Rate Coefficient Measurements and Theoretical Analysis of the OH + (*E*)-$CF_3CH=CHCF_3$ Reaction

Munkhbayar Baasandorj,[1,2,#] Paul Marshall,[3] Robert L. Waterland,[4]
A.R. Ravishankara,[1,$] and James B. Burkholder[1]*

[1] Earth System Research Laboratory, Chemical Sciences Division, National Oceanic and Atmospheric Administration, 325 Broadway, Boulder, CO 80305-3328
[2] Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309
[3] Department of Chemistry, University of North Texas, P.O. Box 305070, Denton, Texas 76203-5070
[4] DuPont Central R&D, Wilmington, Delaware 19880, United States

Current Address: Utah Division of Air Quality, Salt Lake, UT, USA
$ Current Address: Department of Chemistry and Department of Atmospheric Science, Colorado State University, Fort Collins, CO, 80532 USA

*Corresponding author: James B. Burkholder

e-mail: James.B.Burkholder@noaa.gov

Phone: (303)-497-3252

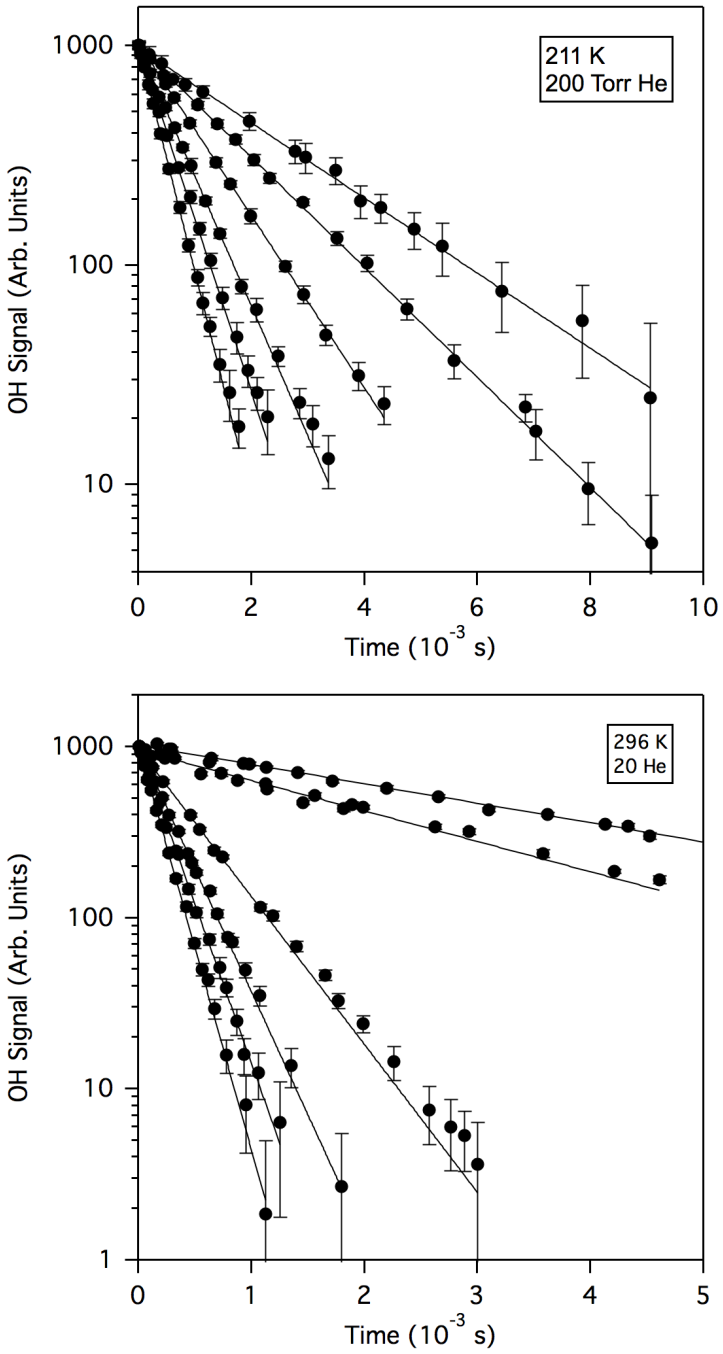


Figure S1. Representative OH temporal profiles measured in the OH + (*E*)-$CF_3CH{=}CHCF_3$ reaction at 211 K (200 Torr, He) and 296 K (20 Torr, He) for (*E*)-$CF_3CH{=}CHCF_3$ concentrations of 0, 2.21, 6.95, 13.4, 20.2 and 29.0 × 10^{15} molecule cm^{-3} and 0, 1.02, 12.4, 22.5, 30.8 and 38.0 × 10^{15} molecule cm^{-3} (from top to bottom), respectively. The data has been normalized to the same initial OH signal. The lines are least-squares fits of the data. The error bars are the 2σ precision of the OH signal measurement.

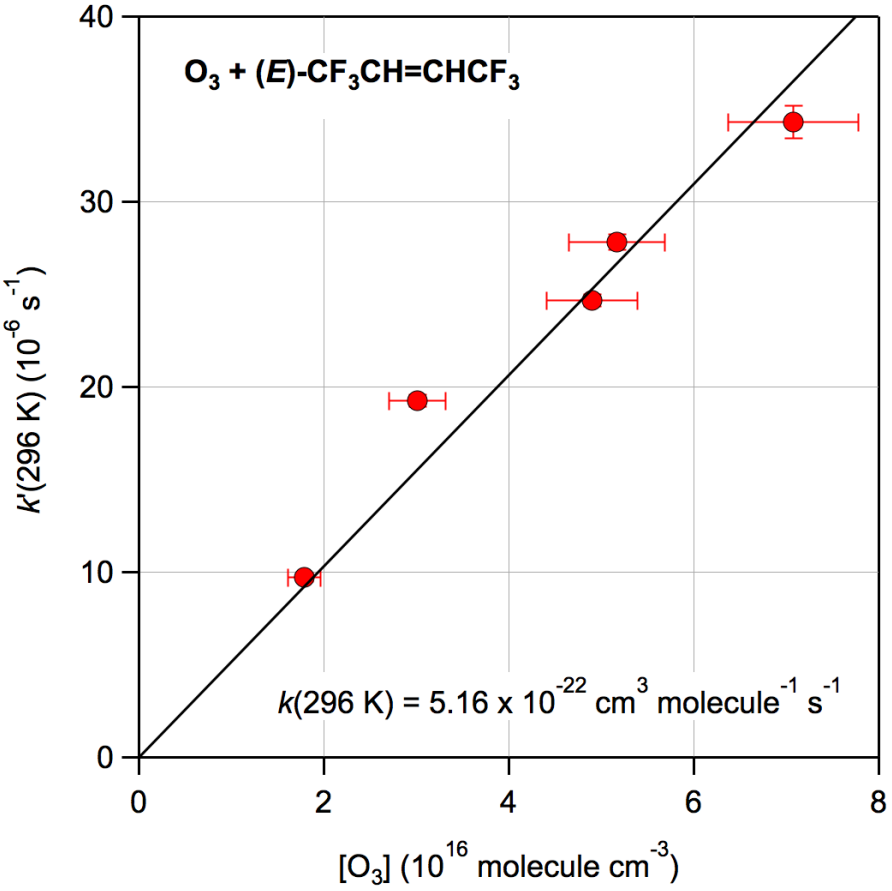
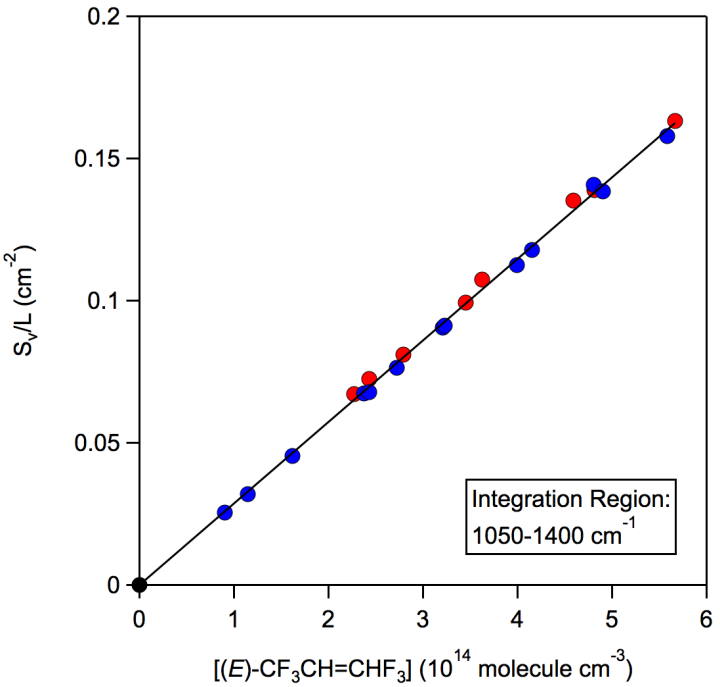
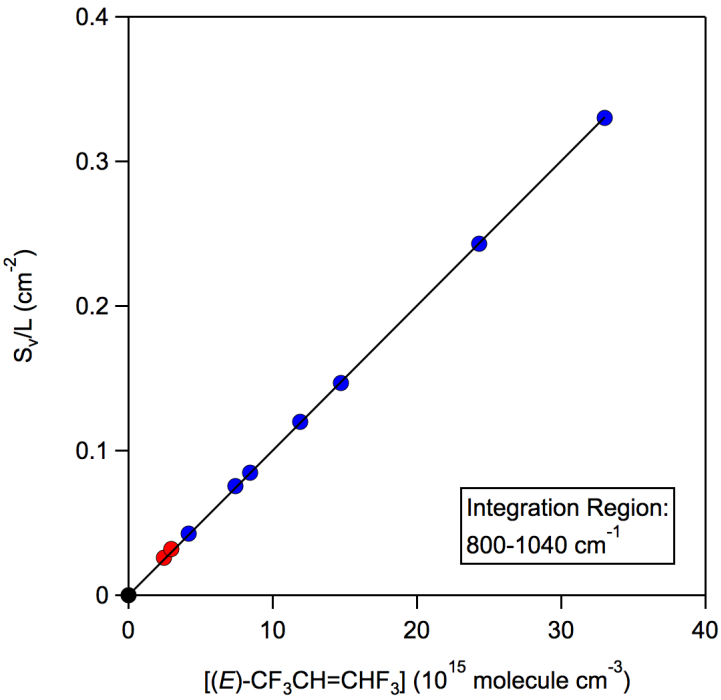


Figure S2. O_3 + (*E*)-$CF_3CH{=}CHCF_3$ reaction rate coefficient determination data.


0.2
0.15
0.1
0.05
0
0
1
2
3
4
5
6
S_v/L (cm^{-2})
[(*E*)-$CF_3CH=CHF_3$] (10^{14} molecule cm^{-3})
Integration Region:
1050-1400 cm^{-1}


0.4
0.3
0.2
0.1
0
0
10
20
30
40
S_v/L (cm^{-2})
[(*E*)-$CF_3CH=CHF_3$] (10^{15} molecule cm^{-3})
Integration Region:
800-1040 cm^{-1}

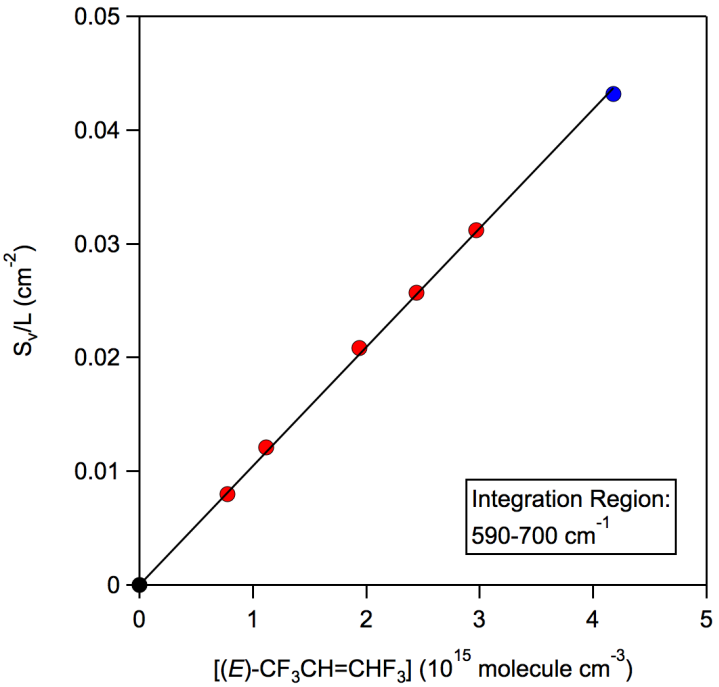


Figure S3. Beer's law plots of the infrared band strengths of (*E*)-$CF_3CH=CHCF_3$ over the wavenumber regions indicated on the graphs. The different colored symbols represent independent measurements using different samples. The band strength results are given in Table 4.

Table S1. Geometries computed with UMP2/cc-pVTZ theory, given as the atomic number followed by x, y and z coordinates (in units of 10^{-10} m) for each atom

Hydroxyl radical (OH)

8	0.000000000	0.000000000	0.107498000
1	0.000000000	0.000000000	-0.859987000

E **$CF_3CH=CHCF_3$**

6	0.032365000	1.931525000	0.000000000
6	-0.424682000	0.509984000	0.000000000
6	0.424682000	-0.509984000	0.000000000
6	-0.032365000	-1.931525000	0.000000000
1	-1.494184000	0.364756000	0.000000000
1	1.494184000	-0.364756000	0.000000000
9	-0.432610000	2.575004000	-1.079438000
9	-0.432610000	2.575004000	1.079438000
9	1.364029000	2.045243000	0.000000000
9	0.432610000	-2.575004000	-1.079438000
9	0.432610000	-2.575004000	1.079438000
9	-1.364029000	-2.045243000	0.000000000

TS for OH addition to *E* $CF_3CH=CHCF_3$

6	1.185521000	1.471252000	0.270033000
6	1.026467000	-0.011073000	0.199117000
6	-0.156343000	-0.596588000	0.242705000
6	-0.275675000	-2.093825000	0.339858000
1	1.939176000	-0.573139000	0.073017000
1	-1.054634000	-0.043671000	0.463976000
9	2.013697000	1.804757000	1.270822000
9	1.726618000	1.944735000	-0.863133000
9	0.028315000	2.104380000	0.467755000
9	-0.223682000	-2.449700000	1.634094000
9	-1.427412000	-2.538974000	-0.148997000
9	0.724465000	-2.717904000	-0.291036000
8	-0.549539000	-0.400798000	-1.733387000
1	0.324506000	-0.470204000	-2.148326000

Z **$CF_3CH=CHCF_3$**

6	0.003389000	1.571916000	0.017776000
6	-0.003389000	0.665859000	1.215065000
6	0.003389000	-0.665859000	1.215065000
6	-0.003389000	-1.571916000	0.017776000
1	-0.015404000	1.188577000	2.159725000
1	0.015404000	-1.188577000	2.159725000

9	-1.230790000	1.765885000	-0.462509000
9	0.485116000	2.771531000	0.377770000
9	0.766610000	1.115726000	-0.977124000
9	1.230790000	-1.765885000	-0.462509000
9	-0.485116000	-2.771531000	0.377770000
9	-0.766610000	-1.115726000	-0.977124000

OH + (Z)-$CF_3CH=CHCF_3$ entrance adduct

6	1.579859000	-0.281229000	0.039217000
6	0.669401000	0.248129000	1.107991000
6	-0.663834000	0.212946000	1.111423000
6	-1.552880000	-0.335956000	0.033517000
1	1.184255000	0.700437000	1.941877000
1	-1.195693000	0.628971000	1.953385000
9	1.720839000	0.599015000	-0.971613000
9	2.799047000	-0.486862000	0.551830000
9	1.160601000	-1.432277000	-0.485588000
9	-1.701357000	-1.661764000	0.140666000
9	-2.768567000	0.213688000	0.134952000
9	-1.093885000	-0.074420000	-1.196794000
8	-0.178448000	2.846604000	-0.047089000
1	0.193641000	2.418006000	-0.832516000

TS for OH addition to *Z* $CF_3CH=CHCF_3$

6	-1.639110000	-0.117287000	-0.035435000
6	-0.683913000	0.524138000	-0.999409000
6	0.636281000	0.500240000	-0.941544000
6	1.486595000	-0.350800000	-0.027607000
1	-1.161788000	1.096884000	-1.777354000
1	1.199846000	0.949721000	-1.743176000
9	-1.710482000	0.568709000	1.122799000
9	-2.868377000	-0.121679000	-0.565342000
9	-1.322663000	-1.376995000	0.264266000
9	1.533105000	-1.604227000	-0.501733000
9	2.736543000	0.109703000	0.001634000
9	1.030628000	-0.400190000	1.223525000
8	0.804013000	2.241901000	0.104789000
1	0.141943000	2.102546000	0.799840000

Table S2. Infrared vibrational band centers (unscaled) and band strengths for (*E*)-$CF_3CH=CHCF_3$ computed with B3LYP/6-311G(d,p) theory

	Band Center (cm^{-1})	Band Strength (10^{-18} cm^2 $molecule^{-1}$ cm^{-1})
1	34	0.00
2	96	0.35
3	114	0.00
4	131	0.61
5	233	0.00
6	315	0.00
7	336	0.00
8	436	1.35
9	439	0.36
10	525	0.00
11	536	0.00
12	591	0.75
13	608	0.00
14	619	9.90
15	706	0.00
16	853	4.79
17	879	0.00
18	890	0.00
19	1007	7.35
20	1128	63.61
21	1148	0.00
22	1162	102.04
23	1175	0.00
24	1265	61.59
25	1308	0.00
26	1329	71.94
27	1332	0.00
28	1766	0.00
29	3200	0.00
30	3203	0.47

Table S3: Infrared vibrational band centers (unscaled) and band strengths for (*E*)-$CF_3CH=CHCF_3$ computed with M06-2X/aug-cc-pVTZ theory

	Band Center (cm^{-1})	Band Strength (10^{-18} cm^2 $molecule^{-1}$ cm^{-1})
1	36	0.00
2	97	0.37
3	112	0.00
4	135	0.61
5	236	0.00
6	322	0.00
7	342	0.00
8	443	1.32
9	449	0.47
10	537	0.00
11	548	0.00
12	603	0.45
13	622	0.01
14	633	11.05
15	725	0.00
16	887	3.32
17	904	0.00
18	909	0.00
19	1012	7.52
20	1165	44.49
21	1211	0.00
22	1224	95.32
23	1226	0.00
24	1301	54.28
25	1330	0.00
26	1358	91.19
27	1359	0.00
28	1809	0.00
29	3227	0.00
30	3228	1.27

Table S4: Unscaled frequencies obtained via UM06-2X/aug-cc-pVDZ theory, in units of cm^{-1}.

OH	E reactant	E TS	Z reactant	OH + Z adduct	Z TS
3733	49	422 i	37	45	438 i
	98	39	75	60	62
	101	66	132	82	91
	136	82	187	94	113
	238	118	224	139	135
	320	143	323	141	153
	331	157	355	189	199
	438	225	479	222	232
	444	245	487	271	323
	530	321	527	321	371
	540	378	527	363	378
	595	421	587	448	465
	616	439	613	479	490
	626	528	646	487	526
	715	546	766	526	542
	880	593	777	526	587
	887	594	825	585	611
	902	624	892	612	614
	988	713	1010	643	745
	1151	750	1147	766	776
	1203	850	1199	779	787
	1216	881	1210	825	829
	1216	902	1231	891	893
	1289	994	1267	1007	980
	1314	1155	1280	1149	1149
	1361	1198	1348	1191	1189
	1361	1205	1438	1207	1209
	1812	1232	1797	1221	1221
	3225	1284	3216	1271	1262
	3225	1303	3231	1275	1280
		1335		1342	1341
		1362		1440	1445
		1711		1789	1693
		3235		3238	3247
		3254		3252	3259
		3760		3735	3758