

Heavy-Atom Tunnelling on XeF₆ Pseudorotation

Supporting Information

Itzhak Sedgi,^{†,‡} and Sebastian Kozuch,^{*,†}

[†] Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 841051, Israel.

[‡] Department of Analytical Chemistry, Nuclear Research Center Negev. P.O Box 9001, Beer-Sheva, Israel.

Table of Contents

Energy Benchmark	S2
Rate Constants	S3
KIE	S9
Example of Polyrate input file	S10
XYZ optimized geometries	S11
¹⁸ F monosubstituted IR spectra	S12
References	S13

Energy Benchmark

As mentioned in the main text, the energy barrier of XeF₆ (C_{3v}) pseudorotation, was benchmarked against the results of Peterson¹ et al. (which were energetically confirmed later by Stanton et al.²). In order to find the most compatible functional and basis set combination that will offer the highest accuracy at a reasonable cost, we examined various functionals with the Karlsruhe family basis sets up to the triple-zeta level. Table S1 summarizes those results and confirms the compatibility of BMK/def2tzvp to the energy benchmark. To achieve maximum accuracy, the energy profile was further matched to the exact benchmark energies using the interpolated single point energy (ISPE)³ method.

Table S1. ΔE^\ddagger (kJ·mol⁻¹) for XeF₆ (C_{3v}) pseudorotation. Null values indicate failure to obtain the C_{3v} geometry as the ground state.

Functional	Basis-Set	ΔE^\ddagger
TPSSh	Def2-SV	-
	Def2-TZVP	-
MN15	Def2-SV	2.80
	Def2-TZVP	3.18
MN15L	Def2-SV	-
	Def2-TZVP	3.18
M062X	Def2-SV	5.40
	Def2-TZVP	6.07
ω B97X	Def2-SV	2.13
	Def2-TZVP	2.97
PBE0	Def2-SV	-
	Def2-TZVP	2.05
PBE	Def2-SV	-
	Def2-TZVP	-
B97D3	Def2-SV	-
	Def2-TZVP	-
TPSSTPSS	Def2-SV	-
	Def2-TZVP	-
BMK	Def2-SV	3.47
	Def2-TZVP	4.44
Ref.		4.52

Table S2. CVT and CVT+SCT rate constants (in s⁻¹) not including symmetry numbers correction.

XeF ₆			XeF ₆ [¹⁸ F _{α+β+γ}]		
T(K)	CVT	CVT+SCT	T(K)	CVT	CVT+SCT
4	1.80E-33	4.74E+02	4	4.48E-33	9.81E+02
5	1.22E-24	4.74E+02	5	2.53E-24	9.81E+02
6	9.74E-19	4.74E+02	6	1.79E-18	9.81E+02
7	1.64E-14	4.74E+02	7	2.75E-14	9.82E+02
8	2.46E-11	4.75E+02	8	3.88E-11	9.83E+02
9	7.39E-09	4.78E+02	9	1.11E-08	9.89E+02
10	7.16E-07	4.89E+02	10	1.03E-06	1.01E+03
12	7.00E-04	5.63E+02	12	9.48E-04	1.12E+03
14	9.80E-02	8.24E+02	14	1.27E-01	1.55E+03
16	4.05E+00	1.66E+03	16	5.09E+00	2.85E+03
18	7.42E+01	4.36E+03	18	9.09E+01	6.93E+03
20	7.67E+02	1.31E+04	20	9.21E+02	1.98E+04
22	5.21E+03	4.54E+04	22	6.16E+03	6.18E+04
24	2.59E+04	1.40E+05	24	3.02E+04	1.82E+05
26	1.01E+05	3.94E+05	26	1.16E+05	4.95E+05
28	3.24E+05	1.00E+06	28	3.70E+05	1.23E+06
30	8.93E+05	2.32E+06	30	1.01E+06	2.78E+06
40	3.16E+07	5.17E+07	40	3.49E+07	5.86E+07
50	2.73E+08	3.70E+08	50	2.96E+08	4.08E+08
75	5.00E+09	5.70E+09	75	5.31E+09	6.10E+09
77.36	5.98E+09	6.77E+09	77.36	6.35E+09	7.22E+09
100	2.21E+10	2.38E+10	100	2.32E+10	2.51E+10
125	5.52E+10	5.78E+10	125	5.75E+10	6.04E+10
150	1.03E+11	1.06E+11	150	1.06E+11	1.10E+11
175	1.61E+11	1.65E+11	175	1.67E+11	1.71E+11
194.7	2.12E+11	2.16E+11	194.7	2.19E+11	2.24E+11
200	2.26E+11	2.31E+11	200	2.34E+11	2.38E+11
225	2.96E+11	3.01E+11	225	3.06E+11	3.10E+11
250	3.68E+11	3.73E+11	250	3.79E+11	3.84E+11
273.15	4.35E+11	4.40E+11	273.15	4.48E+11	4.53E+11
275	4.41E+11	4.45E+11	275	4.54E+11	4.58E+11
298.15	5.07E+11	5.11E+11	298.15	5.21E+11	5.26E+11
300	5.12E+11	5.16E+11	300	5.27E+11	5.31E+11
325	5.82E+11	5.86E+11	325	5.98E+11	6.03E+11
350	6.50E+11	6.54E+11	350	6.68E+11	6.72E+11
373.15	7.11E+11	7.15E+11	373.15	7.30E+11	7.34E+11
375	7.16E+11	7.19E+11	375	7.35E+11	7.39E+11
400	7.79E+11	7.82E+11	400	8.00E+11	8.03E+11

XeF₆ [¹⁸F_α]

T(K)	CVT	CVT+SCT
4	3.20E-33	8.59E+02
5	1.93E-24	8.59E+02
6	1.43E-18	8.59E+02
7	2.27E-14	8.59E+02
8	3.28E-11	8.60E+02
9	9.52E-09	8.65E+02
10	9.00E-07	8.80E+02
12	8.47E-04	9.84E+02
14	1.15E-01	1.35E+03
16	4.68E+00	2.50E+03
18	8.43E+01	6.12E+03
20	8.60E+02	1.80E+04
22	5.79E+03	5.66E+04
24	2.85E+04	1.69E+05
26	1.10E+05	4.62E+05
28	3.52E+05	1.15E+06
30	9.66E+05	2.63E+06
40	3.36E+07	5.62E+07
50	2.87E+08	3.94E+08
75	5.19E+09	5.95E+09
77.36	6.21E+09	7.06E+09
100	2.28E+10	2.46E+10
125	5.67E+10	5.95E+10
150	1.05E+11	1.09E+11
175	1.65E+11	1.69E+11
194.7	2.17E+11	2.21E+11
200	2.32E+11	2.36E+11
225	3.03E+11	3.07E+11
250	3.76E+11	3.81E+11
273.15	4.44E+11	4.49E+11
275	4.50E+11	4.54E+11
298.15	5.17E+11	5.22E+11
300	5.23E+11	5.27E+11
325	5.94E+11	5.98E+11
350	6.63E+11	6.67E+11
373.15	7.25E+11	7.29E+11
375	7.30E+11	7.34E+11
400	7.94E+11	7.98E+11

XeF₆ [¹⁸F_β]

T(K)	CVT	CVT+SCT
4	1.75E-33	4.56E+02
5	1.19E-24	4.56E+02
6	9.55E-19	4.56E+02
7	1.61E-14	4.56E+02
8	2.43E-11	4.57E+02
9	7.29E-09	4.61E+02
10	7.08E-07	4.71E+02
12	6.93E-04	5.44E+02
14	9.72E-02	8.03E+02
16	4.02E+00	1.63E+03
18	7.38E+01	4.31E+03
20	7.62E+02	1.30E+04
22	5.19E+03	4.53E+04
24	2.58E+04	1.40E+05
26	1.00E+05	3.93E+05
28	3.23E+05	1.00E+06
30	8.90E+05	2.31E+06
40	3.15E+07	5.16E+07
50	2.72E+08	3.69E+08
75	4.99E+09	5.69E+09
77.36	5.97E+09	6.76E+09
100	2.21E+10	2.38E+10
125	5.51E+10	5.77E+10
150	1.02E+11	1.06E+11
175	1.61E+11	1.65E+11
194.7	2.12E+11	2.16E+11
200	2.26E+11	2.31E+11
225	2.96E+11	3.01E+11
250	3.68E+11	3.73E+11
273.15	4.35E+11	4.40E+11
275	4.41E+11	4.45E+11
298.15	5.07E+11	5.11E+11
300	5.12E+11	5.16E+11
325	5.82E+11	5.86E+11
350	6.50E+11	6.54E+11
373.15	7.11E+11	7.15E+11
375	7.16E+11	7.19E+11
400	7.79E+11	7.82E+11

XeF₆ [¹⁸F_γ]

T(K)	CVT	CVT+SCT
4	2.62E-33	5.56E+02
5	1.64E-24	5.56E+02
6	1.25E-18	5.56E+02
7	2.02E-14	5.56E+02
8	2.96E-11	5.57E+02
9	8.71E-09	5.61E+02
10	8.31E-07	5.72E+02
12	7.92E-04	6.54E+02
14	1.09E-01	9.46E+02
16	4.45E+00	1.88E+03
18	8.06E+01	4.95E+03
20	8.26E+02	1.48E+04
22	5.58E+03	5.04E+04
24	2.76E+04	1.54E+05
26	1.07E+05	4.28E+05
28	3.42E+05	1.08E+06
30	9.40E+05	2.48E+06
40	3.29E+07	5.43E+07
50	2.82E+08	3.84E+08
75	5.12E+09	5.85E+09
77.36	6.13E+09	6.94E+09
100	2.26E+10	2.43E+10
125	5.60E+10	5.87E+10
150	1.04E+11	1.07E+11
175	1.63E+11	1.67E+11
194.7	2.14E+11	2.19E+11
200	2.29E+11	2.33E+11
225	2.99E+11	3.04E+11
250	3.72E+11	3.76E+11
273.15	4.39E+11	4.43E+11
275	4.44E+11	4.49E+11
298.15	5.11E+11	5.15E+11
300	5.16E+11	5.21E+11
325	5.87E+11	5.91E+11
350	6.55E+11	6.59E+11
373.15	7.16E+11	7.20E+11
375	7.21E+11	7.25E+11
400	7.84E+11	7.88E+11

XeF₆ [¹²⁹Xe]

T(K)	CVT	CVT+SCT
4	1.85E-33	5.10E+02
5	1.24E-24	5.10E+02
6	9.89E-19	5.10E+02
7	1.66E-14	5.10E+02
8	2.49E-11	5.11E+02
9	7.46E-09	5.15E+02
10	7.23E-07	5.25E+02
12	7.06E-04	6.01E+02
14	9.86E-02	8.67E+02
16	4.08E+00	1.72E+03
18	7.46E+01	4.49E+03
20	7.70E+02	1.34E+04
22	5.24E+03	4.66E+04
24	2.60E+04	1.43E+05
26	1.01E+05	4.01E+05
28	3.25E+05	1.02E+06
30	8.96E+05	2.35E+06
40	3.17E+07	5.21E+07
50	2.73E+08	3.72E+08
75	5.01E+09	5.72E+09
77.36	5.99E+09	6.79E+09
100	2.22E+10	2.39E+10
125	5.52E+10	5.79E+10
150	1.03E+11	1.06E+11
175	1.61E+11	1.65E+11
194.7	2.12E+11	2.17E+11
200	2.27E+11	2.31E+11
225	2.97E+11	3.01E+11
250	3.69E+11	3.73E+11
273.15	4.36E+11	4.40E+11
275	4.41E+11	4.46E+11
298.15	5.08E+11	5.12E+11
300	5.13E+11	5.17E+11
325	5.83E+11	5.87E+11
350	6.51E+11	6.55E+11
373.15	7.12E+11	7.16E+11
375	7.17E+11	7.20E+11
400	7.80E+11	7.83E+11

XeF₆ [¹³¹Xe]

T(K)	CVT	CVT+SCT
4	1.82E-33	4.61E+02
5	1.23E-24	4.61E+02
6	9.79E-19	4.61E+02
7	1.64E-14	4.61E+02
8	2.47E-11	4.62E+02
9	7.41E-09	4.66E+02
10	7.18E-07	4.77E+02
12	7.02E-04	5.53E+02
14	9.82E-02	8.22E+02
16	4.06E+00	1.68E+03
18	7.44E+01	4.45E+03
20	7.68E+02	1.34E+04
22	5.22E+03	4.67E+04
24	2.59E+04	1.43E+05
26	1.01E+05	4.01E+05
28	3.24E+05	1.02E+06
30	8.94E+05	2.35E+06
40	3.16E+07	5.21E+07
50	2.73E+08	3.71E+08
75	5.00E+09	5.71E+09
77.36	5.99E+09	6.78E+09
100	2.22E+10	2.39E+10
125	5.52E+10	5.78E+10
150	1.03E+11	1.06E+11
175	1.61E+11	1.65E+11
194.7	2.12E+11	2.16E+11
200	2.27E+11	2.31E+11
225	2.97E+11	3.01E+11
250	3.69E+11	3.73E+11
273.15	4.36E+11	4.40E+11
275	4.41E+11	4.45E+11
298.15	5.07E+11	5.11E+11
300	5.12E+11	5.17E+11
325	5.82E+11	5.86E+11
350	6.50E+11	6.54E+11
373.15	7.11E+11	7.15E+11
375	7.16E+11	7.20E+11
400	7.79E+11	7.83E+11

XeF₆ [¹³²Xe]

T(K)	CVT	CVT+SCT
4	1.80E-33	4.73E+02
5	1.22E-24	4.73E+02
6	9.74E-19	4.73E+02
7	1.64E-14	4.73E+02
8	2.46E-11	4.74E+02
9	7.39E-09	4.78E+02
10	7.16E-07	4.88E+02
12	7.00E-04	5.62E+02
14	9.80E-02	8.23E+02
16	4.05E+00	1.66E+03
18	7.42E+01	4.36E+03
20	7.67E+02	1.31E+04
22	5.21E+03	4.54E+04
24	2.59E+04	1.40E+05
26	1.01E+05	3.94E+05
28	3.24E+05	1.00E+06
30	8.93E+05	2.32E+06
40	3.16E+07	5.17E+07
50	2.73E+08	3.70E+08
75	5.00E+09	5.70E+09
77.36	5.98E+09	6.77E+09
100	2.21E+10	2.38E+10
125	5.52E+10	5.78E+10
150	1.03E+11	1.06E+11
175	1.61E+11	1.65E+11
194.7	2.12E+11	2.16E+11
200	2.26E+11	2.31E+11
225	2.96E+11	3.01E+11
250	3.68E+11	3.73E+11
273.15	4.35E+11	4.40E+11
275	4.41E+11	4.45E+11
298.15	5.07E+11	5.11E+11
300	5.12E+11	5.16E+11
325	5.82E+11	5.86E+11
350	6.50E+11	6.54E+11
373.15	7.11E+11	7.15E+11
375	7.16E+11	7.19E+11
400	7.79E+11	7.82E+11

XeF₆ [¹³⁴Xe]

T(K)	CVT	CVT+SCT
4	1.78E-33	4.92E+02
5	1.21E-24	4.92E+02
6	9.64E-19	4.92E+02
7	1.62E-14	4.92E+02
8	2.44E-11	4.93E+02
9	7.34E-09	4.97E+02
10	7.12E-07	5.08E+02
12	6.96E-04	5.82E+02
14	9.75E-02	8.45E+02
16	4.04E+00	1.69E+03
18	7.40E+01	4.42E+03
20	7.64E+02	1.33E+04
22	5.20E+03	4.58E+04
24	2.58E+04	1.41E+05
26	1.01E+05	3.97E+05
28	3.23E+05	1.01E+06
30	8.91E+05	2.33E+06
40	3.15E+07	5.18E+07
50	2.72E+08	3.70E+08
75	4.99E+09	5.70E+09
77.36	5.98E+09	6.77E+09
100	2.21E+10	2.38E+10
125	5.51E+10	5.78E+10
150	1.02E+11	1.06E+11
175	1.61E+11	1.65E+11
194.7	2.12E+11	2.16E+11
200	2.26E+11	2.30E+11
225	2.96E+11	3.00E+11
250	3.68E+11	3.72E+11
273.15	4.35E+11	4.39E+11
275	4.40E+11	4.45E+11
298.15	5.07E+11	5.11E+11
300	5.12E+11	5.16E+11
325	5.82E+11	5.86E+11
350	6.50E+11	6.53E+11
373.15	7.10E+11	7.14E+11
375	7.15E+11	7.19E+11
400	7.78E+11	7.82E+11

XeF₆ [¹³⁶Xe]

T(K)	CVT	CVT+SCT
4	1.75E-33	4.48E+02
5	1.19E-24	4.48E+02
6	9.54E-19	4.48E+02
7	1.61E-14	4.48E+02
8	2.42E-11	4.49E+02
9	7.29E-09	4.53E+02
10	7.07E-07	4.63E+02
12	6.93E-04	5.36E+02
14	9.71E-02	7.91E+02
16	4.02E+00	1.60E+03
18	7.37E+01	4.25E+03
20	7.62E+02	1.28E+04
22	5.18E+03	4.50E+04
24	2.57E+04	1.39E+05
26	1.00E+05	3.92E+05
28	3.22E+05	9.97E+05
30	8.89E+05	2.31E+06
40	3.15E+07	5.15E+07
50	2.72E+08	3.69E+08
75	4.99E+09	5.69E+09
77.36	5.97E+09	6.75E+09
100	2.21E+10	2.38E+10
125	5.51E+10	5.77E+10
150	1.02E+11	1.06E+11
175	1.61E+11	1.64E+11
194.7	2.12E+11	2.16E+11
200	2.26E+11	2.30E+11
225	2.96E+11	3.00E+11
250	3.68E+11	3.72E+11
273.15	4.35E+11	4.39E+11
275	4.40E+11	4.44E+11
298.15	5.06E+11	5.10E+11
300	5.11E+11	5.15E+11
325	5.81E+11	5.85E+11
350	6.49E+11	6.53E+11
373.15	7.10E+11	7.13E+11
375	7.15E+11	7.18E+11
400	7.77E+11	7.81E+11

IF₆⁻

T(K)	CVT	CVT+SCT
4	3.51E-24	2.68E+03
5	3.30E-17	2.68E+03
6	1.52E-12	2.68E+03
7	3.33E-09	2.68E+03
8	1.09E-06	2.70E+03
9	9.93E-05	2.76E+03
10	3.72E-03	2.91E+03
12	8.74E-01	3.97E+03
14	4.41E+01	8.20E+03
16	8.50E+02	2.55E+04
18	8.59E+03	8.69E+04
20	5.50E+04	3.05E+05
22	2.53E+05	9.56E+05
24	9.08E+05	2.64E+06
26	2.68E+06	6.46E+06
28	6.81E+06	1.43E+07
30	1.53E+07	2.87E+07
40	2.63E+08	3.69E+08
50	1.48E+09	1.82E+09
75	1.52E+10	1.67E+10
77.36	1.76E+10	1.92E+10
100	5.04E+10	5.31E+10
125	1.05E+11	1.08E+11
150	1.73E+11	1.76E+11
175	2.47E+11	2.51E+11
194.7	3.09E+11	3.13E+11
200	3.25E+11	3.29E+11
225	4.03E+11	4.07E+11
250	4.79E+11	4.83E+11
273.15	5.47E+11	5.51E+11
275	5.53E+11	5.56E+11
298.15	6.18E+11	6.21E+11
300	6.23E+11	6.26E+11
325	6.89E+11	6.93E+11
350	7.53E+11	7.56E+11
373.15	8.08E+11	8.11E+11
375	8.12E+11	8.15E+11
400	8.69E+11	8.71E+11

TeF₆²⁻

T(K)	CVT	CVT+SCT
4	1.96E+02	5.56E+08
5	1.31E+04	5.56E+08
6	2.22E+05	5.58E+08
7	1.72E+06	5.70E+08
8	8.11E+06	6.13E+08
9	2.75E+07	7.22E+08
10	7.39E+07	9.47E+08
12	3.33E+08	1.46E+09
14	9.95E+08	2.85E+09
16	2.29E+09	5.04E+09
18	4.43E+09	8.16E+09
20	7.55E+09	1.23E+10
22	1.17E+10	1.75E+10
24	1.70E+10	2.37E+10
26	2.33E+10	3.09E+10
28	3.06E+10	3.90E+10
30	3.89E+10	4.79E+10
40	9.08E+10	1.02E+11
50	1.53E+11	1.65E+11
75	3.16E+11	3.27E+11
77.36	3.31E+11	3.41E+11
100	4.62E+11	4.71E+11
125	5.85E+11	5.92E+11
150	6.87E+11	6.93E+11
175	7.73E+11	7.77E+11
194.7	8.30E+11	8.34E+11
200	8.45E+11	8.49E+11
225	9.06E+11	9.10E+11
250	9.59E+11	9.62E+11
273.15	1.00E+12	1.00E+12
275	1.01E+12	1.01E+12
298.15	1.04E+12	1.05E+12
300	1.05E+12	1.05E+12
325	1.08E+12	1.08E+12
350	1.11E+12	1.12E+12
373.15	1.14E+12	1.14E+12
375	1.14E+12	1.14E+12
400	1.17E+12	1.17E+12

Table S3. Kinetic isotope effect from CVT+SCT rate constants.

T(K)	F $\alpha+\beta+\gamma$	F α	F β	F γ	$^{129}\text{Xe}/^{136}\text{Xe}$	$^{129}\text{Xe}/^{134}\text{Xe}$	$^{129}\text{Xe}/^{132}\text{Xe}$	$^{129}\text{Xe}/^{131}\text{Xe}$
4	2.07	1.81	0.96	1.17	1.14	1.04	1.08	1.11
5	2.07	1.81	0.96	1.17	1.14	1.04	1.08	1.11
6	2.07	1.81	0.96	1.17	1.14	1.04	1.08	1.11
7	2.07	1.81	0.96	1.17	1.14	1.04	1.08	1.11
8	2.07	1.81	0.96	1.17	1.14	1.04	1.08	1.11
9	2.07	1.81	0.96	1.17	1.14	1.04	1.08	1.11
10	2.07	1.80	0.96	1.17	1.13	1.03	1.08	1.10
12	1.99	1.75	0.97	1.16	1.12	1.03	1.07	1.09
14	1.88	1.64	0.97	1.15	1.10	1.03	1.05	1.05
16	1.72	1.51	0.98	1.13	1.08	1.02	1.04	1.02
18	1.59	1.40	0.99	1.14	1.06	1.02	1.03	1.01
20	1.51	1.37	0.99	1.13	1.05	1.01	1.02	1.00
22	1.36	1.25	1.00	1.11	1.04	1.02	1.03	1.00
24	1.30	1.21	1.00	1.10	1.03	1.01	1.02	1.00
26	1.26	1.17	1.00	1.09	1.02	1.01	1.02	1.00
28	1.23	1.15	1.00	1.08	1.02	1.01	1.02	1.00
30	1.20	1.13	1.00	1.07	1.02	1.01	1.01	1.00
40	1.13	1.09	1.00	1.05	1.01	1.01	1.01	1.00
50	1.10	1.06	1.00	1.04	1.01	1.01	1.01	1.00
75	1.07	1.04	1.00	1.03	1.01	1.00	1.00	1.00
77.36	1.07	1.04	1.00	1.03	1.01	1.00	1.00	1.00
100	1.05	1.03	1.00	1.02	1.00	1.00	1.00	1.00
125	1.04	1.03	1.00	1.02	1.00	1.00	1.00	1.00
150	1.04	1.03	1.00	1.01	1.00	1.00	1.00	1.00
175	1.04	1.02	1.00	1.01	1.01	1.00	1.00	1.00
194.7	1.04	1.02	1.00	1.01	1.00	1.00	1.00	1.00
200	1.03	1.02	1.00	1.01	1.00	1.00	1.00	1.00
225	1.03	1.02	1.00	1.01	1.00	1.00	1.00	1.00
250	1.03	1.02	1.00	1.01	1.00	1.00	1.00	1.00
273.15	1.03	1.02	1.00	1.01	1.00	1.00	1.00	1.00
275	1.03	1.02	1.00	1.01	1.00	1.00	1.00	1.00
298.15	1.03	1.02	1.00	1.01	1.00	1.00	1.00	1.00
300	1.03	1.02	1.00	1.01	1.00	1.00	1.00	1.00
325	1.03	1.02	1.00	1.01	1.00	1.00	1.00	1.00
350	1.03	1.02	1.00	1.01	1.00	1.00	1.00	1.00
373.15	1.03	1.02	1.00	1.01	1.00	1.00	1.00	1.00
375	1.03	1.02	1.00	1.01	1.00	1.00	1.00	1.00
400	1.03	1.02	1.00	1.01	1.00	1.00	1.00	1.00

Example of Polyrate input file (.dat file):

```

*GENERAL                                     *PATH                                     373.15
TITLE                                       SYMMETRY                                   375
  QMT_calculation_for_XeF6                 INTMU 3                                   400
END                                          SSTEP 0.001                              END
#DL ISPE                                   RPM pagem
ATOMS                                       SRANGE                                    ANALYSIS
1 Xe                                        SLP 20.                                  4
2 F                                         SLM -20.                                 5
3 F                                         END                                       6
4 F                                         SPECSTOP                                  7
5 F                                         CURVE VMEP                               8
6 F                                         PERCENTDOWN 99                          9
7 F                                         END                                       10
END                                          PRPATH                                    12
                                           coord 1 2                                14
                                           xmol                                     16
                                           freq 15                                 18
                                           END                                       20
NOSUPERMOL                                *TUNNEL                                  24
*SECOND                                     ZCT                                       26
HESSCAL hhook                              SCT                                       28
FPRINT                                       QRST                                    30
                                           harmonic                                40
*OPTIMIZATION                              mode 15                                  50
                                           states all                              75
PRINT                                       END                                       77.355
                                           100
OPTMIN ohook                               *RATE                                    125
OPTTS ohook                               FORWARDK                                  150
*REACT1                                     SIGMAF 1                                  175
INITGEO hooks                              TST                                       194.7
GEOM                                         CVT                                       200
1                                             PRDELG                                  225
2                                             PRPART rtp                              250
3                                             TEMP                                     273.15
4                                             4                                       275
5                                             5                                       298.15
6                                             6                                       300
7                                             7                                       300
END                                           8                                       325
                                           9                                       325
SPECIES nonlinrp                            10                                      350
                                           12                                      373.15
                                           14                                      375
*PROD1                                     16                                      400
INITGEO hooks                              18                                      END
GEOM                                         20                                      EACT
1                                             22                                      6. 10.
2                                             24                                      10. 20.
3                                             26                                      20. 50.
4                                             28                                      50. 100.
5                                             30                                      200. 225.
6                                             40                                      300. 325.
7                                             50                                      END
END                                           50                                      GTLOG
SPECIES nonlinrp                            75
                                           77.355
*START                                     100
INITGEO hooks                              125
GEOM                                         150
1                                             175
2                                             194.7
3                                             200
4                                             225
5                                             250
6                                             273.15
7                                             275
END                                           298.15
SPECIES nonlints                            300
PROJECT                                     325
                                           350

```

XYZ optimized geometries at the BMK/def2tzvp level with superfine integral grid.

XeF₆

Reactant/Product				Transition state			
Xe	0.000000	0.000000	0.139158	Xe	0.000000	0.000000	0.123763
F	0.000000	1.847480	0.789863	F	-1.874920	0.000000	-0.130337
F	1.599965	-0.923740	0.789863	F	0.000000	1.738399	1.066699
F	-1.599965	-0.923740	0.789863	F	-0.000000	-1.738399	1.066699
F	1.215111	0.701545	-1.068180	F	0.000000	1.176827	-1.307650
F	-0.000000	-1.403090	-1.068180	F	1.874920	-0.000000	-0.130337
F	-1.215111	0.701545	-1.068180	F	-0.000000	-1.176827	-1.307650

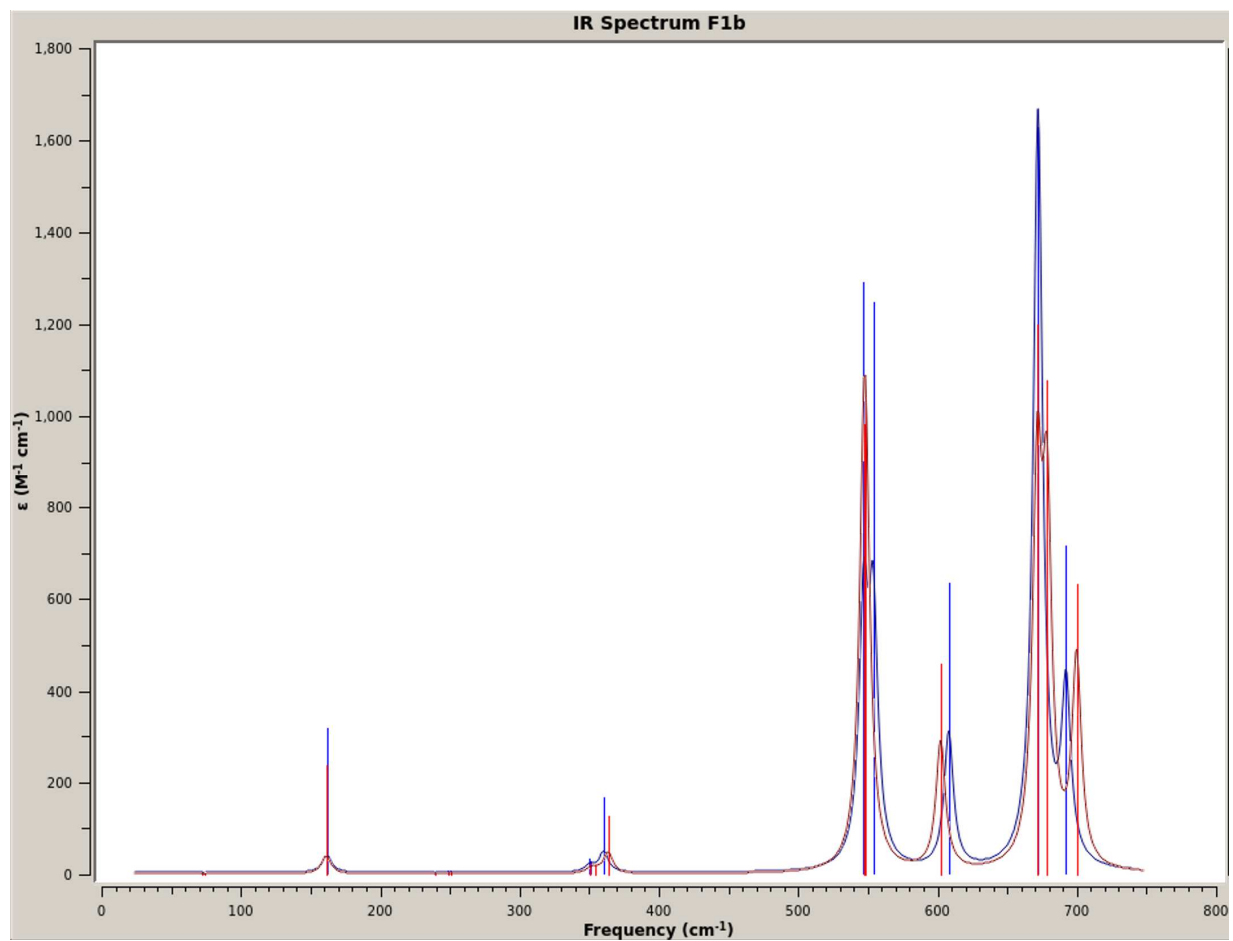
IF₆⁻

Reactant/Product				Transition state			
I	0.000000	0.000000	0.138016	I	0.000000	0.000000	0.123054
F	0.000000	1.930389	0.823095	F	-1.931513	0.000000	-0.153677
F	1.671766	-0.965194	0.823095	F	0.000000	1.820924	1.123921
F	-1.671766	-0.965194	0.823095	F	-0.000000	-1.820924	1.123921
F	1.243163	0.717741	-1.094016	F	0.000000	1.206505	-1.332569
F	-0.000000	-1.435481	-1.094016	F	1.931513	-0.000000	-0.153677
F	-1.243163	0.717741	-1.094016	F	-0.000000	-1.206505	-1.332569

TeF₆²⁻

Reactant/Product				Transition state			
Te	0.000000	0.000000	0.110884	Te	0.000000	0.000000	0.098639
F	0.000000	2.038859	0.948281	F	-2.036903	0.000000	-0.189951
F	1.765703	-1.019429	0.948281	F	0.000000	1.904130	1.298736
F	-1.765703	-1.019429	0.948281	F	-0.000000	-1.904130	1.298736
F	1.304524	0.753167	-1.161835	F	0.000000	1.277336	-1.393742
F	-0.000000	-1.506335	-1.161835	F	2.036903	-0.000000	-0.189951
F	-1.304524	0.753167	-1.161835	F	-0.000000	-1.277336	-1.393742

Computed ^{18}F monosubstituted IR spectra (blue for F_V , red for F_O):



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