Mechanisms of Radiation-Induced Degradation of $CFCl_3$ and CF_2Cl_2 in Noble-Gas Matrixes: An Evidence for "Hot" Ionic Channels in the Solid Phase.

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Supporting Information.

Table S1. Strong absorption bands (cm^{-1}) of $CFCl_3$ in different matrices after deposition at 7 K.

Approximate type of mode	Ne	Ar	Kr	Xe	Gas phase literature data[a)]
CCl_3 d-deform	~ 845-848[*]	837.5	834.8	832.7	847
CF stretch	1075.5-1077.5	1070	1069.2	1067-1068.7	1085

[a)] – see Ref. 40
[*] - out of scale

Table S2. Absorption bands (maxima position, cm^{-1}) used for quantitative estimates of the product formation in the $CFCl_3$/Ng systems.

Species	Matrix			
	Ne	Ar	Kr	Xe
$CFCl_3^{+\bullet}$	1214	1212	1214-1222	1217
$CFCl_3^{-\bullet}$	1057.5	1055.5	–	–
CCl_3^{+}	1047	1036.5	1035.5	–
$CCl_3^{\bullet}$	903 + 909 (after photolysis)	898	895	890.5-893.5
$CFCl^{\bullet\bullet}$	750	739	735.9	731.3-733
$CFCl_2^{\bullet}$	920.5+926.5	915.5-918.5	915	914.5
$CFCl_2^{+}$	1359	1351	1351	1337-1347 + 1352.3

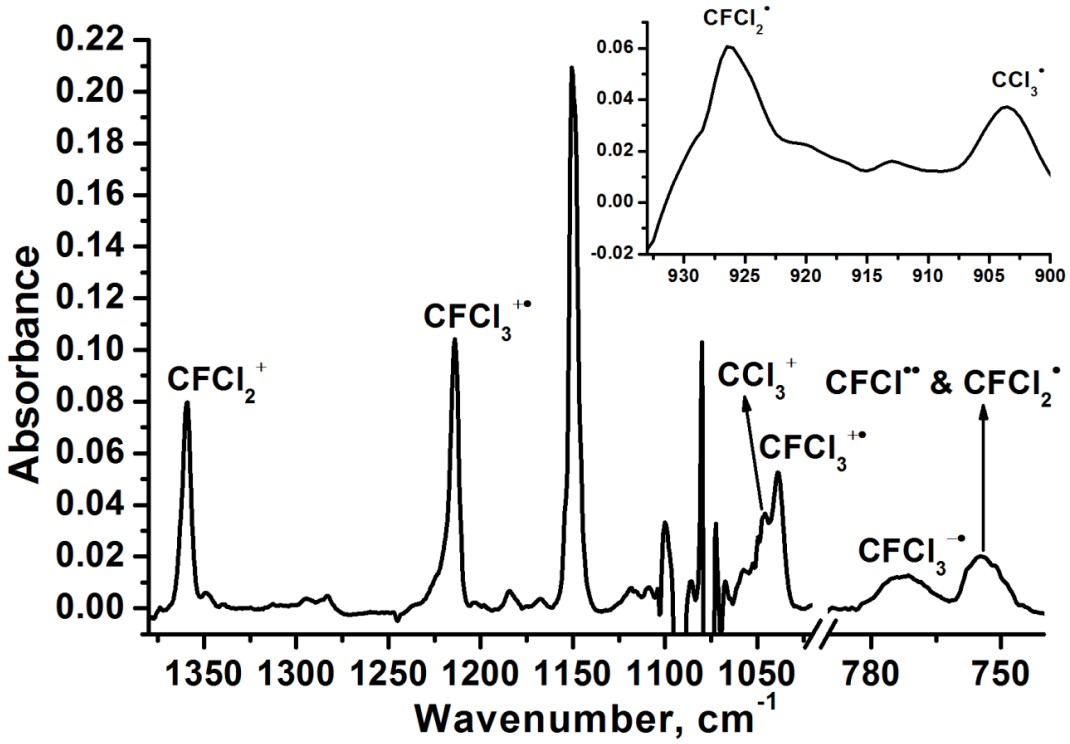

Figure S1. Difference IR spectrum demonstrating the radiation-induced absorptions for $CFCl_3$/Ne system (1/1000) irradiated with X-rays at 7 K.

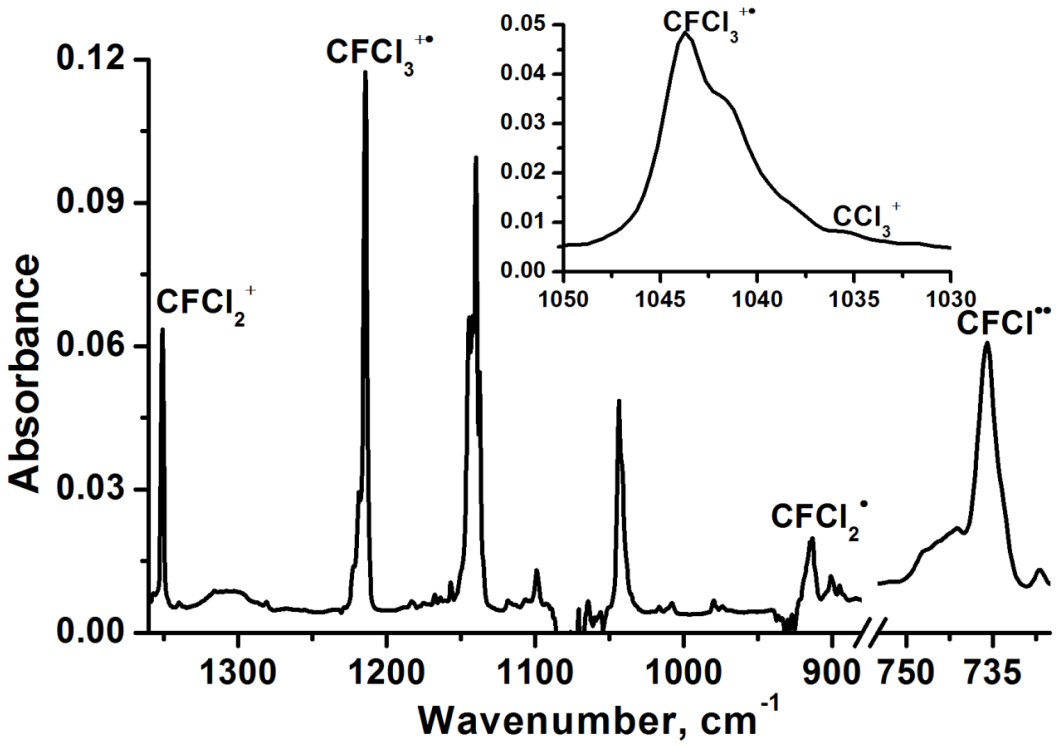

Figure S2. Difference IR spectrum demonstrating the radiation-induced absorptions for $CFCl_3$/Kr system (1/1000) irradiated with X-rays at 7 K.

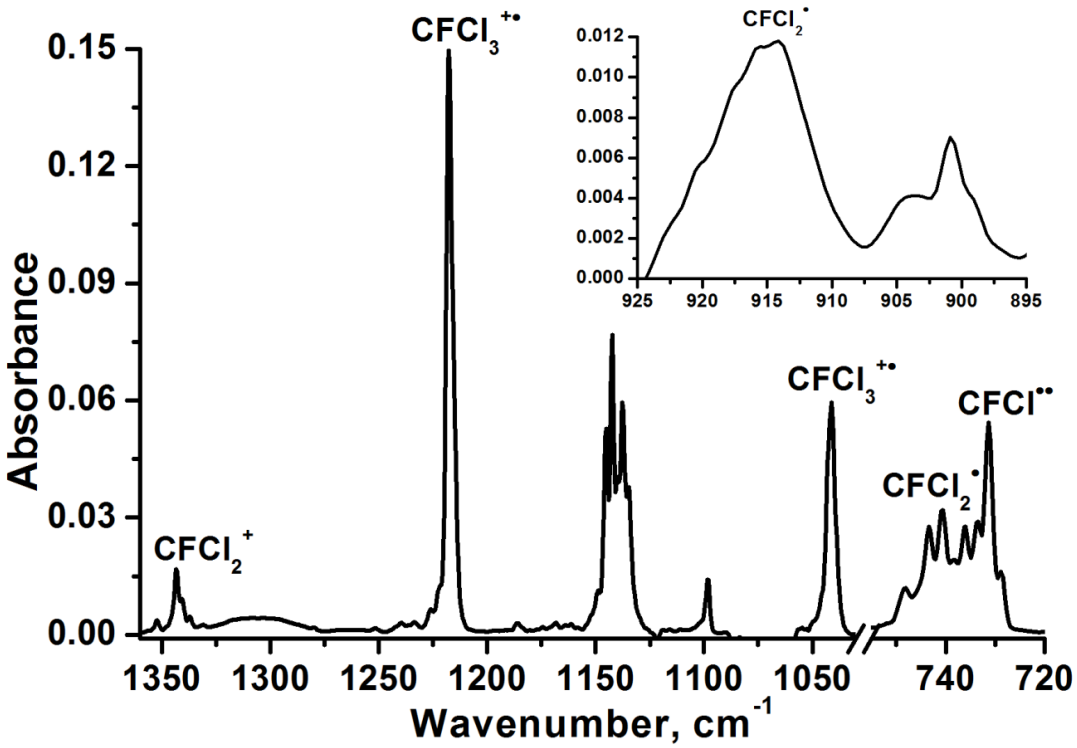

Figure S3. Difference IR spectrum demonstrating the radiation-induced absorptions for $CFCl_3$/Xe system (1/1000) irradiated with X-rays at 7 K.

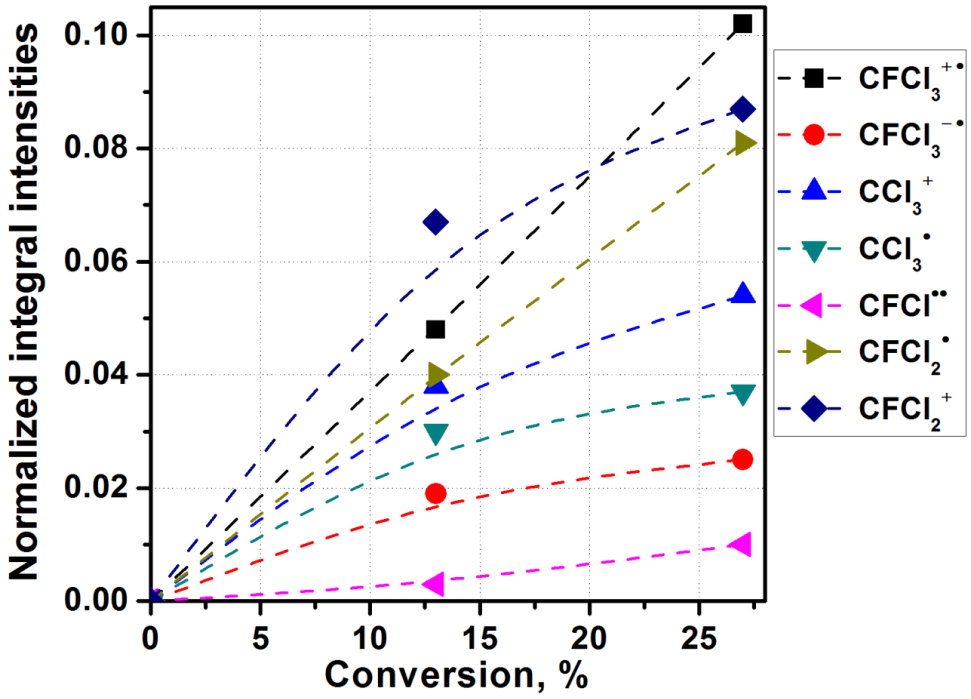

Figure S4. Accumulation of the radiation-induced species under X-rays irradiation of the $CFCl_3$/Ne system (1/1000) at 7 K.

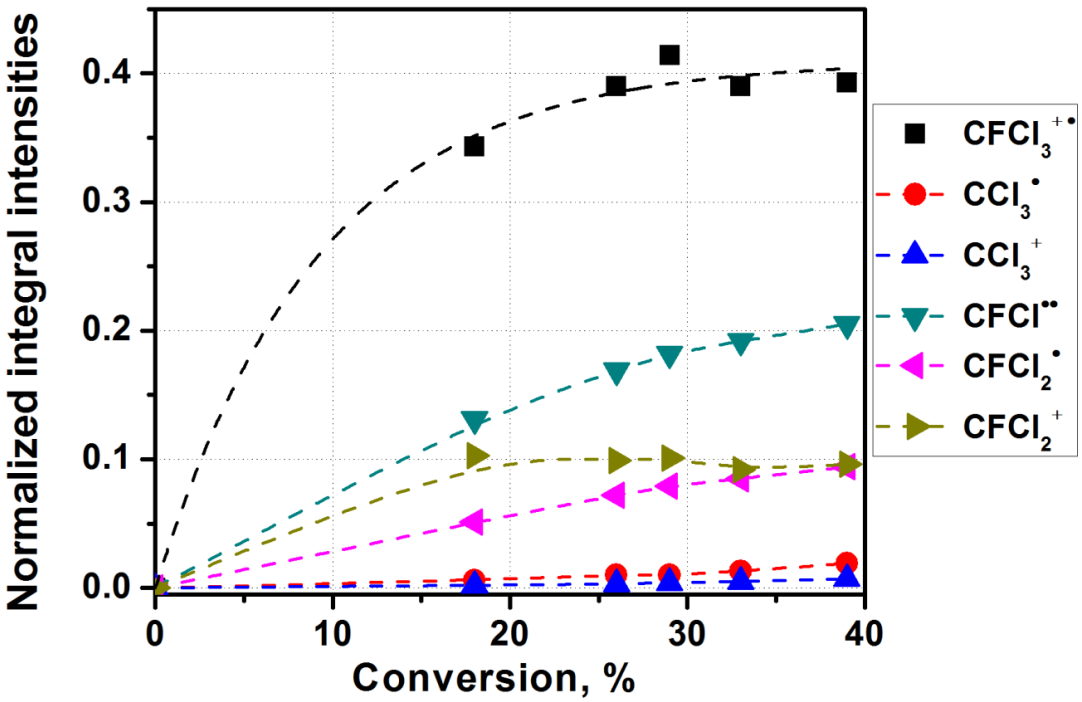

Figure S5. Accumulation of the radiation-induced species under X-rays irradiation of the $CFCl_3$/Kr system (1/1000) at 7 K.

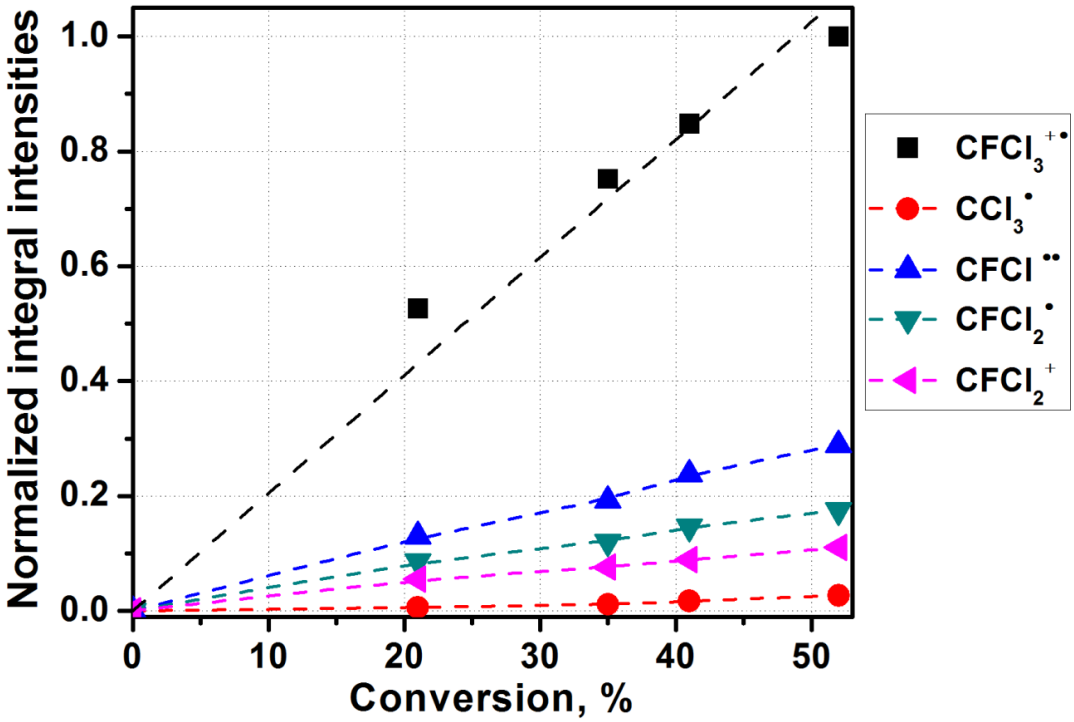

Figure S6. Accumulation of the radiation-induced species under X-rays irradiation of the $CFCl_3$/Xe system (1/1000) at 7 K.

Table S3. The relative integral intensities of selected product absorptions of irradiated Freon-11 in noble gas matrices.

Matrix	**Ne**		**Ar**					**Kr**					**Xe**			
Conversion, %	**13**	**27**	**4**	**14**	**24**	**32**	**40**	**18**	**26**	**29**	**33**	**39**	**21**	**35**	**41**	**52**
Species	***I***															
$CFCl_3^{+\bullet}$	0.048	0.102	0.094	0.146	0.193	0.223	0.242	0.343	0.390	0.414	0.39	0.393	0.526	0.752	0.848	1
$CFCl_3^{-\bullet}$	0.019	0.025	0.020	0.021	0.017	0.014	0.007	0	0	0	0	0	0	0	0	0
CCl_3^{+}	0.038	0.054	0.005	0.007	0.009	0.013	0.019	0.002	0.003	0.004	0.005	0.007	0	0	0	0
$CCl_3^{\bullet}$	0.030	0.037	0.003	0.011	0.020	0.027	0.033	0.006	0.010	0.010	0.013	0.019	0.006	0.011	0.017	0.027
$CFCl^{\bullet\bullet}$	0.003	0.010	0.020	0.038	0.057	0.067	0.071	0.131	0.169	0.182	0.192	0.205	0.130	0.192	0.238	0.289
$CFCl_2^{\bullet}$	0.040	0.081	0.030	0.063	0.095	0.106	0.115	0.051	0.072	0.079	0.085	0.094	0.086	0.120	0.146	0.175
$CFCl_2^{+}$	0.067	0.087	0.030	0.029	0.028	0.031	0.030	0.103	0.099	0.101	0.092	0.096	0.055	0.076	0.089	0.110
900.9								0.017	0.018	0.017	0.015	0.013				
903.5			0.034	0.041	0.058	0.063	0.053									
904								0.003	0.003	0.003	0.003	0.002				
901-904													0.027	0.033	0.036	0.037
913	0.012	0.027														
1097.5			0.003	0.003	0.004	0.004	0.004									
1098.5													0.023	0.029	0.032	0.033
1099								0.021	0.021	0.021	0.020	0.018				
1099.5	0.008	0.020														

Table S4. Strong absorption bands (cm^{-1}) of CF_2Cl_2 in different matrices after deposition at 7 K.

Approximate type of mode	Ne	Ar	Kr	Xe	Gas phase literature data[a)]
CCl_2 a-stretch	883.5-888.5	877.7-882.7	877.1-881.4	885.5-890	882
CCl_2 a-stretch	~ 919-921[*]	908.5-912.7	905.9-910.6	912.5-916.5	922
CF_2 s-stretch	1096-1100.5	1089.8-1094.8	1089-1092.3	1087	1101
CF_2 a-stretch	1147.4-1155.5	1144.9-1149.8	1149.8-1151.6	1142.5-1146	1159

[a)] – see Ref. 40
[*] - out of scale

Table S5. Absorption bands (maxima position, cm^{-1}) used for quantitative estimates of the product formation in the CF_2Cl_2/Ng systems.

Species	Matrix			
	Ne	Ar	Kr	Xe
$CF_2Cl_2^{+\bullet}$	1237	1233	1232.0	–
$CF_2Cl_2^{-\bullet}$	568	563.2	561.7	560.4
"X"	1220	1219.1	1216.9	1213.3
$CF_2^{\bullet\bullet}$	1222	–	–	–
$CFCl_2^{+}$	1361	1354.2	–	–
CF_2Cl^{+}	1411.5	1406.2-1409.4	1408-1411	–
$CFCl_2^{\bullet}$	752.5	–	–	–
$CF_2Cl^{\bullet}$	1212.5	1206.6	1203.7	1200
$CFCl^{\bullet\bullet}$	746.5	739.9	737.2	730.6
"Y"	1251.5	1254.4	1253.3	1249.4

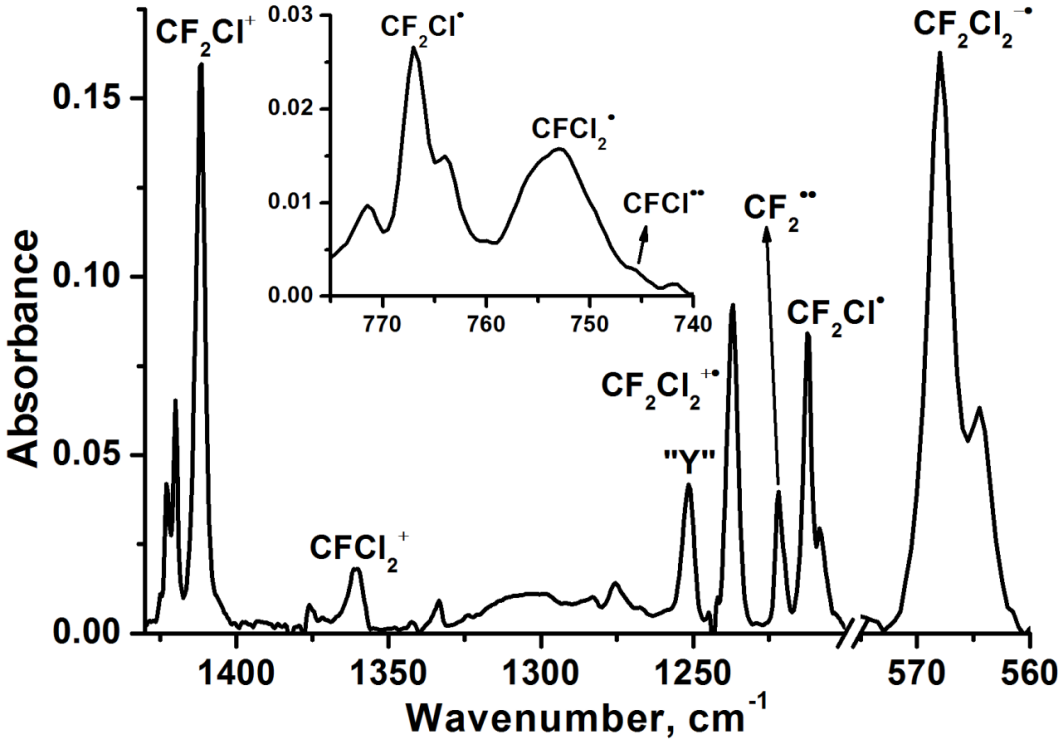

Figure S7. Difference IR spectrum demonstrating the radiation-induced absorptions for CF_2Cl_2/Ne system (1/1000) irradiated with X-rays at 7 K.

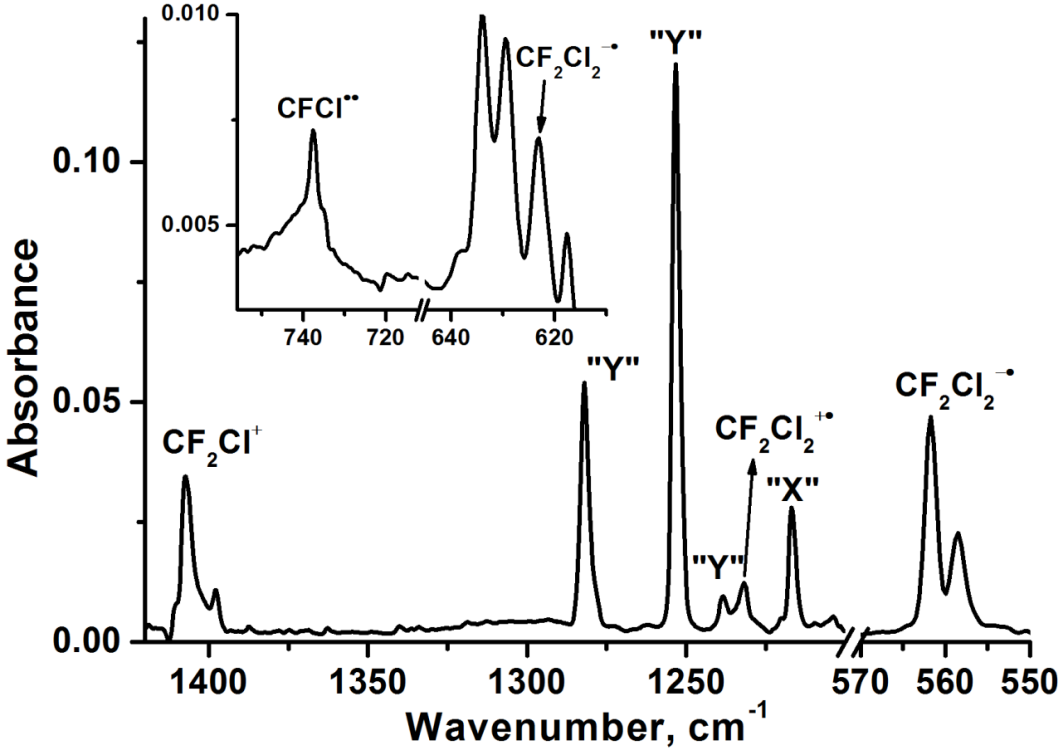

Figure S8. Difference IR spectrum demonstrating the radiation-induced absorptions for CF_2Cl_2/Kr system (1/1000) irradiated with X-rays at 7 K.

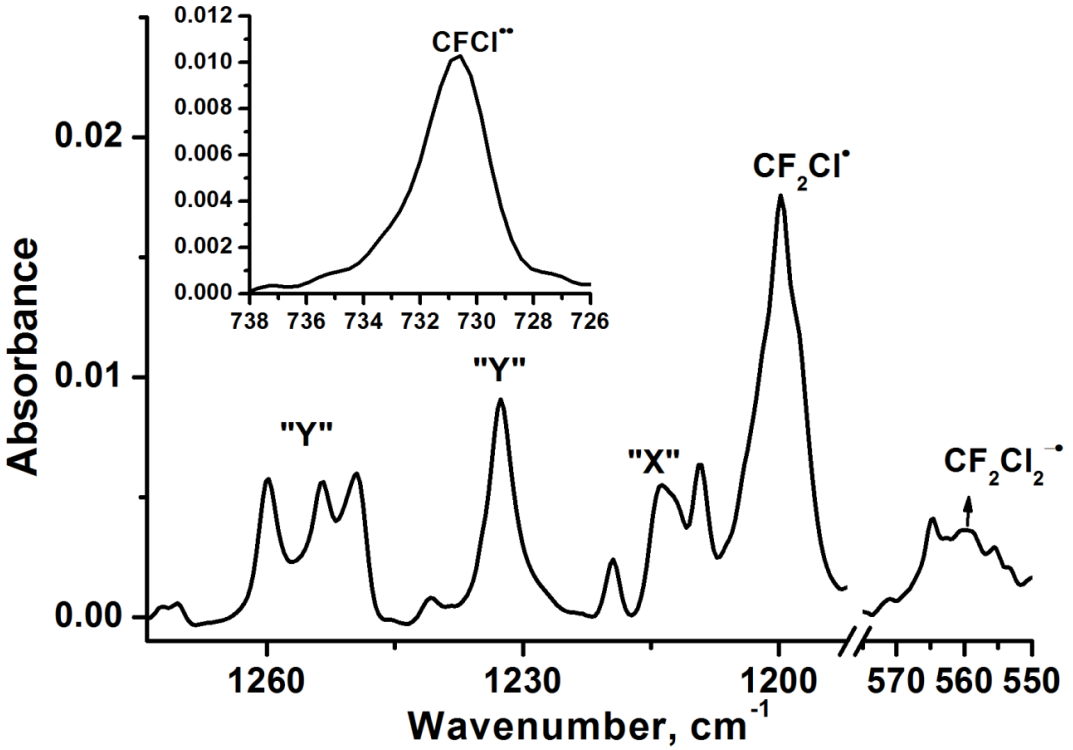

Figure S9. Difference IR spectrum demonstrating the radiation-induced absorptions for CF_2Cl_2/Xe system (1/1000) irradiated with X-rays at 7 K.

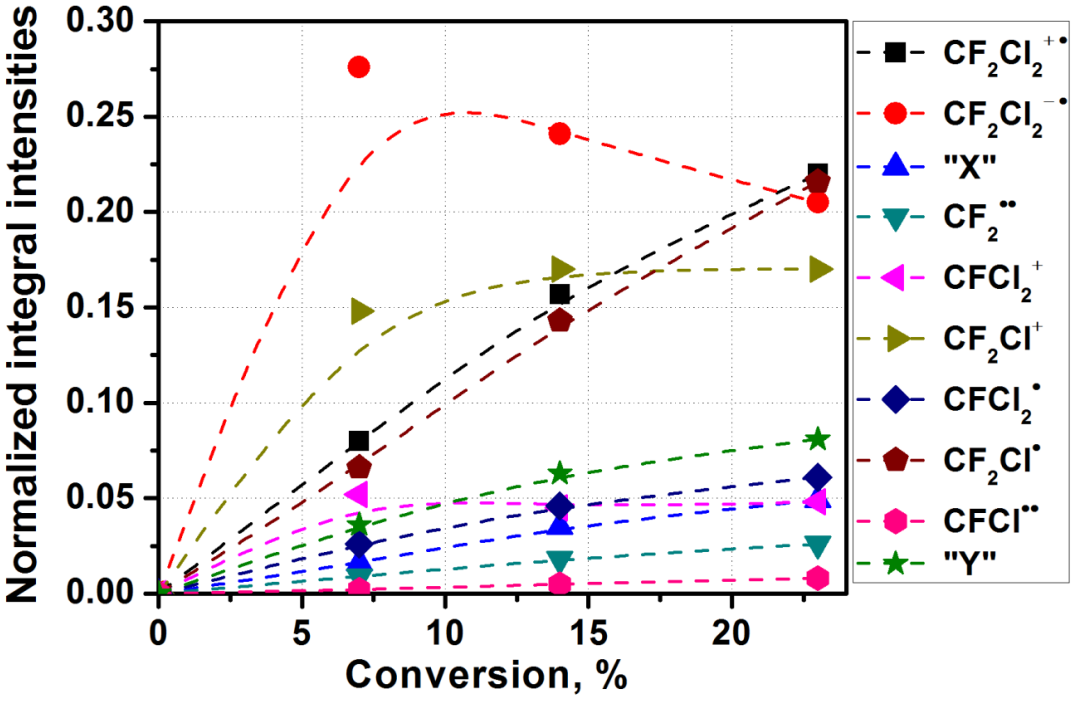

Figure S10. Accumulation of the radiation-induced species under X-rays irradiation of the CF_2Cl_2/Ne system (1/1000) at 7 K.

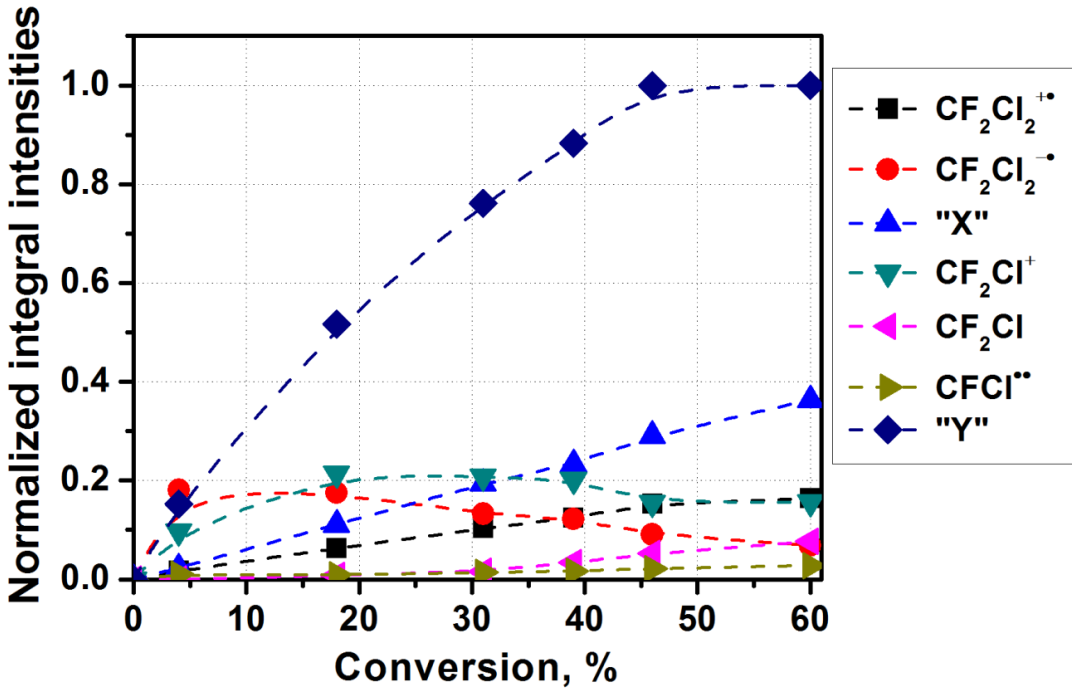

Figure S11. Accumulation of the radiation-induced species under X-rays irradiation of the CF_2Cl_2/Kr system (1/1000) at 7 K.

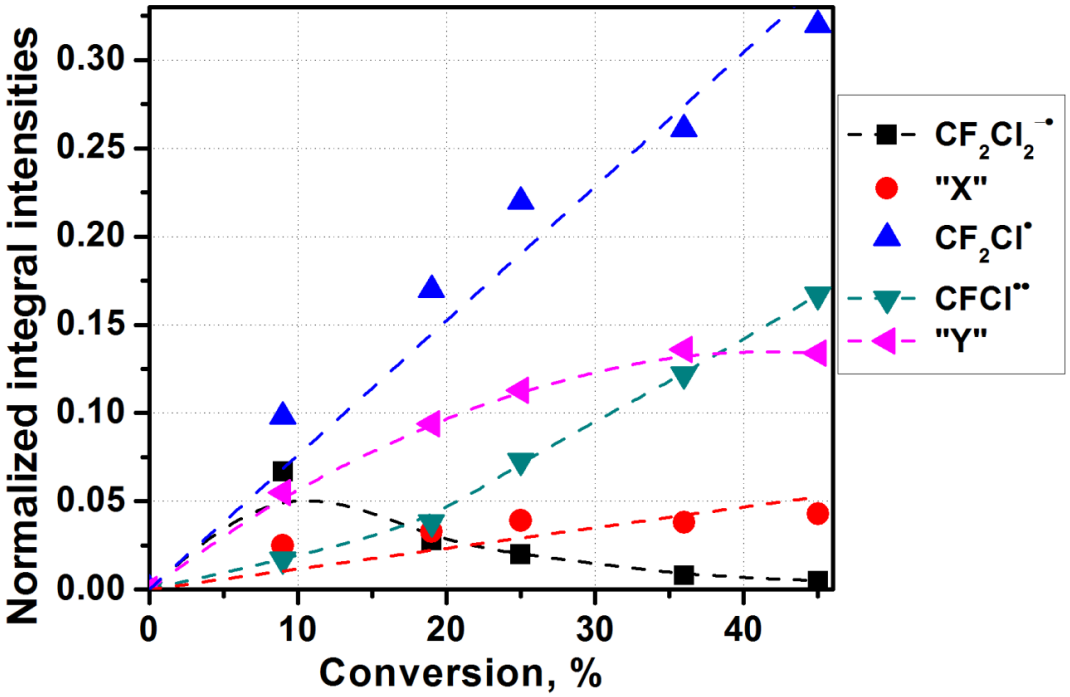

Figure S12. Accumulation of the radiation-induced species under X-rays irradiation of the CF_2Cl_2/Xe system (1/1000) at 7 K.

Table S6. The relative integral intensities of selected product absorptions of irradiated Freon-12 in noble gas matrices.

Matrix	**Ne**			**Ar**				**Kr**						**Xe**				
Conversion, %	**7**	**14**	**23**	**<1**	**14**	**23**	**30**	**4**	**18**	**31**	**39**	**46**	**60**	**9**	**19**	**25**	**36**	**45**
Species	**I**																	
$CF_2Cl_2^{+\bullet}$	0.08	0.157	0.22	0.023	0.074	0.088	0.093	0.017	0.063	0.103	0.125	0.153	0.164	0	0	0	0	0
$CF_2Cl_2^{-\bullet}$	0.276	0.241	0.205	0.152	0.108	0.084	0.070	0.181	0.175	0.133	0.122	0.091	0.069	0.067	0.028	0.02	0.008	0.005
$CF_2^{\bullet\bullet}$	0.009	0.018	0.026	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$CFCl_2^{+}$	0.052	0.045	0.048	0.007	0.009	0.01	0.009	0	0	0	0	0	0	0	0	0	0	0
CF_2Cl^{+}	0.148	0.170	0.170	0.118	0.142	0.134	0.124	0.097	0.214	0.208	0.202	0.155	0.156	0	0	0	0	0
$CFCl_2^{\bullet}$	0.026	0.046	0.061	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$CF_2Cl^{\bullet}$	0.066	0.143	0.216	0.005	0.037	0.061	0.079	0	0.008	0.016	0.034	0.052	0.077	0.098	0.170	0.22	0.261	0.32
$CFCl^{\bullet\bullet}$	0.002	0.005	0.008	0.021	0.044	0.049	0.049	0.011	0.009	0.014	0.017	0.022	0.028	0.017	0.038	0.073	0.122	0.167
“X”	0.016	0.035	0.049	0.090	0.255	0.315	0.341	0.023	0.111	0.194	0.233	0.291	0.363	0.025	0.033	0.039	0.038	0.043
“Y”	0.036	0.063	0.081	0.03	0.052	0.058	0.063	0.153	0.517	0.761	0.883	1	1	0.055	0.094	0.113	0.136	0.134
1131	0.150	0.278	0.368															
1240.8				0	0.002	0.01	0.01											
1131.8								0.02	0.086	0.092	0.188	0.139	0.208					
1238.0								0.019	0.036	0.064	0.081	0.108	0.122					
1281.9								0.077	0.259	0.389	0.439	0.503	0.519					
1125.4														0.017	0.047	0.108	0.158	0.172

Calculated harmonic vibrational frequencies (cm^{-1}), IR intensities (km/mol), molecular geometries and energies for freons and related intermediates

Molecular geometries were fully optimized (tolerance on gradient: 10^{-6} a.u.) at the unrestricted CCSD(T)/L1a level of theory (only the valence electrons are correlated). Basis set contraction scheme: C - {4,3,2}/{11,8,4}; F -{4,3,2}/{11,8,4}; Cl - {5,4,2}/{15,12,4}.

abbreviations:

E –energy (a.u.),

ZPVE –zero point vibration energy (a.u.),

E0 –ZPVE corrected energy (a.u.),

Mode – Mode number

Freq. – Harmonic Frequencies (cm^{-1}),

Mass.- Reduced Masses (a.m.u.),

IR Int. - IR Intensities (km/mol).

$CFCl_3$

Mode	Freq.	Mass.	IR Int.
1	246.26	29.91	0.060
2	246.27	29.91	0.061
3	349.49	25.59	0.267
4	396.73	25.29	0.000
5	396.74	25.29	0.000
6	527.35	22.59	1.064
7	842.48	12.88	217.424
8	842.49	12.88	217.393
9	1083.61	13.69	160.705

```
$molecule
 z-matrix
 set=L1a
  6
  9   1   1.34780714
 17   1   1.77939209   2   108.373773
 17   1   1.77939209   2   108.373773   3   120.000000
 17   1   1.77939209   2   108.373773   3  -120.000000
$end

$molecule
 cartesian
 set=L1a
  6    0.00000000  -0.00000000   0.06697285
  9    0.00000000  -0.00000000   1.41477999
 17     0.00000000   1.68867939  -0.49391762
 17    -1.46243925  -0.84433970  -0.49391762
 17     1.46243925  -0.84433970  -0.49391762
$end
```

E = -1516.800747; E0 = -1516.789512; ZPVE = 0.011235

$CFCl_3^{+\bullet}$

Mode	Freq.	Mass.	IR Int.
1	219.05	29.45	0.281
2	246.31	30.49	0.408
3	328.39	24.99	0.037
4	354.33	27.09	8.012
5	404.04	24.41	0.667
6	528.07	22.14	9.457
7	823.31	12.79	1026.508
8	883.49	13.23	302.465
9	1217.62	13.78	193.443

```
$molecule
 charge=1 mult=2
 z-matrix
 set=L1a
  6
  9   1   1.30474868
 17   1   1.71000235   2   114.389901
 17   1   1.83493998   2   110.474444   3   131.681467
 17   1   1.83494009   2   110.474443   3  -131.681468
$end

$molecule
 charge=1 mult=2
 cartesian
 set=L1a
  6    0.16239134  -0.00000000   0.11684140
  9    0.33248471   0.00000004   1.41045547
 17     1.61444116  -0.00000021  -0.78629721
 17    -1.05465840   1.28385868  -0.37049989
 17    -1.05465880  -1.28385851  -0.37049977
$end
```

E = -1516.386082; E0 = -1516.374680; ZPVE = 0.011401

$CFCl_2^{\bullet}$

Mode	Freq.	Mass.	IR Int.
1	282.08	26.86	0.013
2	379.04	23.28	0.328
3	462.09	17.58	0.359
4	610.23	15.66	8.526
5	910.59	13.19	264.914
6	1149.81	13.76	221.239

```
$molecule
 mult=2
 z-matrix
 set=L1a
  6
  9   1   1.33529083
 17   1   1.73521198   2   112.960093
 17   1   1.73521198   2   112.960093   3   136.096397
$end

$molecule
 mult=2
 cartesian
 set=L1a
  6    0.00000000   0.09281400  -0.28388794
  9    0.00000000   1.36826457   0.11136823
 17   -1.48190439  -0.73053928   0.08625985
 17    1.48190439  -0.73053928   0.08625985
$end
```

E = -1057.049237; E0 = -1057.040594; ZPVE = 0.008643

$CFCl_2^+$

Mode	Freq.	Mass.	IR Int.
1	330.00	26.00	0.048
2	445.88	23.07	1.951
3	589.32	12.85	2.942
4	640.78	23.93	2.210
5	1129.66	13.15	460.412
6	1365.68	13.64	281.946

```
$molecule
 charge=1
 z-matrix
 set=L1a
  6
  9   1   1.27239234
 17   1   1.64660688   2   117.922267
 17   1   1.64660688   2   117.922267   3   -179.999993
$end

$molecule
 charge=1
 cartesian
 set=L1a
  6   -0.00000000   0.06743288   0.00000004
  9   -0.00000000   1.33982522  -0.00000002
 17   -1.45491502  -0.70362905  -0.00000001
 17    1.45491502  -0.70362905  -0.00000001
$end
```

E = -1056.750525; E0 = -1056.740270; ZPVE = 0.010255

($CFCl_2^{\bullet}...Cl^-$)

Mode	Freq.	Mass.	IR Int.
1	60.09	31.49	0.287
2	107.21	22.25	1.084
3	164.77	29.56	78.711
4	262.73	28.39	0.785
5	349.35	23.82	6.030
6	436.33	21.40	3.460
7	478.06	13.15	569.027
8	744.12	12.98	274.956
9	1038.18	13.87	201.174

```
$molecule
 charge=-1 mult=2
 z-matrix
 set=L1a
  6
  9   1   1.35055356
 17   1   1.81286019   2   107.735295
 17   1   1.81286019   2   107.735295   3   118.802276
 17   1   2.48419706   2   102.684176   3  -120.598862
$end

$molecule
 charge=-1 mult=2
 cartesian
 set=L1a
  6   -0.13685300   0.00000000   0.05082299
  9   -0.22733020   0.00000000   1.39834249
 17   -0.97681629   1.48626262  -0.55905171
 17   -0.97681629  -1.48626262  -0.55905171
 17    2.31781578   0.00000000  -0.33106206
$end
```

E = -1516.828172,E0 = -1516.819877, ZPVE = 0.008294

CCl_3^+

Mode	Freq.	Mass.	IR Int.
1	311.21	31.74	0.089
2	311.21	31.74	0.089
3	517.45	12.87	0.062
4	534.56	34.97	0.000
5	1027.86	13.37	302.435
6	1027.86	13.37	302.435

```
$molecule
 charge=1
 z-matrix
 set=L1a
  6
 17   1   1.66283931
 17   1   1.66284011   2   120.000014
 17   1   1.66284011   2   120.000014   3   -179.999999
$end

$molecule
 charge=1
 cartesian
 set=L1a
  6    0.00000000   0.00000038   0.00000001
 17    0.00000000   1.66283969  -0.00000000
 17   -1.44006157  -0.83142003  -0.00000000
 17    1.44006157  -0.83142003  -0.00000000
$end
```

E = -1416.744071; E0 = -1416.735573; ZPVE = 0.008498

$CCl_3^{\bullet}$

Mode	Freq.	Mass.	IR Int.
1	271.98	31.85	0.032
2	271.98	31.85	0.036
3	350.03	16.00	0.213
4	493.98	22.82	0.051
5	880.50	13.42	163.443
6	880.50	13.42	163.295

```
$molecule
 mult=2
 z-matrix
 set=L1a
  6
 17   1   1.73103925
 17   1   1.73103947   2   116.445361
 17   1   1.73103947   2   116.445360   3   143.409941
$end

$molecule
 mult=2
 cartesian
 set=L1a
  6   -0.00000001  -0.00000020  -0.24782191
 17    0.01092242   1.69917435   0.08260728
 17   -1.47699001  -0.84012798   0.08260732
 17    1.46606760  -0.85904616   0.08260732
$end
```

E = -1417.036199; E0 = -1417.029025; ZPVE = 0.007174

CFCl singlet

Mode	Freq.	Mass.	IR Int.
1	435.63	21.69	14.454
2	732.61	13.46	238.240
3	1142.63	14.01	260.429

```
$molecule
 z-matrix
 set=L1a
   6
   9    1    1.30862413
  17    1    1.76955661    2    106.291768
$end

$molecule
 cartesian
 set=L1a
   6     0.22965061  -0.58404154   0.00000000
   9     1.12176173   0.37336896   0.00000000
  17    -1.35141234   0.21067257   0.00000000
$end
```

E = -597.325461; E0 = -597.320197; ZPVE = 0.005265

CF_2Cl_2

Mode	Freq.	Mass.	IR Int.
1	262.60	27.34	0.122
2	322.80	21.20	0.000
3	434.20	25.64	0.002
4	434.52	18.57	0.068
5	453.34	25.67	0.114
6	663.14	18.26	8.523
7	911.67	12.72	348.665
8	1102.56	13.55	272.949
9	1155.30	13.39	192.171

```
$molecule
 z-matrix
 set=L1a
  6
  9   1   1.33942236
  9   1   1.33942236   2   107.772500
 17   1   1.77463762   2   109.298843   3   118.683061
 17   1   1.77463762   2   109.298843   3  -118.683061
$end

$molecule
 cartesian
 set=L1a
  6   -0.00000000   0.08226791   0.00000000
  9   -0.00000000   0.87171040   1.08205029
  9    0.00000000   0.87171037  -1.08205031
 17   -1.46938433  -0.91284433   0.00000001
 17    1.46938433  -0.91284433   0.00000001
$end
```

E = -1156.827580; E0 = -1156.814503; ZPVE = 0.013077

$CF_2Cl_2^{+\bullet}$

Mode	Freq.	Mass.	IR Int.
1	262.11	28.03	0.071
2	278.27	21.71	0.000
3	394.31	26.89	7.994
4	404.67	18.31	0.783
5	446.80	25.47	0.069
6	683.20	17.46	30.970
7	1008.82	12.73	2141.803
8	1184.95	13.90	373.234
9	1341.95	13.47	213.600

```
$molecule
 charge=1 mult=2
 z-matrix
 set=L1a
  6
  9   1   1.29362378
  9   1   1.29362378   2   112.918677
 17   1   1.81797382   2   112.809578   3   129.376619
 17   1   1.81797382   2   112.809565   3  -129.376589
$end

$molecule
 charge=1 mult=2
 cartesian
 set=L1a
  6    0.22431087   0.00000020   0.00000000
  9    0.93907510   0.00000039   1.07822752
  9    0.93907500   0.00000039  -1.07822758
 17   -1.05123118   1.29538481   0.00000002
 17   -1.05122979  -1.29538579   0.00000003
$end
```

E = -1156.402292; E0 = -1156.388611; ZPVE = 0.013681

$CF_2Cl^{\bullet}$

Mode	Freq.	Mass.	IR Int.
1	363.76	19.40	0.136
2	419.95	23.59	0.062
3	597.01	16.38	3.451
4	766.30	14.06	66.300
5	1151.16	13.73	324.762
6	1206.01	13.49	255.425

```
$molecule
 mult=2
 z-matrix
 set=L1a
   6
   9    1    1.32860715
   9    1    1.32860717    2    110.201491
  17    1    1.74303723    2    113.852202    3    129.332069
$end

$molecule
 mult=2
 cartesian
 set=L1a
   6    -0.10435771  -0.00000019  -0.29888677
   9    -0.74611047   1.08967054   0.10850501
   9    -0.74611445  -1.08966855   0.10850512
  17     1.59658263  -0.00000180   0.08187664
$end
```

E = -697.066876; E0 = -697.056615; ZPVE = 0.010261

CF_2Cl^+

Mode	Freq.	Mass.	IR Int.
1	423.42	19.20	1.795
2	519.53	22.90	3.308
3	676.97	12.84	19.188
4	812.93	19.15	20.556
5	1404.79	13.47	536.295
6	1522.44	13.43	295.421

```
$molecule
 charge=1
 z-matrix
 set=L1a
   6
   9    1    1.25538019
   9    1    1.25538028    2    116.019209
  17    1    1.62980617    2    121.990393    3   -179.999968
$end

$molecule
 charge=1
 cartesian
 set=L1a
   6    -0.07491569   0.00000001   0.00000017
   9    -0.73998718   1.06473441  -0.00000006
   9    -0.73998760  -1.06473423  -0.00000006
  17     1.55489048  -0.00000020  -0.00000005
$end
```

E = -696.755762; E0 = -696.743551; ZPVE = 0.012211

($CF_2Cl^{\bullet}\cdots Cl^-$)

Mode	Freq.	Mass.	IR Int.
1	72.23	24.52	7.842
2	133.40	19.13	0.485
3	166.02	27.23	110.295
4	329.01	24.89	72.240
5	335.38	19.54	0.075
6	567.39	13.96	579.119
7	609.19	16.12	231.717
8	1013.16	13.88	312.485
9	1079.21	13.50	223.729

```
$molecule
 charge=-1 mult=2
 z-matrix
 set=L1a
  6
  9   1   1.34914024
  9   1   1.34914024   2   106.474982
 17   1   1.86890920   2   107.083924   3   114.291649
 17   1   2.46431193   2   104.007002   3  -109.506417
$end

$molecule
 charge=-1 mult=2
 cartesian
 set=L1a
  6   -0.13275133   0.04006261  -0.00000000
  9   -0.25567841   0.83811037   1.08082750
  9   -0.25567841   0.83811038  -1.08082750
 17   -1.60239339  -1.11448224  -0.00000000
 17    2.24650154  -0.60180112   0.00000000
$end
```

E = -1156.847583; E0 = -1156.837776; ZPVE = 0.009807

$CF_2^{\bullet\bullet}$

Mode	Freq.	Mass.	IR Int.
1	658.40	17.82	2.491
2	1088.28	13.69	392.999
3	1208.04	13.79	120.075

```
$molecule
 z-matrix
 set=L1a
  6
  9   1   1.31339283
  9   1   1.31339283   2   104.507959
$end

$molecule
 cartesian
 set=L1a
  6    0.00000000  -0.53600644   0.00000000
  9    1.03854186   0.26800322   0.00000000
  9   -1.03854186   0.26800322   0.00000000
$end
```

E = -237.358968; E0 = -237.352237; ZPVE = 0.006731