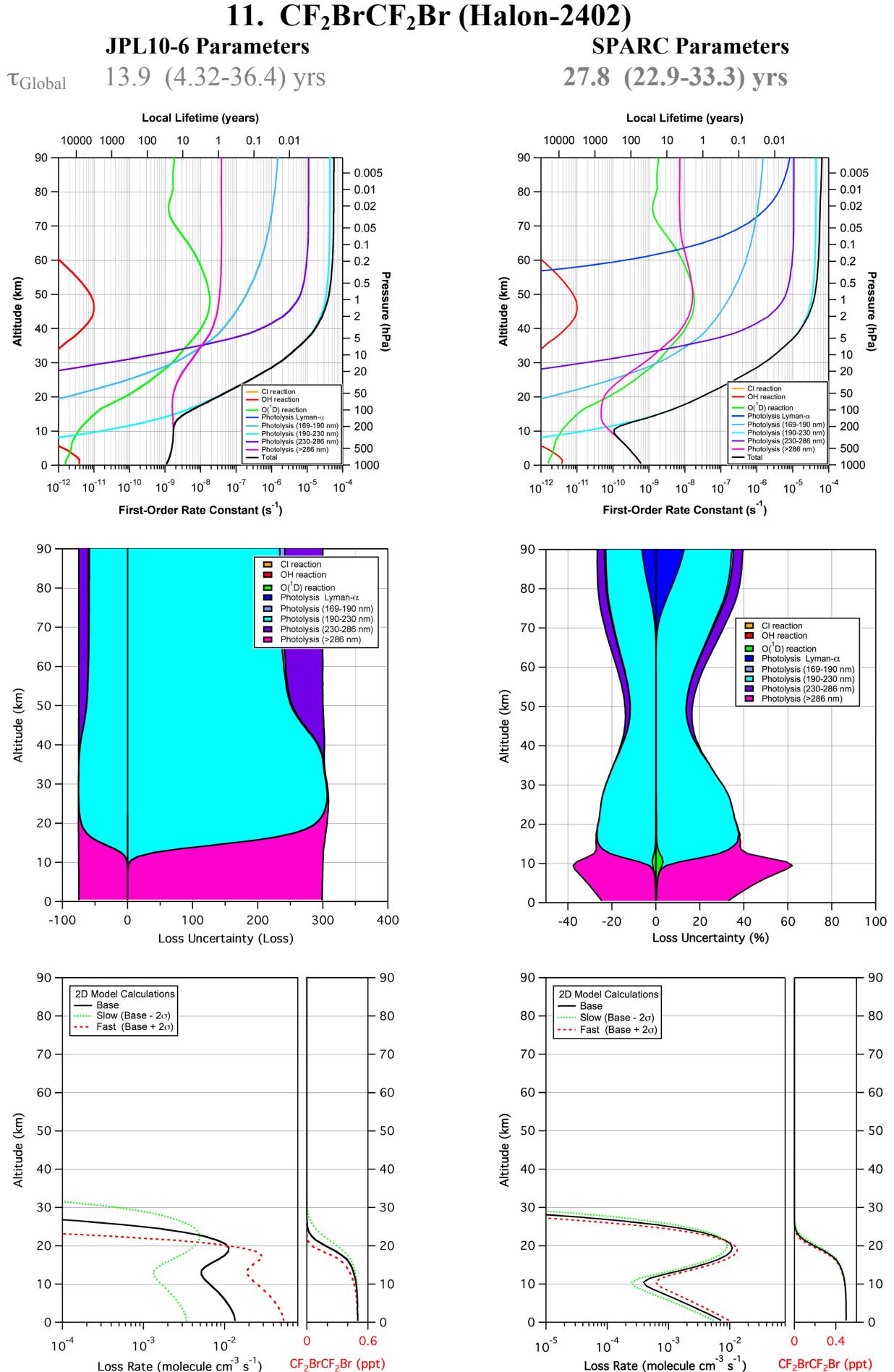
Molecular Loss Rates, Uncertainties, and Profiles



Gas-Phase Loss Processes

Estimated Uncertainties

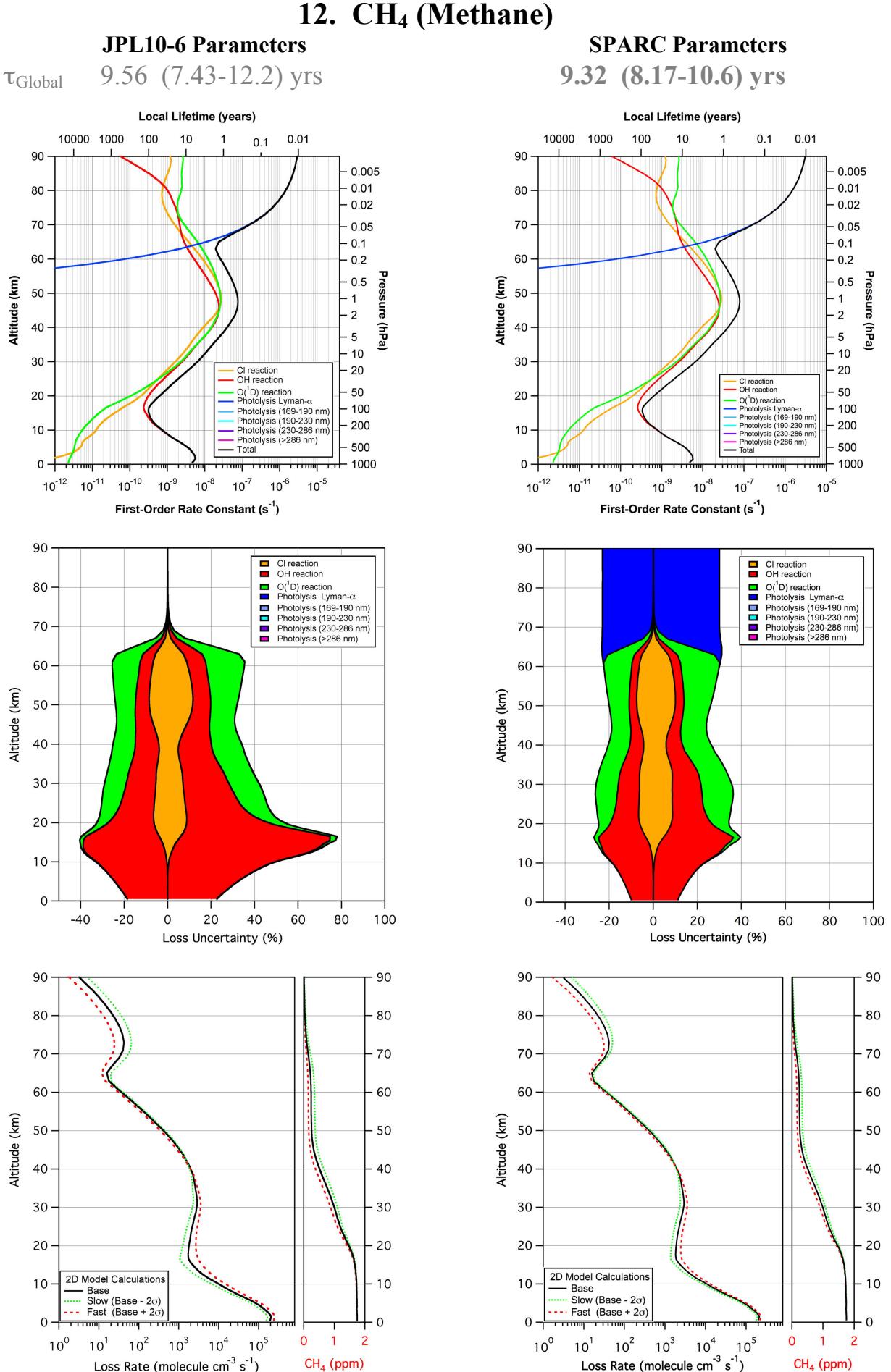
Molecular Loss Rates, Uncertainties, and Profiles



Gas-Phase Loss Processes

Estimated Uncertainties

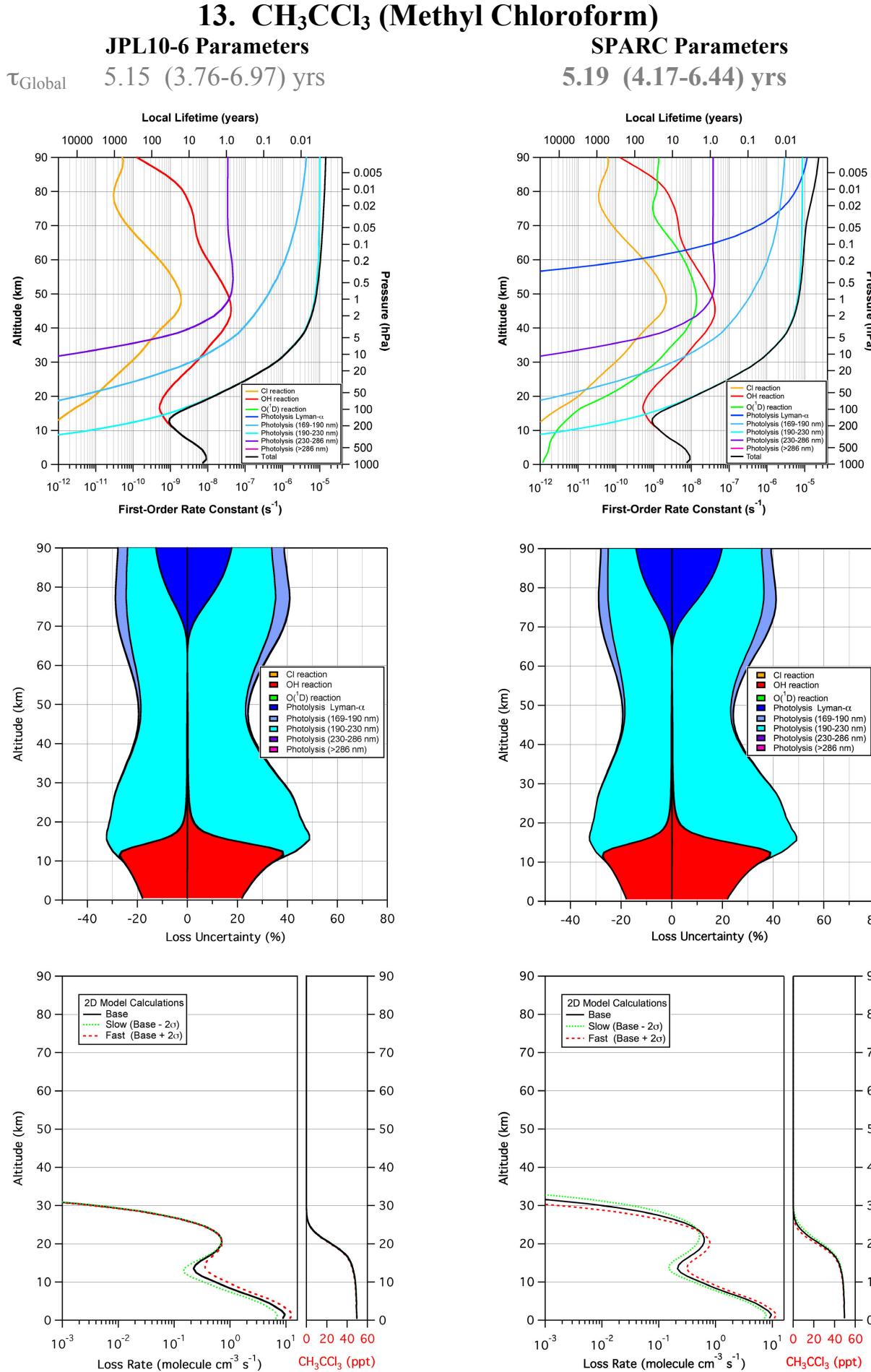
Molecular Loss Rates, Uncertainties, and Profiles



Gas-Phase Loss Processes

Estimated Uncertainties

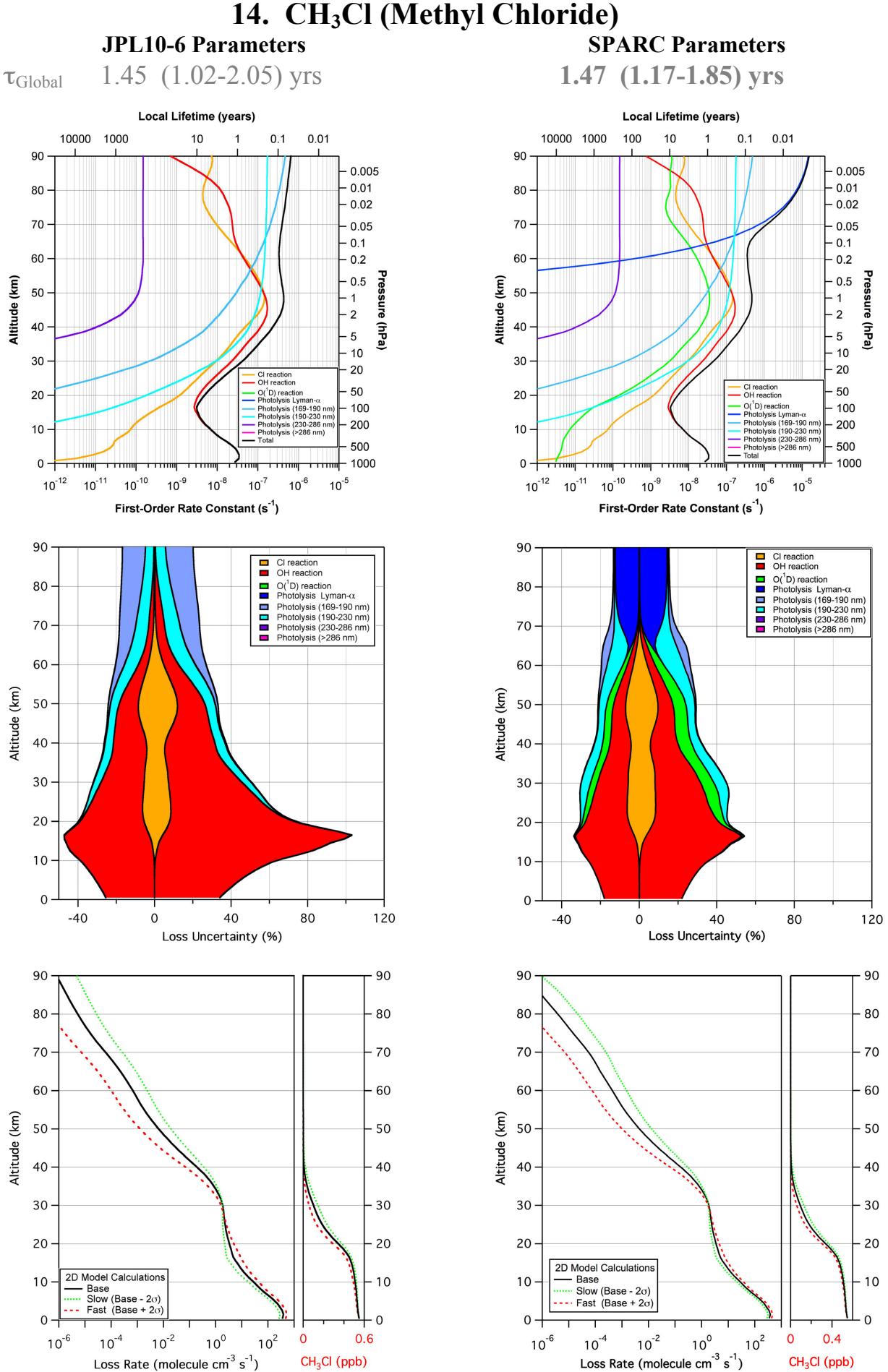
Molecular Loss Rates, Uncertainties, and Profiles



Gas-Phase Loss Processes

Estimated Uncertainties

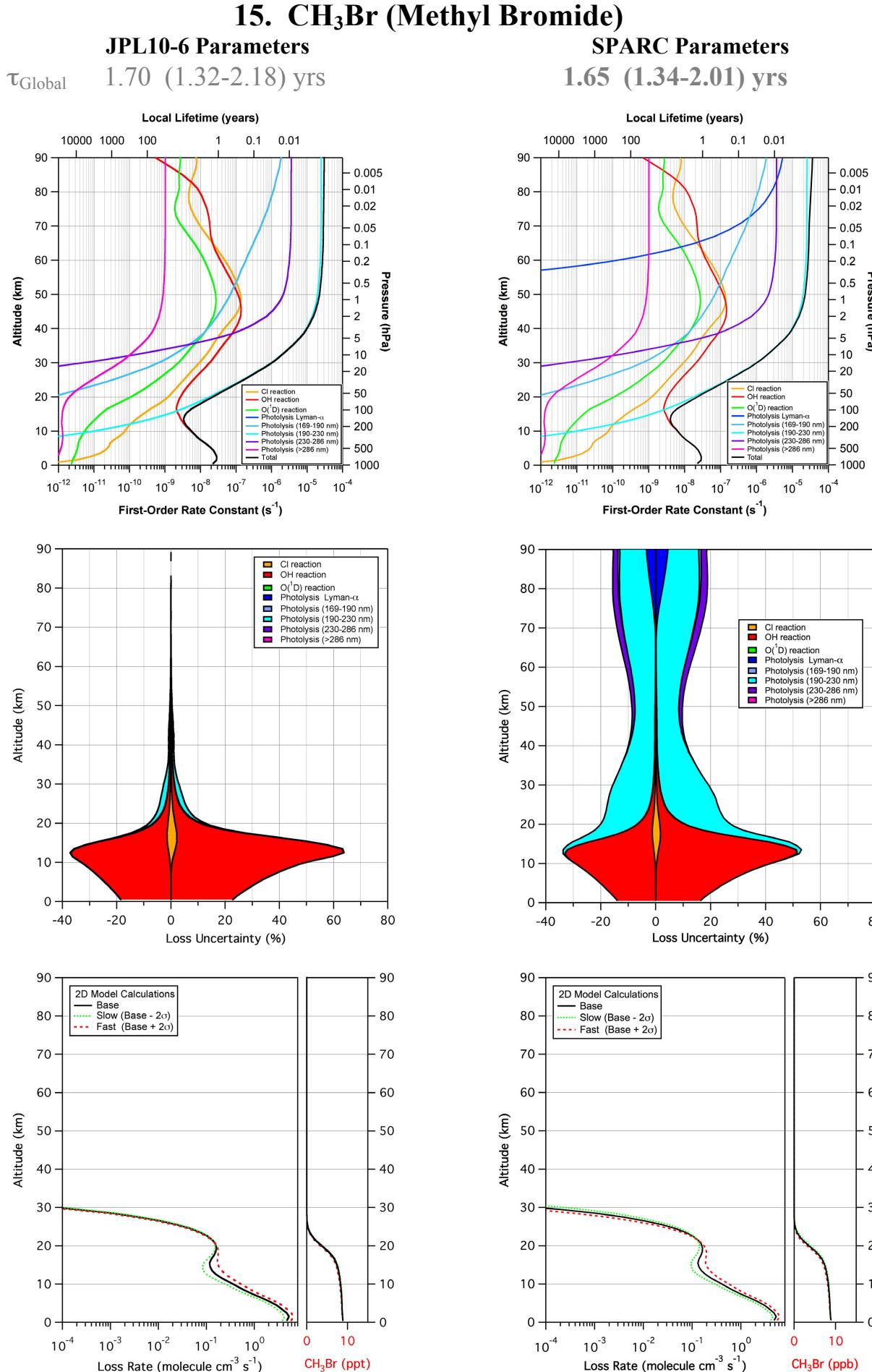
Molecular Loss Rates, Uncertainties, and Profiles



Gas-Phase Loss Processes

Estimated Uncertainties

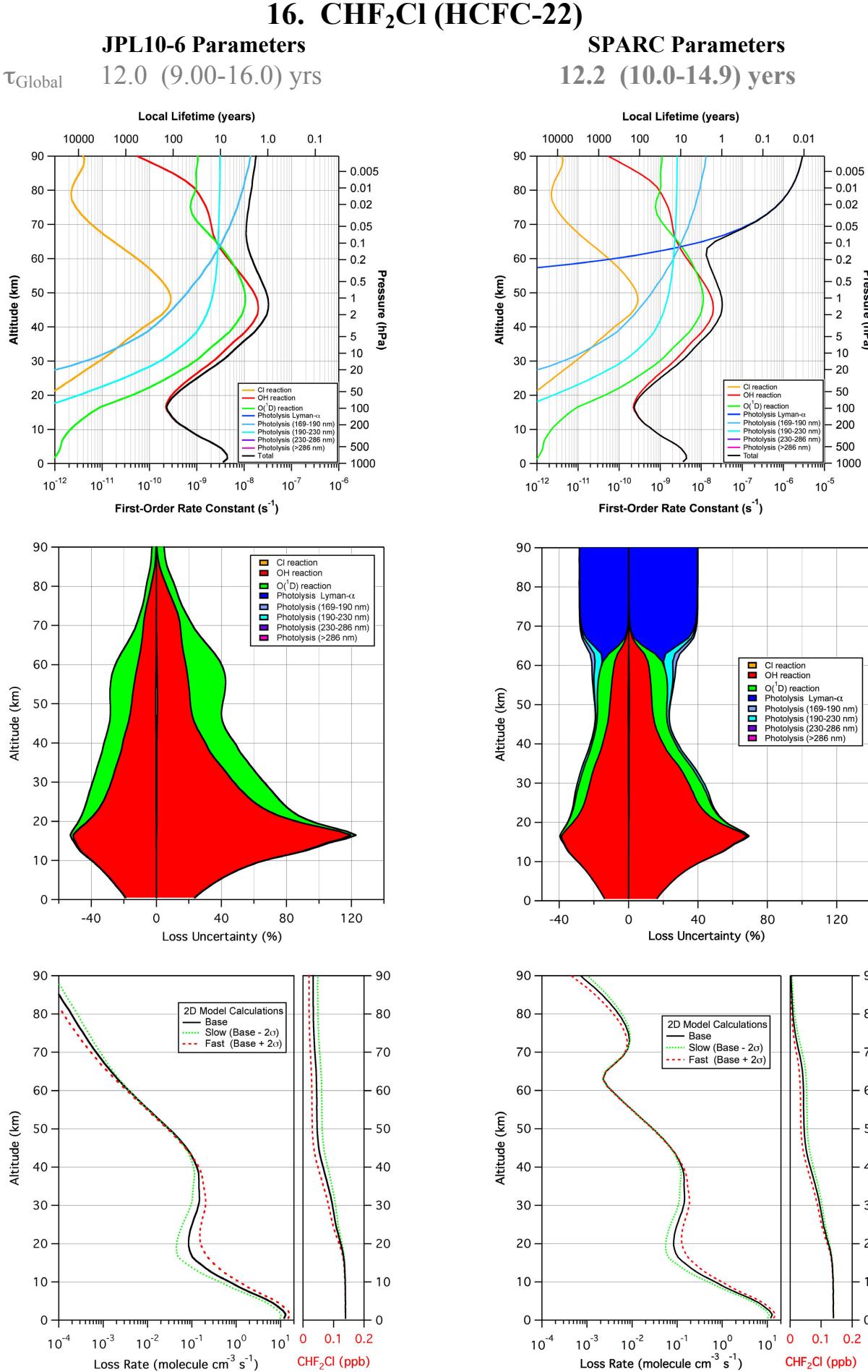
Molecular Loss Rates, Uncertainties, and Profiles



Gas-Phase Loss Processes

Estimated Uncertainties

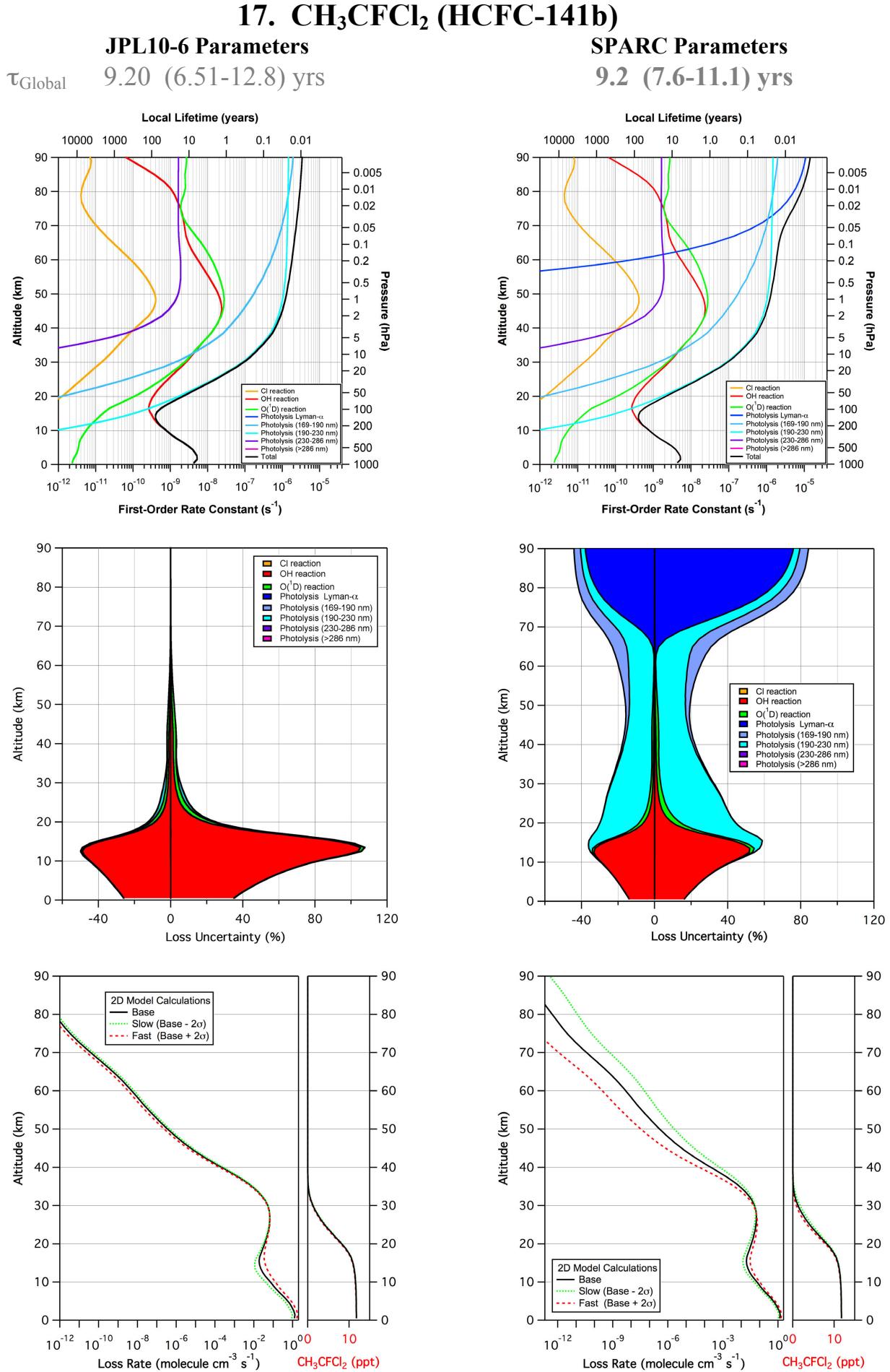
Molecular Loss Rates, Uncertainties, and Profiles



Gas-Phase Loss Processes

Estimated Uncertainties

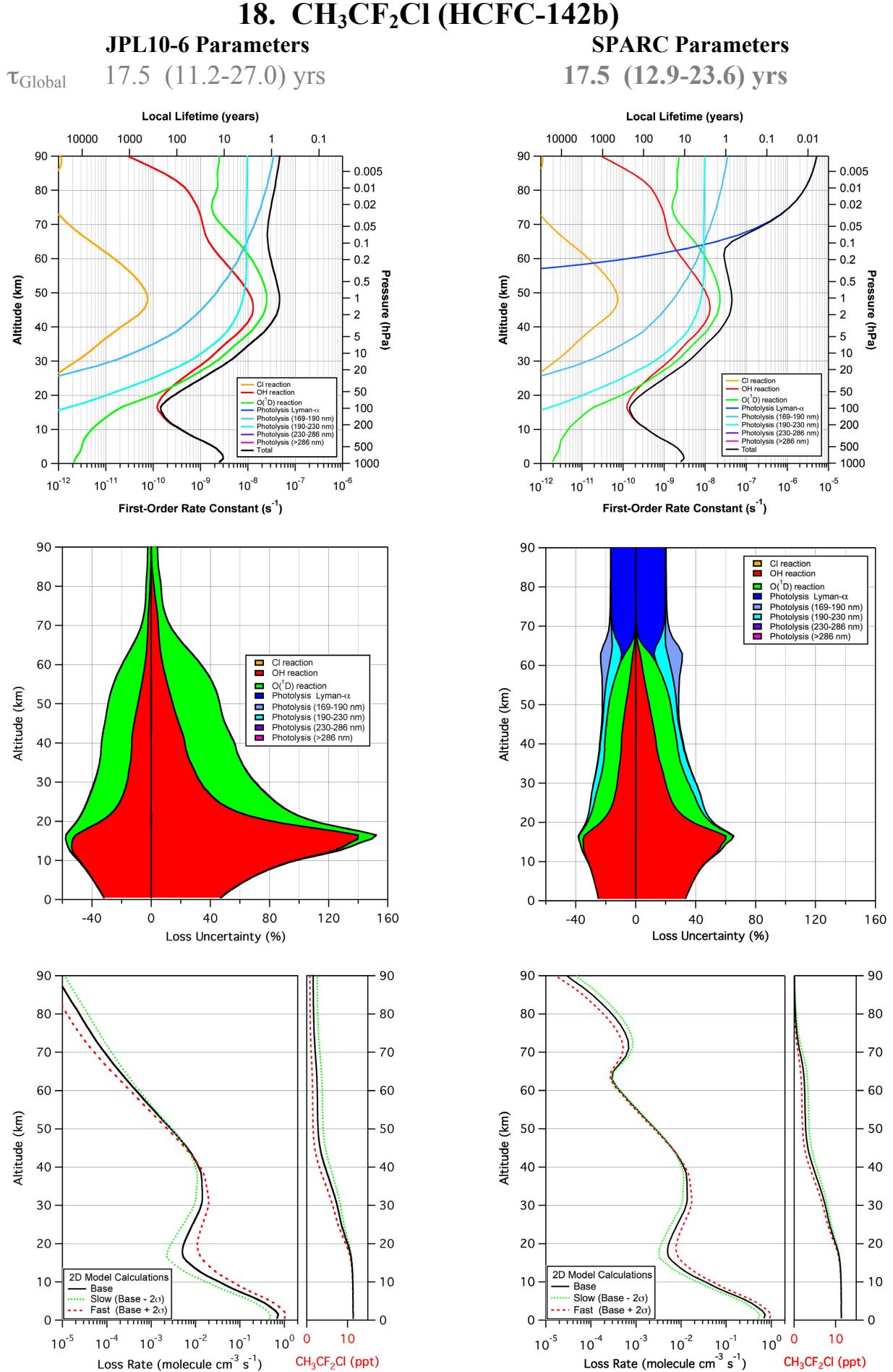
Molecular Loss Rates, Uncertainties, and Profiles



Gas-Phase Loss Processes

Estimated Uncertainties

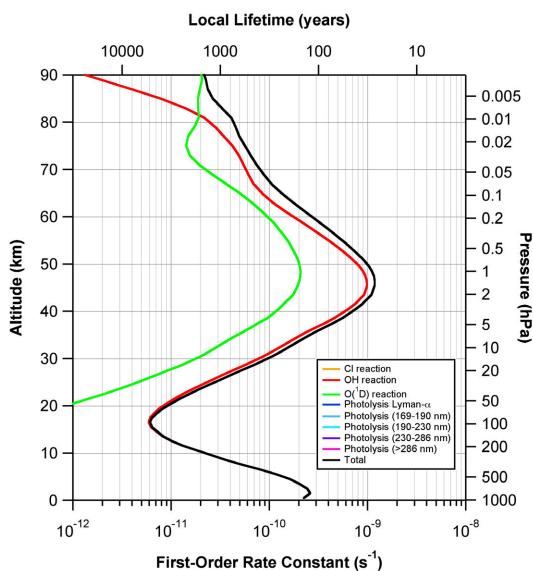
Molecular Loss Rates, Uncertainties, and Profiles



19. CHF₃ (HFC-23)

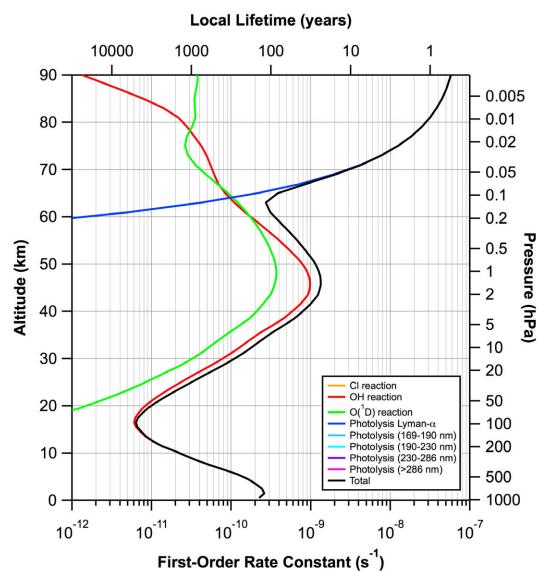
JPL10-6 Parameters

τ_{Global} 226.4 (160.2-319.5) yrs



SPARC Parameters

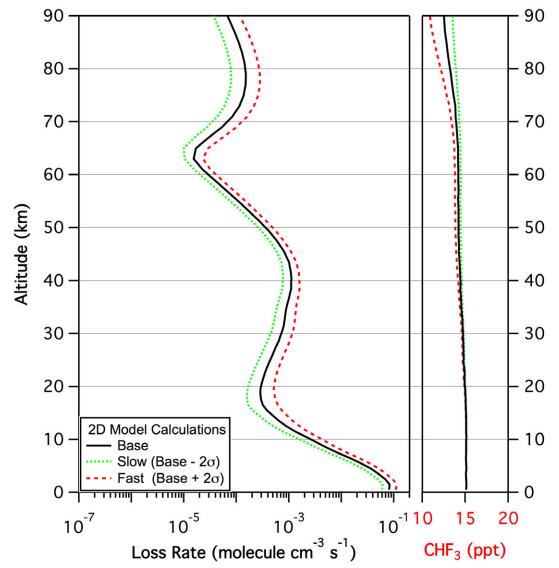
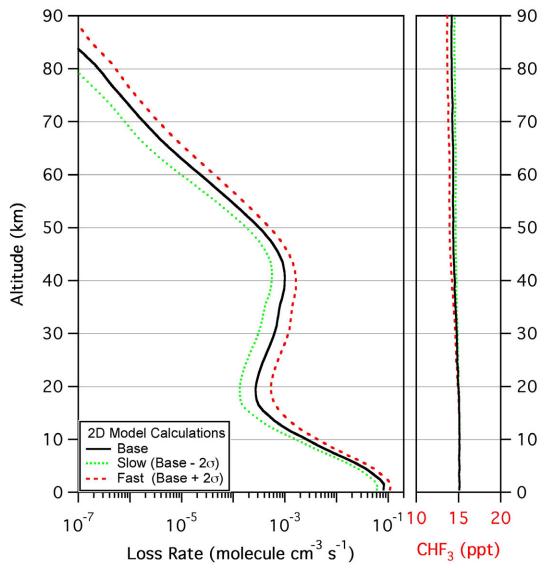
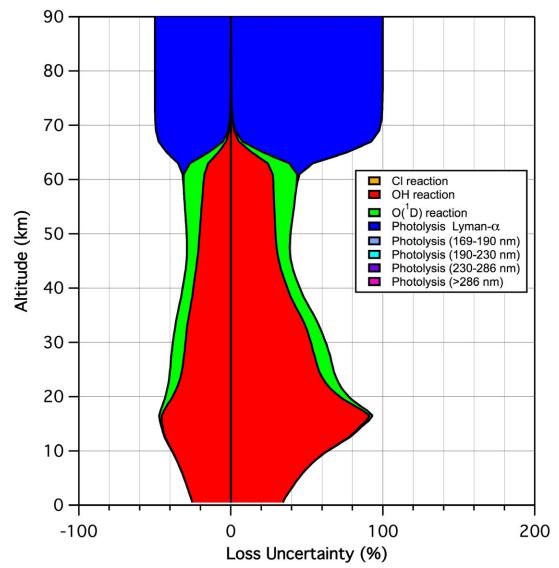
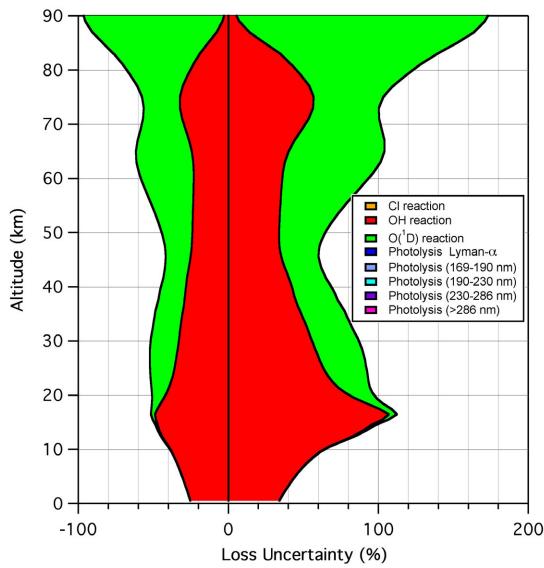
223.8 (159.4-313.3) yrs



Gas-Phase Loss Processes

Estimated Uncertainties

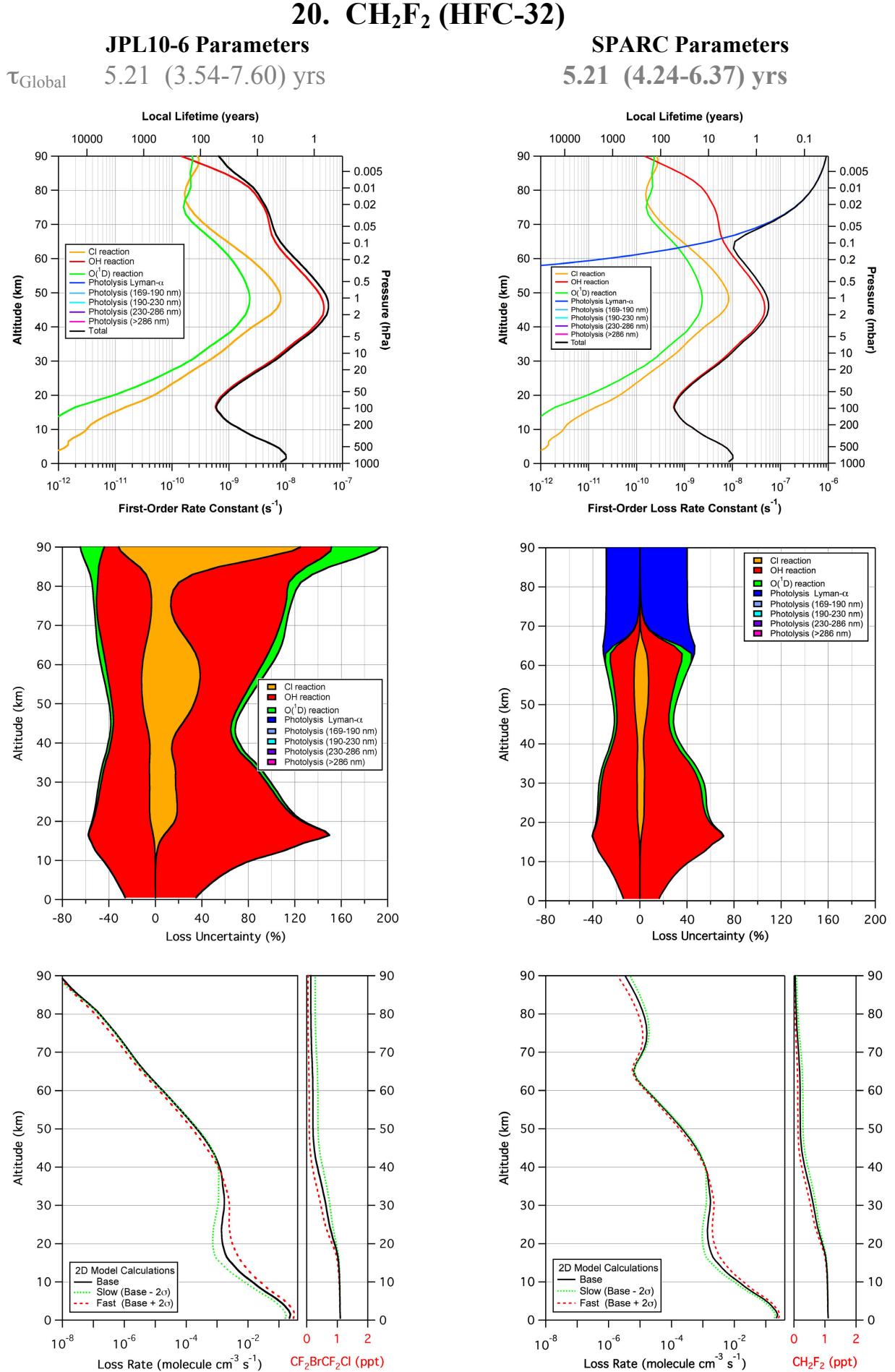
Molecular Loss Rates, Uncertainties, and Profiles

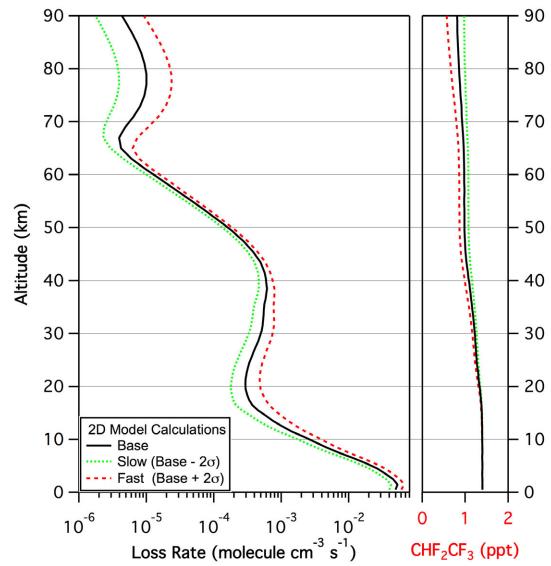
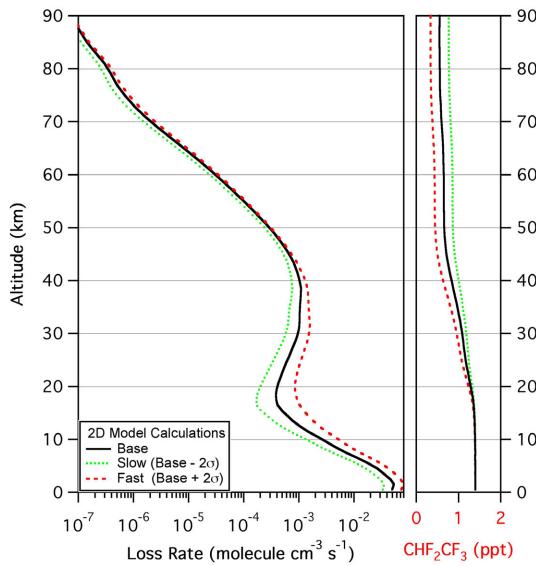
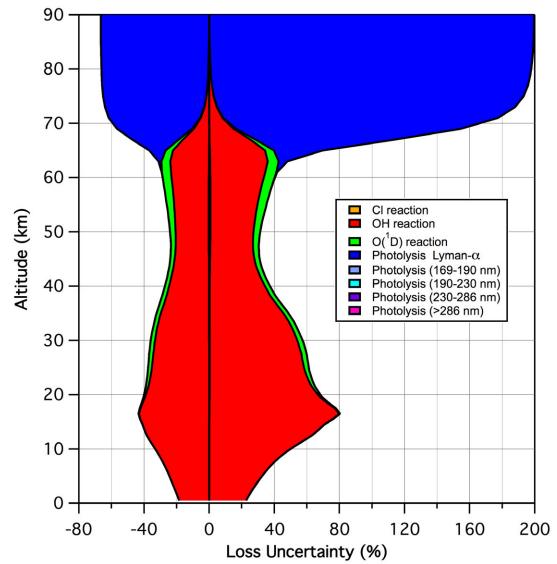
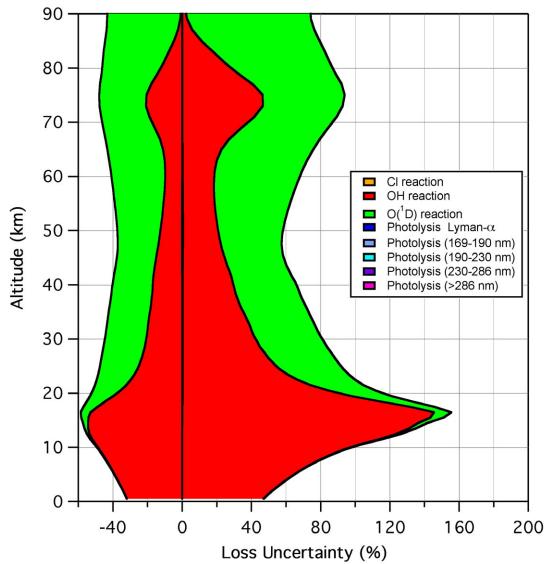
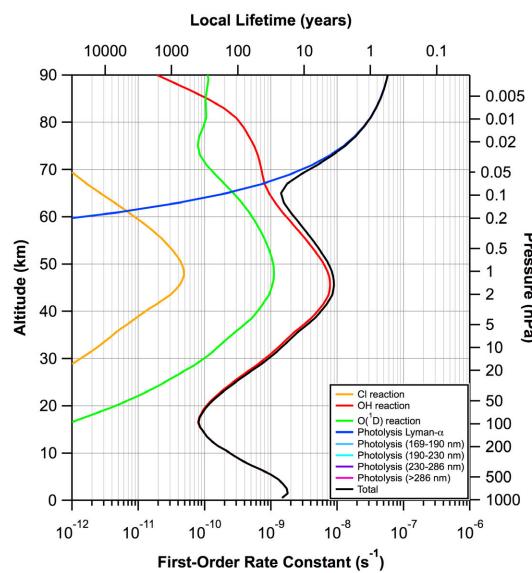
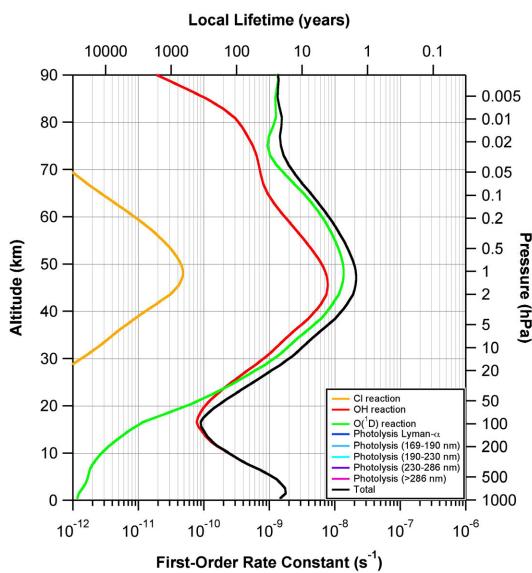


Gas-Phase Loss Processes

Estimated Uncertainties

Molecular Loss Rates, Uncertainties, and Profiles

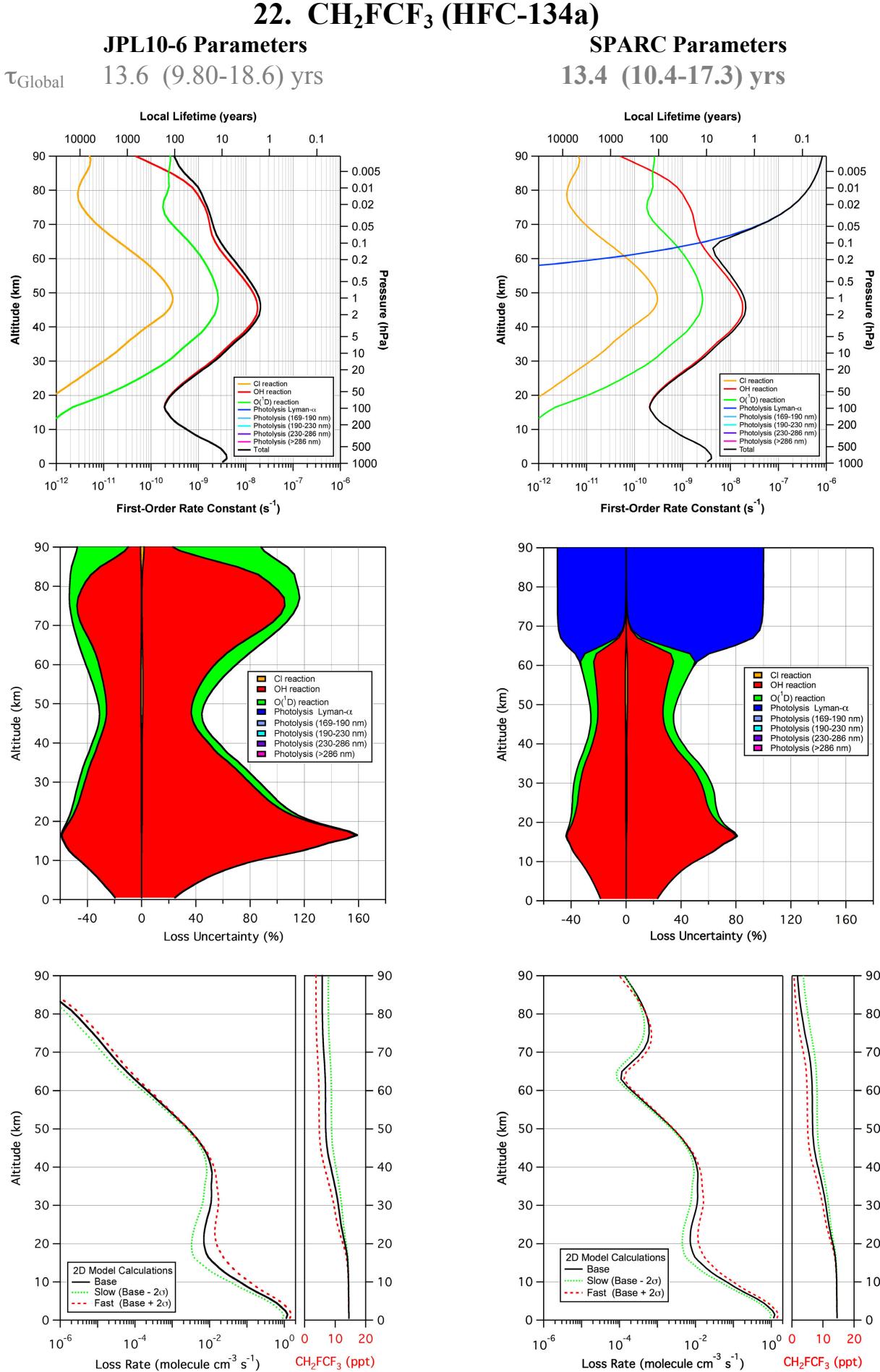


Gas-Phase Loss Processes**Estimated Uncertainties****Molecular Loss Rates,
Uncertainties, and Profiles****21. CHF₂CF₃ (HFC-125)****JPL10-6 Parameters** $\tau_{\text{Global}} = 29.3 \text{ (18.6-46.0) yrs}$ **SPARC Parameters** $\tau_{\text{Global}} = 30.6 \text{ (23.7-39.5) yrs}$ 

Gas-Phase Loss Processes

Estimated Uncertainties

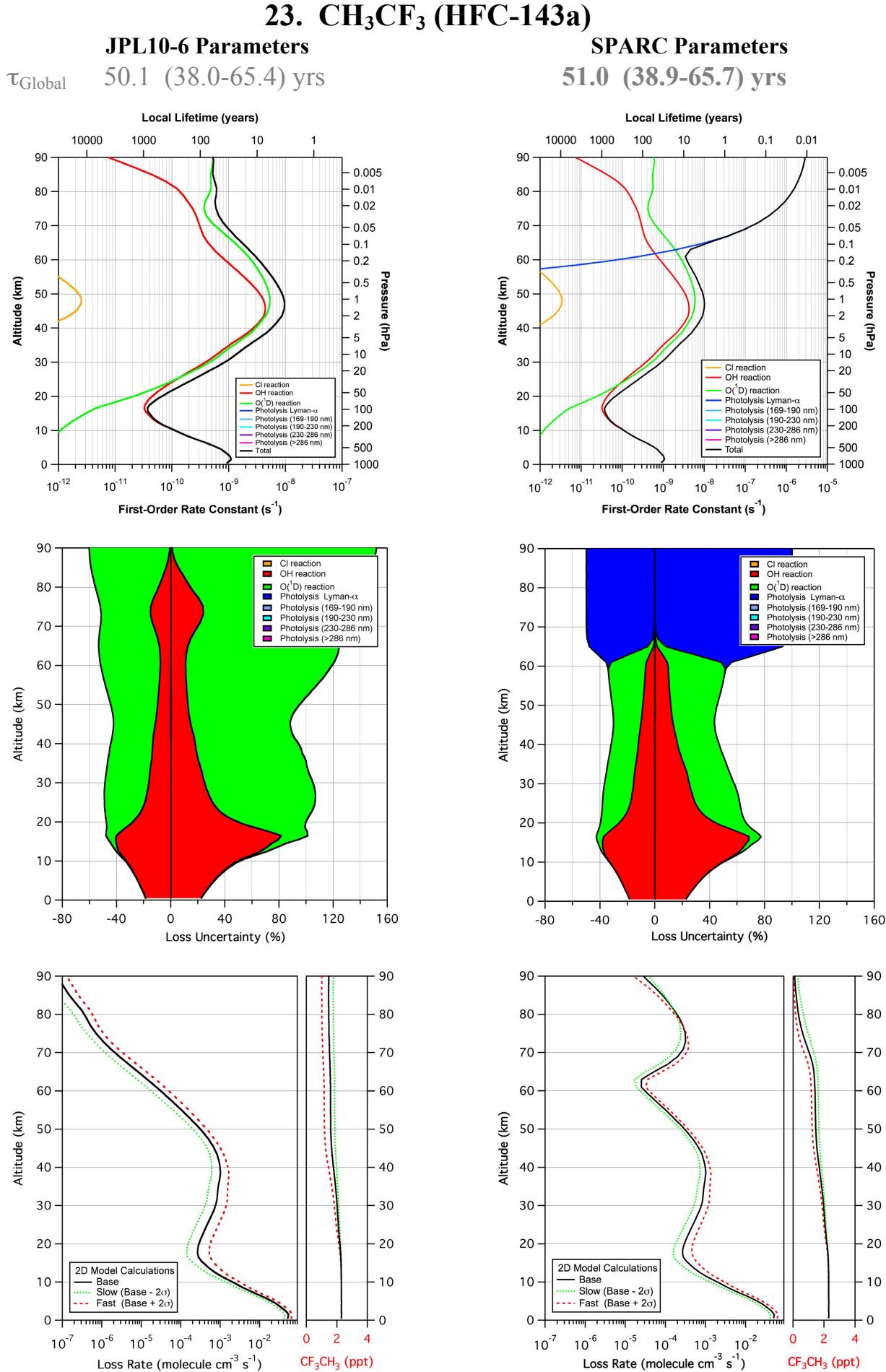
Molecular Loss Rates, Uncertainties, and Profiles



Gas-Phase Loss Processes

Estimated Uncertainties

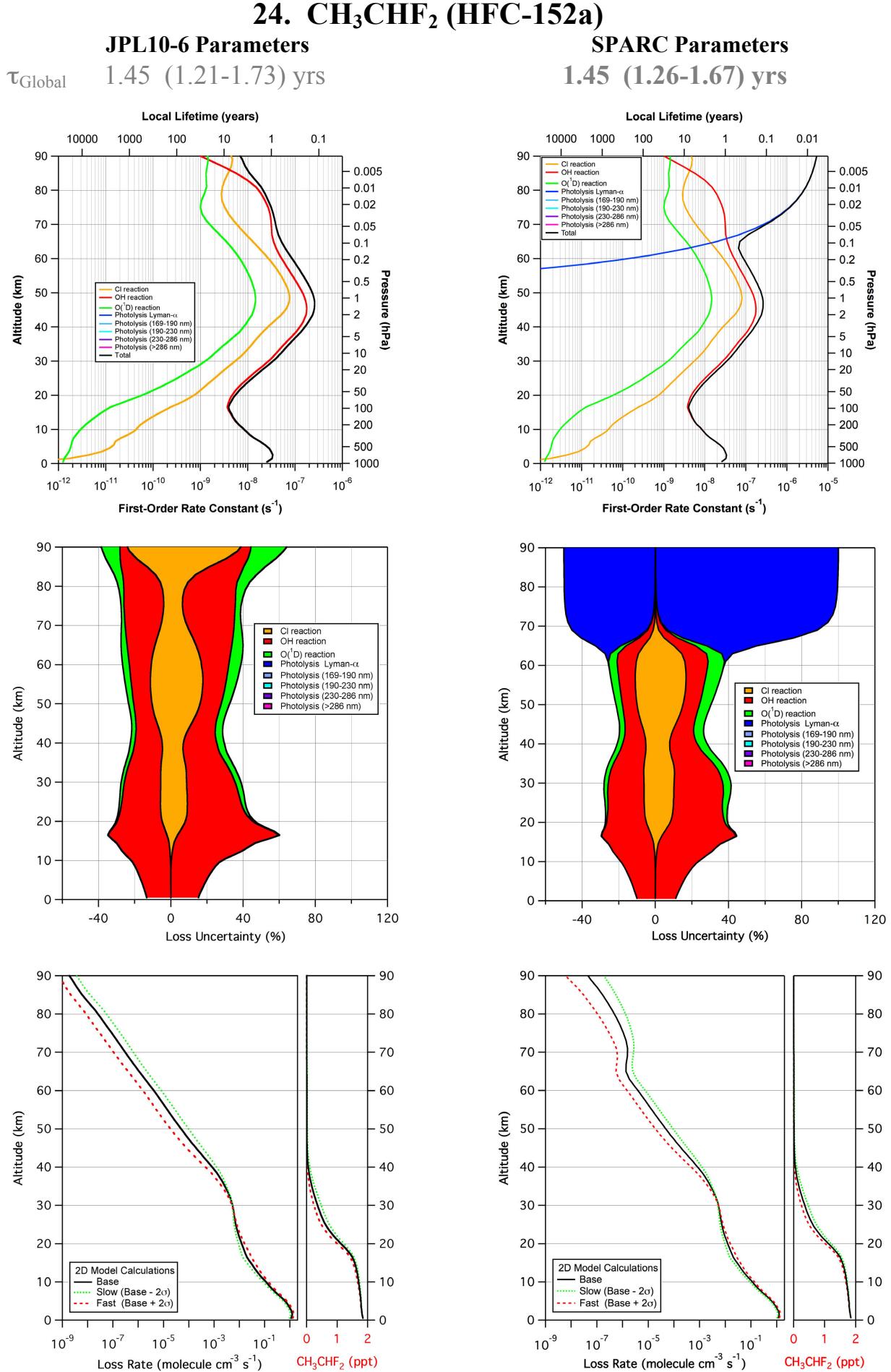
Molecular Loss Rates, Uncertainties, and Profiles



Gas-Phase Loss Processes

Estimated Uncertainties

Molecular Loss Rates, Uncertainties, and Profiles



Gas-Phase Loss Processes

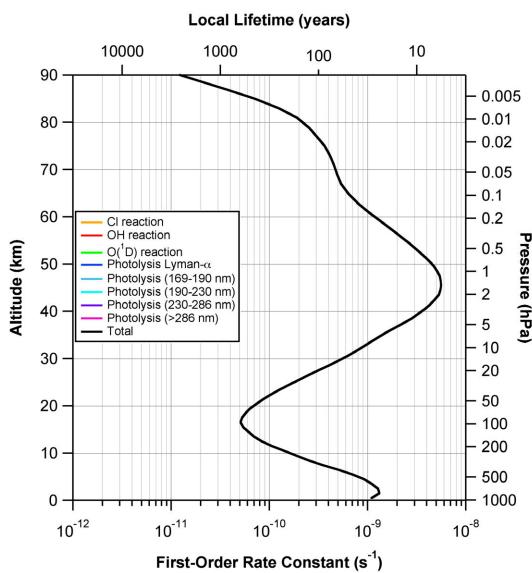
Estimated Uncertainties

Molecular Loss Rates, Uncertainties, and Profiles

25. $\text{CF}_3\text{CHFCF}_3$ (HFC-227ea)

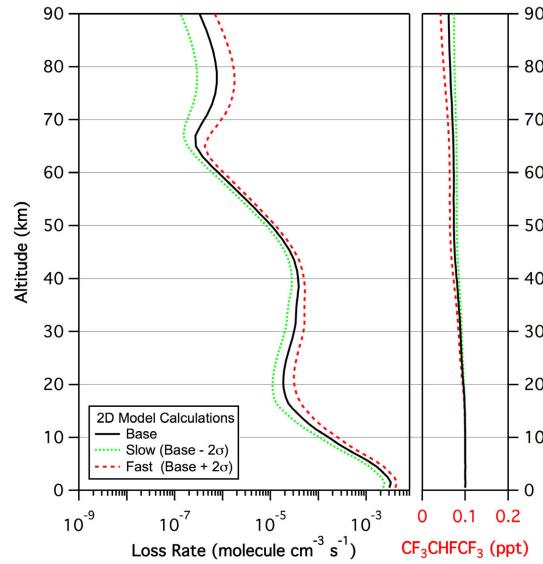
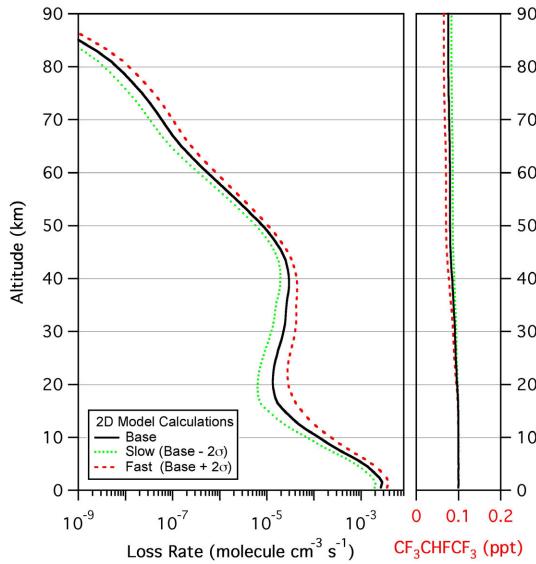
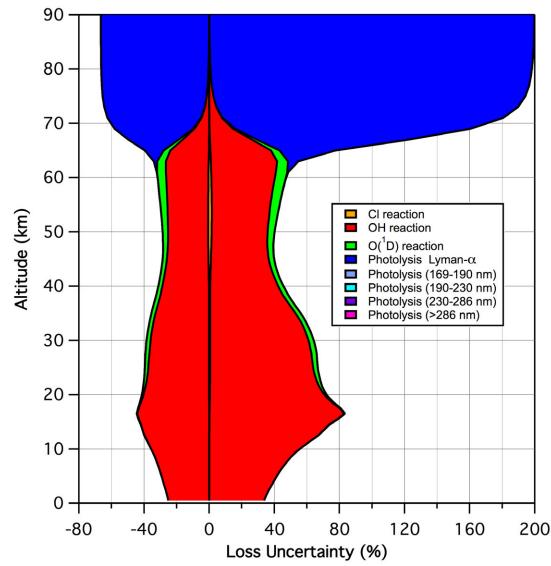
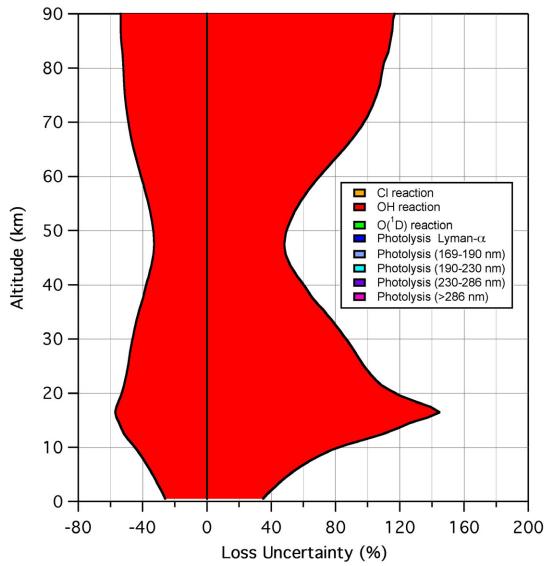
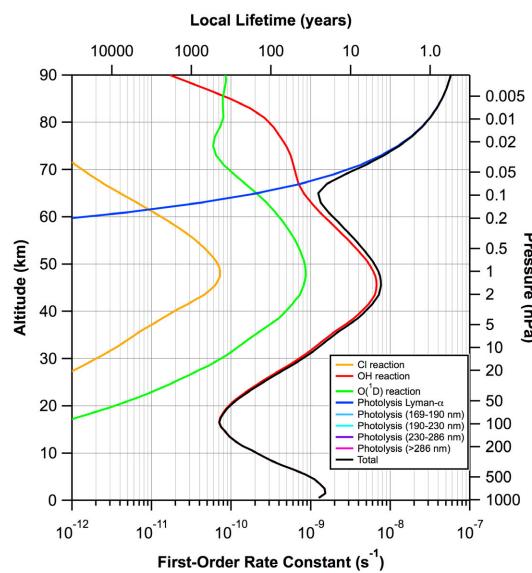
JPL10-6 Parameters

τ_{Global} 42.3 (29.0-61.3) yrs



SPARC Parameters

35.6 (25.6-49.4) yrs



Gas-Phase Loss Processes

Estimated Uncertainties

Molecular Loss Rates, Uncertainties, and Profiles

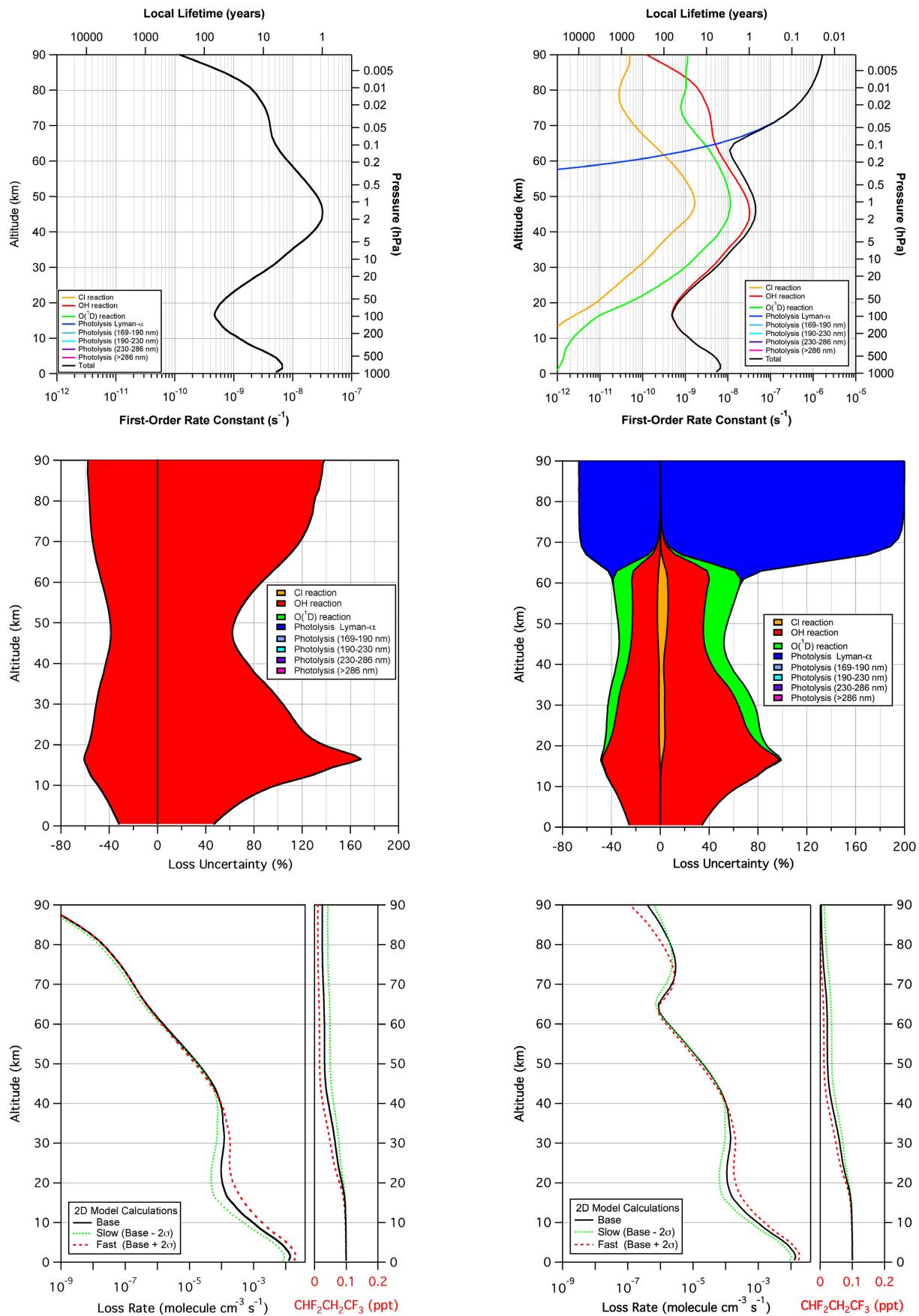
26. CHF₂CH₂CF₃ (HFC-245fa)

JPL10-6 Parameters

$\tau_{\text{Global}} = 7.79 \text{ (4.85-12.4) yrs}$

SPARC Parameters

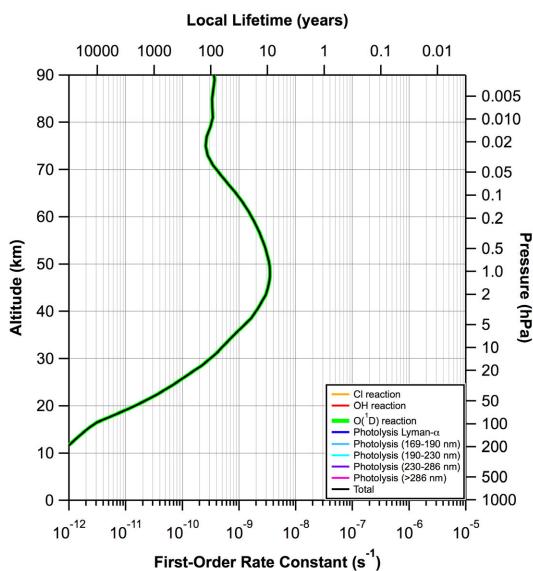
$\tau_{\text{Global}} = 7.73 \text{ (5.44-10.9) yrs}$



27. NF₃

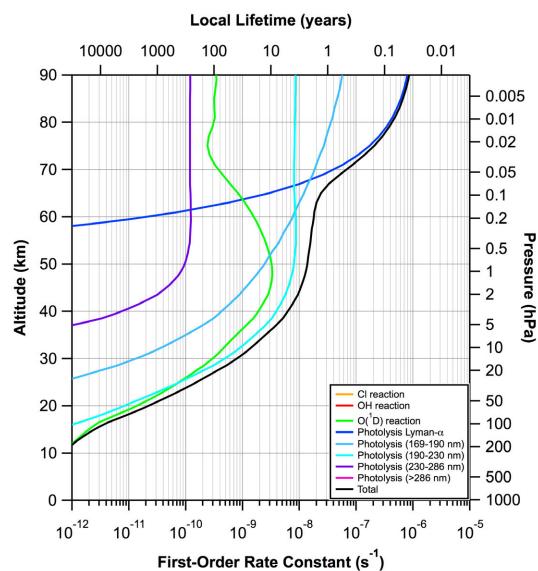
JPL10-6 Parameters

τ_{Global} 1588 (1031-2951) yrs



SPARC Parameters

569.2 (493.8-679.2) yrs



Gas-Phase Loss Processes

Estimated Uncertainties

Molecular Loss Rates, Uncertainties, and Profiles

