

**Table S1.** Fitted transition frequencies for CH<sub>2</sub><sup>35</sup>ClF-H<sup>12</sup>C<sup>12</sup>CH.

$J'$	$K_a'$	$K_c'$	$F'+1/2$	$J''$	$K_a''$	$K_c''$	$F''+1/2$	Obs. Freq. / MHz	Obs. - Calc. Freq. / MHz
3	1	3	4	2	1	2	4	7722.8710	0.0015
3	1	3	2	2	1	2	1	7727.7098	0.0023
3	1	3	3	2	1	2	2	7729.1439	-0.0001
3	1	3	5	2	1	2	4	7730.6938	-0.0013
3	1	3	3	2	1	2	3	7735.7857	-0.0055
3	1	3	2	2	1	2	2	7736.9967	0.0008
4	0	4	3	3	1	3	2	7820.5190	0.0012
4	0	4	6	3	1	3	5	7824.9761	0.0030
4	0	4	4	3	1	3	3	7830.5523	0.0049
4	0	4	5	3	1	3	4	7834.9561	0.0016
3	0	3	3	2	0	2	3	8163.8380	0.0009
3	0	3	4	2	0	2	3	8165.8320	0.0010
3	0	3	5	2	0	2	4	8167.5213	-0.0027
3	0	3	3	2	0	2	2	8168.0908	0.0029
3	0	3	2	2	0	2	1	8169.7786	0.0025
3	0	3	4	2	0	2	4	8171.8165	-0.0028
3	2	2	2	2	2	1	1	8248.9037	-0.0069
3	2	2	5	2	2	1	4	8254.0017	-0.0053
3	2	2	3	2	2	1	2	8256.0379	-0.0057
3	2	2	4	2	2	1	3	8261.1219	-0.0031
3	2	1	2	2	2	0	1	8336.9117	-0.0007
3	2	1	5	2	2	0	4	8342.4860	-0.0048
3	2	1	3	2	2	0	2	8345.6900	-0.0026
3	2	1	3	2	2	0	3	8349.9609	-0.0049
3	2	1	4	2	2	0	3	8351.3101	-0.0004
3	1	2	2	2	1	1	2	8739.5309	0.0043
3	1	2	3	2	1	1	3	8745.5829	0.0041
3	1	2	5	2	1	1	4	8752.5079	0.0064
3	1	2	4	2	1	1	3	8753.9133	0.0088
3	1	2	2	2	1	1	1	8755.9084	0.0095
2	1	2	3	1	0	1	2	8867.1387	-0.0090
2	1	2	2	1	0	1	2	8873.7832	-0.0117
2	1	2	3	1	0	1	3	8874.2635	-0.0059
2	1	2	4	1	0	1	3	8883.5259	-0.0003
2	1	2	2	1	0	1	1	8886.6214	0.0015
2	1	2	1	1	0	1	1	8895.9069	-0.0014
4	1	4	3	3	1	3	2	10282.4324	0.0024
4	1	4	4	3	1	3	3	10282.6616	0.0031
4	1	4	6	3	1	3	5	10283.4335	0.0035
4	1	4	5	3	1	3	4	10283.6520	0.0058
4	0	4	4	3	0	3	3	10789.1261	-0.0029
4	0	4	6	3	0	3	5	10790.0115	-0.0053
4	0	4	3	3	0	3	2	10791.2538	0.0007
4	0	4	5	3	0	3	5	10792.1690	-0.0036
5	0	5	4	4	1	4	3	10877.2781	-0.0125
5	0	5	7	4	1	4	6	10879.9333	-0.0076
5	0	5	5	4	1	4	4	10884.6979	-0.0089
5	0	5	6	4	1	4	5	10887.2751	-0.0133
4	2	3	3	3	2	2	2	10988.3858	0.0053
4	2	3	6	3	2	2	5	10989.3223	0.0014
4	2	3	4	3	2	2	3	10991.0126	0.0049
4	2	3	5	3	2	2	4	10991.8791	0.0043
3	1	3	4	2	0	2	3	11118.7574	0.0036
3	1	3	3	2	0	2	2	11126.6705	0.0012
3	1	3	5	2	0	2	4	11132.5626	-0.0051
3	1	3	2	2	0	2	2	11134.5293	0.0079
3	1	3	2	2	0	2	1	11140.5030	-0.0085
4	2	2	3	3	2	1	2	11205.8125	-0.0061
4	2	2	6	3	2	1	5	11207.1600	-0.0018
4	2	2	4	3	2	1	4	11209.2088	-0.0020
4	2	2	4	3	2	1	3	11210.5470	-0.0085
4	2	2	5	3	2	1	4	11211.8631	-0.0017
4	1	3	6	3	1	2	5	11642.2435	0.0078
4	1	3	5	3	1	2	4	11642.3680	0.0081
4	1	3	3	3	1	2	2	11644.2901	0.0025
4	1	3	4	3	1	2	3	11644.3887	0.0082
4	1	4	6	3	0	3	5	13248.4721	-0.0016
5	0	5	6	4	0	4	5	13335.9867	0.0066
5	0	5	5	4	0	4	4	13336.8193	0.0014
5	0	5	7	4	0	4	6	13338.4060	0.0083
5	0	5	4	4	0	4	3	13339.2130	0.0102

**Table S2.** Fitted transition frequencies for CH<sub>2</sub><sup>37</sup>ClF-H<sup>12</sup>C<sup>12</sup>CH.

$J'$	$K_a'$	$K_c'$	$F' + 1/2$	$J''$	$K_a''$	$K_c''$	$F'' + 1/2$	Obs. Freq. / MHz	Obs. - Calc. Freq. / MHz
3	1	3	4	2	1	2	4	7658.1570	0.0084
3	1	3	3	2	1	2	2	7663.1065	0.0026
3	1	3	3	2	1	2	3	7668.3396	0.0049
3	0	3	4	2	0	2	3	8100.8261	0.0061
3	0	3	3	2	0	2	2	8102.6056	0.0037
3	0	3	5	2	0	2	4	8102.2059	0.0065
3	0	3	2	2	0	2	1	8103.9854	0.0069
3	0	3	4	2	0	2	4	8105.4482	-0.0095
3	2	2	2	2	2	1	1	8189.4832	0.0048
3	2	2	5	2	2	1	4	8193.4622	0.0014
3	2	2	3	2	2	1	2	8195.0461	-0.0064
3	2	2	4	2	2	1	3	8199.0245	0.0009
3	2	1	5	2	2	0	4	8286.3727	-0.0057
3	2	1	3	2	2	0	2	8288.9227	-0.0018
3	2	1	4	2	2	0	3	8293.3303	0.0045
3	1	2	2	2	1	1	2	8685.6349	-0.0063
3	1	2	3	2	1	1	3	8690.3871	0.0082
3	1	2	5	2	1	1	4	8695.8195	0.0002
3	1	2	4	2	1	1	3	8696.8985	-0.0029
3	1	2	2	2	1	1	1	8698.4983	0.0032
3	1	2	3	2	1	1	2	8699.5861	-0.0018
4	0	4	4	3	0	3	4	10696.0936	-0.0061
4	0	4	5	3	0	3	4	10696.6195	-0.0048
4	0	4	4	3	0	3	3	10697.6052	-0.0083
4	0	4	6	3	0	3	5	10698.3595	-0.0022
4	0	4	3	3	0	3	2	10699.3328	-0.0078
4	0	4	5	3	0	3	5	10699.8817	-0.0008
4	2	3	3	3	2	2	3	10906.6308	-0.0030
4	2	3	6	3	2	2	5	10907.3708	-0.0037
4	2	3	4	3	2	2	4	10908.7088	0.0092
4	2	3	5	3	2	2	4	10909.3558	-0.0026
4	1	4	5	3	1	3	4	10193.9901	0.0102
4	1	4	6	3	1	3	5	10193.8232	-0.0029
4	1	4	3	3	1	3	2	10193.0374	-0.0065
4	1	4	4	3	1	3	3	10193.1959	-0.0103
4	1	3	6	3	1	2	5	11564.9599	0.0024
5	0	5	6	4	0	4	5	13216.0592	-0.0002
5	0	5	5	4	0	4	4	13216.7195	0.0002
5	0	5	7	4	0	4	6	13218.0209	0.0130

**Table S3.** Fitted transition frequencies for CH<sub>2</sub><sup>35</sup>ClF-H<sup>13</sup>C<sup>13</sup>CH.

$J'$	$K_a'$	$K_c'$	$F' + 1/2$	$J''$	$K_a''$	$K_c''$	$F'' + 1/2$	Obs. Freq. / MHz	Obs. - Calc. Freq. / MHz
1	1	1	2	0	0	0	2	6374.2462	-0.0022
1	1	1	3	0	0	0	2	6390.6070	0.0031
1	1	1	1	0	0	0	2	6403.7166	-0.0028
3	0	3	2	2	0	2	2	7807.1130	0.0030
3	0	3	3	2	0	2	3	7807.3264	-0.0014
3	0	3	4	2	0	2	3	7809.4197	-0.0029
3	0	3	5	2	0	2	4	7810.9706	-0.0002
3	0	3	3	2	0	2	2	7811.6328	0.0067
3	0	3	2	2	0	2	1	7813.1680	-0.0001
3	0	3	4	2	0	2	4	7815.4797	-0.0028
3	1	3	2	2	1	2	1	7400.3893	-0.0031
3	1	3	3	2	1	2	2	7401.8488	-0.0007
3	1	3	5	2	1	2	4	7403.3902	0.0007
3	1	3	4	2	1	2	3	7404.8384	-0.0033
3	1	2	5	2	1	1	4	8342.8632	-0.0006
3	1	2	4	2	1	1	3	8344.2930	-0.0015
3	1	2	2	2	1	1	1	8346.2369	-0.0035
3	1	2	3	2	1	1	2	8347.6889	0.0028
2	1	2	3	1	0	1	2	8689.7408	-0.0009
2	1	2	2	1	0	1	2	8696.3877	-0.0002
2	1	2	4	1	0	1	3	8706.0871	0.0035
2	1	2	2	1	0	1	1	8709.1537	0.0015
2	1	2	1	1	0	1	1	8718.4364	-0.0021
4	1	4	3	3	1	3	2	9849.7575	0.0002
4	1	4	4	3	1	3	3	9850.0214	-0.0006
4	1	4	6	3	1	3	5	9850.7664	-0.0006
4	1	4	5	3	1	3	4	9851.0204	0.0001
4	0	4	5	3	0	3	4	10328.0847	0.0035
4	0	4	4	3	0	3	3	10329.2993	0.0007
4	0	4	6	3	0	3	5	10330.0520	0.0010
4	0	4	3	3	0	3	2	10331.2573	0.0031
4	2	3	3	3	2	2	2	10496.9368	0.0003
4	2	3	6	3	2	2	5	10497.8701	0.0003
4	2	3	4	3	2	2	3	10499.5556	-0.0026
4	2	2	5	3	2	2	4	10500.4473	0.0032
4	2	2	6	3	2	1	5	10681.4201	0.0006
4	2	2	4	3	2	1	3	10684.7145	-0.0074
4	2	2	5	3	2	1	4	10685.9401	0.0068
5	1	5	5	4	1	4	4	12281.7254	0.0021
5	1	5	4	4	1	4	3	12281.9028	0.0037
5	1	5	6	4	1	4	5	12282.1837	-0.0009
5	1	5	7	4	1	4	6	12282.3772	-0.0023
5	0	5	6	4	0	4	5	12782.6443	-0.0036
5	0	5	5	4	0	4	4	12783.4670	0.0026
5	0	5	7	4	0	4	6	12784.9064	-0.0003
5	0	5	4	4	0	4	3	12785.6954	-0.0041

**Table S4.** Fitted transition frequencies for CH<sub>2</sub><sup>37</sup>ClF-H<sup>13</sup>C<sup>13</sup>CH.

$J'$	$K_a'$	$K_c'$	$F' + 1/2$	$J''$	$K_a''$	$K_c''$	$F'' + 1/2$	Obs. Freq. / MHz	Obs. - Calc. Freq. / MHz
1	1	1	2	0	0	0	2	6244.7563	0.0038
1	1	1	3	0	0	0	2	6257.5672	-0.0108
1	1	1	1	0	0	0	2	6267.8662	0.0076
3	1	3	4	2	1	2	4	7331.7976	0.0023
3	1	3	2	2	1	2	1	7335.6219	0.0009
3	1	3	3	2	1	2	2	7336.7437	-0.0022
3	1	3	5	2	1	2	4	7337.9715	0.0030
3	1	3	4	2	1	2	3	7339.0906	0.0004
3	1	3	3	2	1	2	3	7341.9770	-0.0025
3	0	3	2	2	0	2	2	7743.5893	0.0001
3	0	3	3	2	0	2	3	7743.6874	-0.0023
3	0	3	4	2	0	2	3	7745.2797	-0.0005
3	0	3	5	2	0	2	4	7746.5354	-0.0035
3	0	3	3	2	0	2	2	7747.0117	-0.0030
3	0	3	2	2	0	2	1	7748.2624	-0.0072
3	0	3	4	2	0	2	4	7749.9603	-0.0014
3	1	2	2	2	1	1	2	8275.3820	0.0004
3	1	2	3	2	1	1	3	8280.1222	-0.0025
3	1	2	5	2	1	1	4	8285.5382	0.0016
3	1	2	4	2	1	1	3	8286.6396	0.0014
3	1	2	2	2	1	1	1	8288.1972	0.0029
3	1	2	3	2	1	1	2	8289.3023	-0.0035
3	1	2	4	2	1	1	4	8299.4802	0.0018
4	1	4	3	3	1	3	2	9761.8202	0.0047
4	1	4	4	3	1	3	3	9762.0125	0.0063
4	1	4	6	3	1	3	5	9762.6129	0.0068
4	1	4	5	3	1	3	4	9762.7957	0.0065
4	0	4	5	3	0	3	4	10238.8293	-0.0041
4	0	4	4	3	0	3	3	10239.7906	-0.0022
4	0	4	6	3	0	3	5	10240.4277	-0.0038
4	0	4	3	3	0	3	2	10241.3792	-0.0023
4	2	3	6	3	2	2	5	10416.0950	-0.0024
4	2	3	5	3	2	2	5	10418.0985	0.0023
4	2	2	6	3	2	1	5	10607.9977	0.0004
4	2	2	4	3	2	1	3	10610.5907	0.0002
4	2	2	5	3	2	1	4	10611.5783	-0.0108
4	1	3	6	3	1	2	5	11022.9714	-0.0003
4	1	3	5	3	1	2	4	11023.1105	0.0135
4	1	3	4	3	1	2	3	11024.6687	0.0032
5	0	5	6	4	0	4	5	12666.1476	-0.0006
5	0	5	5	4	0	4	4	12666.7850	-0.0059
5	0	5	7	4	0	4	6	12667.9703	0.0010
5	0	5	4	4	0	4	3	12668.5944	-0.0008