Supporting Information:

Exploring the Initial Bond Activations of PFAS on Zero-valent Iron

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1 Bader Charges

Table S1: Bader charges for PFBA in the gas-phase.

Atom	Charge
C	1.61
C_α	1.18
C_β	1.18
C_ω	1.82
O_{OH}	–1.04
H	0.61
O	–1.03
F_α	–0.57
F_α	–0.58
F_β	–0.57
F_β	–0.57
F_ω	–0.58
F_ω	–0.58
F_ω	–0.58

Table S2: Bader charges for reaction **R1** in the carbo binding mode.

Atom	Charge[a]		
	Initial	TS	Final
C	0.82	1.01 (0.20)	1.11 (0.30)
C_α	1.12	1.12 (−0.00)	1.13 (0.01)
C_β	1.18	1.22 (0.05)	1.22 (0.04)
C_ω	1.81	1.80 (−0.01)	1.80 (−0.02)
O_{OH}	−1.07	−1.01 (0.07)	−1.06 (0.01)
H	0.60	0.18 (−0.42)	−0.34 (−0.94)
O	−1.08	−1.06 (0.02)	−1.07 (0.00)
F_α	−0.62	−0.63 (−0.00)	−0.63 (−0.00)
F_α	−0.62	−0.62 (0.01)	−0.62 (0.00)
F_β	−0.57	−0.59 (−0.02)	−0.57 (0.00)
F_β	−0.58	−0.58 (0.00)	−0.58 (0.00)
F_ω	−0.58	−0.59 (−0.00)	−0.58 (0.00)
F_ω	−0.56	−0.56 (0.01)	−0.56 (−0.00)
F_ω	−0.58	−0.58 (0.00)	−0.58 (−0.00)
Total[b]	−0.76	−0.87 (−0.11)	−1.34 (−0.59)

[a] Values in parenthesis are the changes in the Bader charges with respect to the initial state.
[b] In order to maintain charge neutrality of the unit cell, the Fe(110) surface will have an equal and opposite charge.

Table S3: Bader charges for reaction **R2** in the carbo binding mode.

Atom	Charge[a]		
	Initial	TS	Final
C	0.82	0.82 (0.00)	0.92 (0.11)
C_α	1.12	0.74 (−0.38)	0.29 (−0.83)
C_β	1.18	1.21 (0.03)	1.18 (0.00)
C_ω	1.81	1.79 (−0.02)	1.78 (−0.04)
O_{OH}	−1.07	−1.01 (0.06)	−1.03 (0.04)
H	0.60	0.59 (−0.01)	0.59 (−0.01)
O	−1.08	−1.03 (0.04)	−1.06 (0.02)
F_α	−0.62	−0.59 (0.03)	−0.69 (−0.07)
F_α	−0.62	−0.63 (−0.00)	−0.60 (0.03)
F_β	−0.57	−0.58 (−0.00)	−0.60 (−0.03)
F_β	−0.58	−0.56 (0.02)	−0.57 (0.01)
F_ω	−0.58	−0.59 (−0.00)	−0.63 (−0.04)
F_ω	−0.56	−0.56 (0.00)	−0.58 (−0.01)
F_ω	−0.58	−0.58 (−0.00)	−0.60 (−0.02)
Total[b]	−0.76	−0.98 (−0.22)	−1.61 (−0.85)

[a] Values in parenthesis are the changes in the Bader charges with respect to the initial state.
[b] In order to maintain charge neutrality of the unit cell, the Fe(110) surface will have an equal and opposite charge.

Table S4: Bader charges for reaction **R4** in the carbo binding mode.

Atom	Charge[a]		
	Initial	TS	Final
C	0.82	0.88 (0.07)	0.84 (0.02)
C_α	1.12	1.08 (−0.04)	0.68 (−0.44)
C_β	1.18	1.19 (0.01)	1.20 (0.02)
C_ω	1.81	1.79 (−0.02)	1.79 (−0.02)
O_{OH}	−1.07	−1.10 (−0.03)	−1.05 (0.02)
H	0.60	0.59 (−0.00)	0.61 (0.01)
O	−1.08	−1.11 (−0.03)	−1.10 (−0.02)
F_α	−0.62	−0.62 (0.00)	−0.61 (0.01)
F_α	−0.62	−0.64 (−0.02)	−0.60 (0.02)
F_β	−0.57	−0.57 (0.00)	−0.61 (−0.04)
F_β	−0.58	−0.59 (−0.01)	−0.61 (−0.03)
F_ω	−0.58	−0.58 (0.01)	−0.58 (0.01)
F_ω	−0.56	−0.56 (−0.00)	−0.57 (−0.00)
F_ω	−0.58	−0.58 (0.00)	−0.59 (−0.01)
Total[b]	−0.76	−0.81 (−0.05)	−1.20 (−0.44)

[a] Values in parenthesis are the changes in the Bader charges with respect to the initial state.
[b] In order to maintain charge neutrality of the unit cell, the Fe(110) surface will have an equal and opposite charge.

Table S5: Bader charges for reaction **R5** in the carbo binding mode.

Atom	Charge[a]		
	Initial	TS	Final
C	0.82	0.26 (−0.55)	0.13 (−0.69)
C_α	1.12	1.09 (−0.03)	1.09 (−0.03)
C_β	1.18	1.22 (0.05)	1.20 (0.02)
C_ω	1.81	1.80 (−0.01)	1.80 (−0.02)
O_{OH}	−1.07	−1.10 (−0.03)	−1.09 (−0.02)
H	0.60	0.61 (0.01)	0.61 (0.01)
O	−1.08	−0.93 (0.15)	−0.97 (0.11)
F_α	−0.62	−0.63 (−0.01)	−0.63 (−0.00)
F_α	−0.62	−0.59 (0.04)	−0.63 (−0.01)
F_β	−0.57	−0.61 (−0.03)	−0.57 (0.01)
F_β	−0.58	−0.59 (−0.01)	−0.59 (−0.01)
F_ω	−0.58	−0.58 (0.00)	−0.58 (0.01)
F_ω	−0.56	−0.57 (−0.01)	−0.57 (−0.01)
F_ω	−0.58	−0.57 (0.01)	−0.58 (0.00)
Total[b]	−0.76	−1.18 (−0.43)	−1.38 (−0.63)

[a] Values in parenthesis are the changes in the Bader charges with respect to the initial state.
[b] In order to maintain charge neutrality of the unit cell, the Fe(110) surface will have an equal and opposite charge.

Table S6: Bader charges for reaction **R6** in the carbo binding mode.

Atom	Charge[a]		
	Initial	TS	Final
C	0.82	0.62 (−0.20)	0.16 (−0.66)
C_α	1.12	1.13 (0.01)	1.07 (−0.06)
C_β	1.18	1.22 (0.05)	1.21 (0.03)
C_ω	1.81	1.82 (0.00)	1.83 (0.01)
O_{OH}	−1.07	−0.98 (0.10)	−1.20 (−0.12)
H	0.60	0.56 (−0.04)	0.61 (0.02)
O	−1.08	−1.11 (−0.03)	−1.03 (0.05)
F_α	−0.62	−0.62 (0.01)	−0.60 (0.03)
F_α	−0.62	−0.62 (0.00)	−0.63 (−0.01)
F_β	−0.57	−0.59 (−0.01)	−0.58 (−0.01)
F_β	−0.58	−0.60 (−0.02)	−0.59 (−0.01)
F_ω	−0.58	−0.59 (−0.00)	−0.59 (−0.00)
F_ω	−0.56	−0.56 (0.00)	−0.58 (−0.01)
F_ω	−0.58	−0.58 (−0.00)	−0.59 (−0.01)
Total[b]	−0.76	−0.89 (−0.14)	−1.51 (−0.75)

[a] Values in parenthesis are the changes in the Bader charges with respect to the initial state.
[b] In order to maintain charge neutrality of the unit cell, the Fe(110) surface will have an equal and opposite charge.

Table S7: Bader charges for reaction **R7** in the carbo binding mode.

Atom	Charge[a]		
	Initial	TS	Final
C	1.11	1.08 (−0.03)	1.31 (0.20)
C_α	1.13	0.89 (−0.24)	0.29 (−0.84)
C_β	1.22	1.23 (0.01)	1.18 (−0.04)
C_ω	1.80	1.82 (0.02)	1.78 (−0.02)
O_{OH}	−1.06	−1.04 (0.02)	−1.08 (−0.02)
H	−0.34	−0.34 (0.00)	−0.32 (0.02)
O	−1.07	−1.06 (0.02)	−1.07 (0.01)
F_α	−0.63	−0.54 (0.09)	−0.68 (−0.05)
F_α	−0.62	−0.62 (0.00)	−0.60 (0.02)
F_β	−0.57	−0.58 (−0.01)	−0.61 (−0.04)
F_β	−0.58	−0.57 (0.01)	−0.57 (0.01)
F_ω	−0.58	−0.58 (−0.00)	−0.64 (−0.06)
F_ω	−0.56	−0.56 (0.00)	−0.57 (−0.01)
F_ω	−0.58	−0.59 (−0.00)	−0.59 (−0.01)
Total[b]	−1.34	−1.46 (−0.11)	−2.18 (−0.83)

[a] Values in parenthesis are the changes in the Bader charges with respect to the initial state.
[b] In order to maintain charge neutrality of the unit cell, the Fe(110) surface will have an equal and opposite charge.

Table S8: Bader charges for reaction **R9** in the carbo binding mode.

Atom	Charge[a]		
	Initial	TS	Final
C	1.11	0.84 (−0.27)	1.02 (−0.09)
C_α	1.13	1.09 (−0.04)	0.69 (−0.43)
C_β	1.22	1.16 (−0.05)	1.19 (−0.02)
C_ω	1.80	1.81 (0.01)	1.78 (−0.02)
O_{OH}	−1.06	−1.07 (−0.01)	−1.02 (0.04)
H	−0.34	0.62 (0.95)	−0.35 (−0.02)
O	−1.07	−1.09 (−0.01)	−1.06 (0.01)
F_α	−0.63	−0.64 (−0.01)	−0.61 (0.02)
F_α	−0.62	−0.64 (−0.01)	−0.62 (0.00)
F_β	−0.57	−0.57 (−0.00)	−0.61 (−0.04)
F_β	−0.58	−0.58 (0.00)	−0.60 (−0.02)
F_ω	−0.58	−0.58 (−0.00)	−0.57 (0.01)
F_ω	−0.56	−0.57 (−0.01)	−0.56 (0.00)
F_ω	−0.58	−0.57 (0.01)	−0.58 (−0.00)
Total[b]	−1.34	−0.78 (0.56)	−1.90 (−0.56)

[a] Values in parenthesis are the changes in the Bader charges with respect to the initial state.
[b] In order to maintain charge neutrality of the unit cell, the Fe(110) surface will have an equal and opposite charge.

Table S9: Bader charges for reaction **R10** in the carbo binding mode.

Atom	Charge[a]		
	Initial	TS	Final
C	1.11	0.83 (−0.28)	0.51 (−0.61)
C_α	1.13	1.12 (−0.01)	1.09 (−0.04)
C_β	1.22	1.22 (0.00)	1.23 (0.02)
C_ω	1.80	1.80 (0.00)	1.82 (0.02)
O_{OH}	−1.06	−1.09 (−0.03)	−1.05 (0.01)
H	−0.34	−0.34 (0.00)	−0.35 (−0.01)
O	−1.07	−0.91 (0.16)	−0.96 (0.11)
F_α	−0.63	−0.62 (0.00)	−0.63 (0.00)
F_α	−0.62	−0.62 (0.00)	−0.62 (0.00)
F_β	−0.57	−0.57 (−0.00)	−0.59 (−0.02)
F_β	−0.58	−0.58 (−0.00)	−0.59 (−0.01)
F_ω	−0.58	−0.58 (0.00)	−0.58 (0.00)
F_ω	−0.56	−0.57 (−0.00)	−0.58 (−0.02)
F_ω	−0.58	−0.58 (0.00)	−0.58 (−0.00)
Total[b]	−1.34	−1.50 (−0.15)	−1.88 (−0.54)

[a] Values in parenthesis are the changes in the Bader charges with respect to the initial state.
[b] In order to maintain charge neutrality of the unit cell, the Fe(110) surface will have an equal and opposite charge.

Table S10: Bader charges for reaction **R1** in the flat binding mode.

Atom	Charge[a]		
	Initial	TS	Final
C	1.55	1.58 (0.03)	1.63 (0.08)
C_α	1.23	1.22 (−0.01)	1.19 (−0.05)
C_β	1.15	1.16 (0.02)	1.16 (0.01)
C_ω	1.83	1.81 (−0.02)	1.83 (−0.00)
O_{OH}	−1.07	−1.04 (0.03)	−1.14 (−0.07)
H	0.53	0.31 (−0.22)	−0.36 (−0.89)
O	−1.18	−1.18 (0.00)	−1.13 (0.05)
F_α	−0.59	−0.58 (0.01)	−0.58 (0.00)
F_α	−0.57	−0.58 (−0.01)	−0.58 (−0.01)
F_β	−0.63	−0.62 (0.01)	−0.61 (0.02)
F_β	−0.57	−0.57 (0.00)	−0.57 (0.01)
F_ω	−0.60	−0.60 (0.00)	−0.60 (0.01)
F_ω	−0.57	−0.55 (0.02)	−0.58 (−0.01)
F_ω	−0.58	−0.58 (0.00)	−0.58 (0.00)
Total[b]	−0.07	−0.23 (−0.15)	−0.91 (−0.84)

[a] Values in parenthesis are the changes in the Bader charges with respect to the initial state.
[b] In order to maintain charge neutrality of the unit cell, the Fe(110) surface will have an equal and opposite charge.

Table S11: Bader charges for reaction **R2** in the flat binding mode.

Atom	Charge[a]		
	Initial	TS	Final
C	1.55	1.36 (−0.19)	1.17 (−0.38)
C_α	1.23	0.86 (−0.38)	0.56 (−0.68)
C_β	1.15	1.19 (0.04)	1.15 (0.00)
C_ω	1.83	1.78 (−0.05)	1.77 (−0.06)
O_{OH}	−1.07	−1.04 (0.03)	−1.07 (0.00)
H	0.53	0.56 (0.03)	0.52 (−0.01)
O	−1.18	−1.17 (0.02)	−1.17 (0.01)
F_α	−0.59	−0.59 (−0.00)	−0.67 (−0.09)
F_α	−0.57	−0.57 (0.00)	−0.57 (0.00)
F_β	−0.63	−0.62 (0.02)	−0.62 (0.02)
F_β	−0.57	−0.57 (0.00)	−0.57 (−0.00)
F_ω	−0.60	−0.62 (−0.02)	−0.60 (0.00)
F_ω	−0.57	−0.56 (0.01)	−0.58 (−0.01)
F_ω	−0.58	−0.58 (0.00)	−0.58 (−0.00)
Total[b]	−0.07	−0.55 (−0.48)	−1.25 (−1.18)

[a] Values in parenthesis are the changes in the Bader charges with respect to the initial state.
[b] In order to maintain charge neutrality of the unit cell, the Fe(110) surface will have an equal and opposite charge.

Table S12: Bader charges for reaction **R3** in the flat binding mode.

Atom	Charge[a]		
	Initial	TS	Final
C	1.55	1.54 (−0.01)	0.91 (−0.64)
C_α	1.23	1.23 (−0.01)	1.10 (−0.13)
C_β	1.15	1.06 (−0.09)	0.27 (−0.88)
C_ω	1.83	1.85 (0.02)	1.67 (−0.16)
O_{OH}	−1.07	−1.08 (−0.01)	−1.06 (0.01)
H	0.53	0.54 (0.01)	0.57 (0.04)
O	−1.18	−1.19 (−0.00)	−1.05 (0.13)
F_α	−0.59	−0.58 (0.00)	−0.62 (−0.03)
F_α	−0.57	−0.58 (−0.01)	−0.58 (−0.01)
F_β	−0.63	−0.56 (0.07)	−0.69 (−0.06)
F_β	−0.57	−0.57 (−0.00)	−0.60 (−0.03)
F_ω	−0.60	−0.61 (−0.00)	−0.61 (−0.01)
F_ω	−0.57	−0.58 (−0.01)	−0.62 (−0.05)
F_ω	−0.58	−0.58 (0.00)	−0.57 (0.02)
Total[b]	−0.07	−0.12 (−0.04)	−1.87 (−1.79)

[a] Values in parenthesis are the changes in the Bader charges with respect to the initial state.
[b] In order to maintain charge neutrality of the unit cell, the Fe(110) surface will have an equal and opposite charge.

Table S13: Bader charges for reaction **R4** in the flat binding mode.

Atom	Charge[a]		
	Initial	TS	Final
C	1.55	1.37 (−0.18)	1.26 (−0.29)
C_α	1.23	0.78 (−0.46)	0.80 (−0.43)
C_β	1.15	1.12 (−0.03)	1.13 (−0.01)
C_ω	1.83	1.81 (−0.02)	1.77 (−0.06)
O_{OH}	−1.07	−1.08 (−0.01)	−1.07 (−0.00)
H	0.53	0.47 (−0.06)	0.47 (−0.06)
O	−1.18	−1.21 (−0.02)	−1.19 (−0.00)
F_α	−0.59	−0.60 (−0.02)	−0.61 (−0.02)
F_α	−0.57	−0.59 (−0.02)	−0.61 (−0.04)
F_β	−0.63	−0.62 (0.01)	−0.62 (0.01)
F_β	−0.57	−0.58 (−0.01)	−0.56 (0.01)
F_ω	−0.60	−0.65 (−0.04)	−0.63 (−0.03)
F_ω	−0.57	−0.60 (−0.03)	−0.60 (−0.03)
F_ω	−0.58	−0.57 (0.01)	−0.56 (0.02)
Total[b]	−0.07	−0.95 (−0.88)	−1.02 (−0.94)

[a] Values in parenthesis are the changes in the Bader charges with respect to the initial state.
[b] In order to maintain charge neutrality of the unit cell, the Fe(110) surface will have an equal and opposite charge.

Table S14: Bader charges for reaction **R5** in the flat binding mode.

Atom	Charge[a]		
	Initial	TS	Final
C	1.55	0.54 (−1.01)	0.33 (−1.22)
C_α	1.23	1.14 (−0.09)	1.11 (−0.13)
C_β	1.15	1.20 (0.05)	1.18 (0.03)
C_ω	1.83	1.79 (−0.04)	1.80 (−0.02)
O_{OH}	−1.07	−1.06 (0.01)	−1.06 (0.01)
H	0.53	0.57 (0.04)	0.57 (0.04)
O	−1.18	−0.93 (0.25)	−0.97 (0.21)
F_α	−0.59	−0.64 (−0.06)	−0.64 (−0.06)
F_α	−0.57	−0.57 (−0.01)	−0.58 (−0.01)
F_β	−0.63	−0.63 (0.00)	−0.63 (−0.00)
F_β	−0.57	−0.59 (−0.02)	−0.57 (−0.00)
F_ω	−0.60	−0.60 (0.01)	−0.62 (−0.02)
F_ω	−0.57	−0.56 (0.01)	−0.57 (−0.00)
F_ω	−0.58	−0.57 (0.01)	−0.57 (0.01)
Total[b]	−0.07	−0.92 (−0.85)	−1.24 (−1.16)

[a] Values in parenthesis are the changes in the Bader charges with respect to the initial state.
[b] In order to maintain charge neutrality of the unit cell, the Fe(110) surface will have an equal and opposite charge.

Table S15: Bader charges for reaction **R6** in the flat binding mode.

Atom	Charge[a]		
	Initial	TS	Final
C	1.55	0.99 (−0.56)	0.74 (−0.81)
C_α	1.23	1.18 (−0.06)	1.16 (−0.07)
C_β	1.15	1.20 (0.05)	1.14 (−0.00)
C_ω	1.83	1.79 (−0.04)	1.79 (−0.04)
O_{OH}	−1.07	−0.98 (0.09)	−1.00 (0.07)
H	0.53	0.60 (0.07)	0.14 (−0.39)
O	−1.18	−1.13 (0.05)	−1.14 (0.04)
F_α	−0.59	−0.57 (0.01)	−0.59 (−0.00)
F_α	−0.57	−0.59 (−0.02)	−0.57 (−0.00)
F_β	−0.63	−0.62 (0.02)	−0.62 (0.01)
F_β	−0.57	−0.57 (0.00)	−0.56 (0.01)
F_ω	−0.60	−0.61 (−0.00)	−0.61 (−0.00)
F_ω	−0.57	−0.58 (−0.01)	−0.58 (−0.02)
F_ω	−0.58	−0.57 (0.01)	−0.56 (0.02)
Total[b]	−0.07	−0.46 (−0.39)	−1.26 (−1.19)

[a] Values in parenthesis are the changes in the Bader charges with respect to the initial state.
[b] In order to maintain charge neutrality of the unit cell, the Fe(110) surface will have an equal and opposite charge.

Table S16: Bader charges for reaction **R7** in the flat binding mode.

Atom	Charge[a]		
	Initial	TS	Final
C	1.63	1.56 (−0.08)	1.19 (−0.45)
C_α	1.19	0.89 (−0.30)	0.56 (−0.63)
C_β	1.16	1.22 (0.06)	1.15 (−0.01)
C_ω	1.83	1.82 (−0.00)	1.78 (−0.05)
O_{OH}	−1.14	−1.11 (0.02)	−1.14 (−0.00)
H	−0.36	−0.36 (−0.00)	−0.36 (−0.00)
O	−1.13	−1.16 (−0.03)	−1.15 (−0.02)
F_α	−0.58	−0.48 (0.11)	−0.69 (−0.11)
F_α	−0.58	−0.56 (0.02)	−0.58 (0.00)
F_β	−0.61	−0.57 (0.04)	−0.62 (−0.01)
F_β	−0.57	−0.57 (−0.00)	−0.57 (−0.00)
F_ω	−0.60	−0.60 (−0.00)	−0.60 (−0.01)
F_ω	−0.58	−0.57 (0.01)	−0.56 (0.02)
F_ω	−0.58	−0.58 (−0.00)	−0.58 (0.00)
Total[b]	−0.91	−1.07 (−0.16)	−2.16 (−1.25)

[a] Values in parenthesis are the changes in the Bader charges with respect to the initial state.
[b] In order to maintain charge neutrality of the unit cell, the Fe(110) surface will have an equal and opposite charge.

Table S17: Bader charges for reaction **R8** in the flat binding mode.

Atom	Charge[a]		
	Initial	TS	Final
C	1.63	1.64 (0.00)	1.08 (−0.55)
C_α	1.19	1.20 (0.01)	1.14 (−0.05)
C_β	1.16	0.80 (−0.36)	0.24 (−0.92)
C_ω	1.83	1.82 (−0.00)	1.71 (−0.11)
O_{OH}	−1.14	−1.14 (−0.00)	−1.11 (0.03)
H	−0.36	−0.36 (−0.00)	−0.35 (0.01)
O	−1.13	−1.13 (0.00)	−1.03 (0.10)
F_α	−0.58	−0.58 (0.01)	−0.60 (−0.02)
F_α	−0.58	−0.58 (0.00)	−0.57 (0.01)
F_β	−0.61	−0.61 (0.01)	−0.68 (−0.07)
F_β	−0.57	−0.56 (0.01)	−0.59 (−0.02)
F_ω	−0.60	−0.59 (0.00)	−0.62 (−0.03)
F_ω	−0.58	−0.59 (−0.01)	−0.62 (−0.04)
F_ω	−0.58	−0.56 (0.02)	−0.58 (−0.01)
Total[b]	−0.91	−1.23 (−0.32)	−2.57 (−1.66)

[a] Values in parenthesis are the changes in the Bader charges with respect to the initial state.
[b] In order to maintain charge neutrality of the unit cell, the Fe(110) surface will have an equal and opposite charge.

Table S18: Bader charges for reaction **R9** in the flat binding mode.

Atom	Charge[a]		
	Initial	TS	Final
C	1.63	1.12 (−0.51)	1.04 (−0.59)
C_α	1.19	0.82 (−0.36)	0.82 (−0.37)
C_β	1.16	1.12 (−0.04)	1.13 (−0.03)
C_ω	1.83	1.81 (−0.02)	1.77 (−0.06)
O_{OH}	−1.14	−1.09 (0.05)	−1.04 (0.10)
H	−0.36	−0.35 (0.01)	−0.35 (0.01)
O	−1.13	−1.02 (0.11)	−1.06 (0.08)
F_α	−0.58	−0.61 (−0.03)	−0.61 (−0.03)
F_α	−0.58	−0.61 (−0.03)	−0.60 (−0.03)
F_β	−0.61	−0.65 (−0.03)	−0.64 (−0.02)
F_β	−0.57	−0.57 (−0.01)	−0.57 (−0.00)
F_ω	−0.60	−0.64 (−0.04)	−0.64 (−0.04)
F_ω	−0.58	−0.60 (−0.02)	−0.56 (0.02)
F_ω	−0.58	−0.57 (0.00)	−0.57 (0.00)
Total[b]	−0.91	−1.84 (−0.92)	−1.88 (−0.97)

[a] Values in parenthesis are the changes in the Bader charges with respect to the initial state.
[b] In order to maintain charge neutrality of the unit cell, the Fe(110) surface will have an equal and opposite charge.

Table S19: Bader charges for reaction **R10** in the flat binding mode.

Atom	Charge[a]		
	Initial	TS	Final
C	1.63	0.74 (−0.89)	0.14 (−1.49)
C_α	1.19	1.19 (−0.00)	1.15 (−0.03)
C_β	1.16	1.19 (0.03)	1.21 (0.05)
C_ω	1.83	1.79 (−0.04)	1.79 (−0.04)
O_{OH}	−1.14	−1.10 (0.04)	−1.03 (0.10)
H	−0.36	−0.35 (0.00)	−0.33 (0.02)
O	−1.13	−0.92 (0.21)	−0.94 (0.20)
F_α	−0.58	−0.61 (−0.03)	−0.63 (−0.04)
F_α	−0.58	−0.59 (−0.01)	−0.58 (−0.00)
F_β	−0.61	−0.58 (0.03)	−0.61 (0.00)
F_β	−0.57	−0.57 (−0.01)	−0.58 (−0.02)
F_ω	−0.60	−0.59 (0.00)	−0.60 (0.00)
F_ω	−0.58	−0.56 (0.02)	−0.56 (0.02)
F_ω	−0.58	−0.57 (0.01)	−0.58 (0.00)
Total[b]	−0.91	−1.54 (−0.62)	−2.14 (−1.23)

[a] Values in parenthesis are the changes in the Bader charges with respect to the initial state.
[b] In order to maintain charge neutrality of the unit cell, the Fe(110) surface will have an equal and opposite charge.

2 Vibrational Spectra

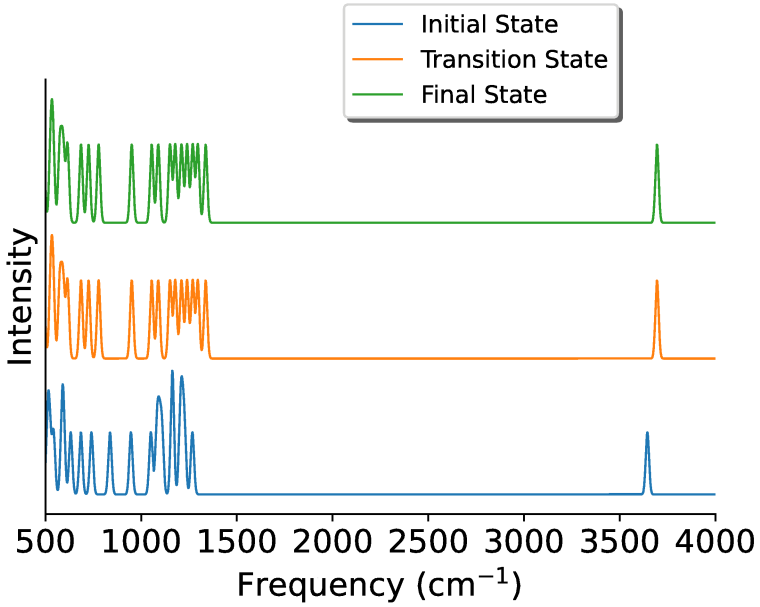

Figure S1: Vibrational spectra of the initial, transition, and final state for reaction **R2** in the carbo binding mode.

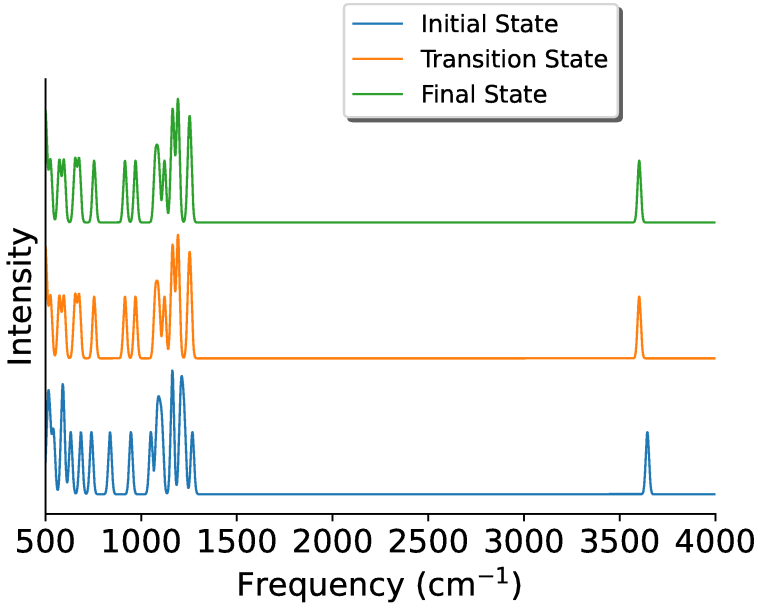

Figure S2: Vibrational spectra of the initial, transition, and final state for reaction **R4** in the carbo binding mode.

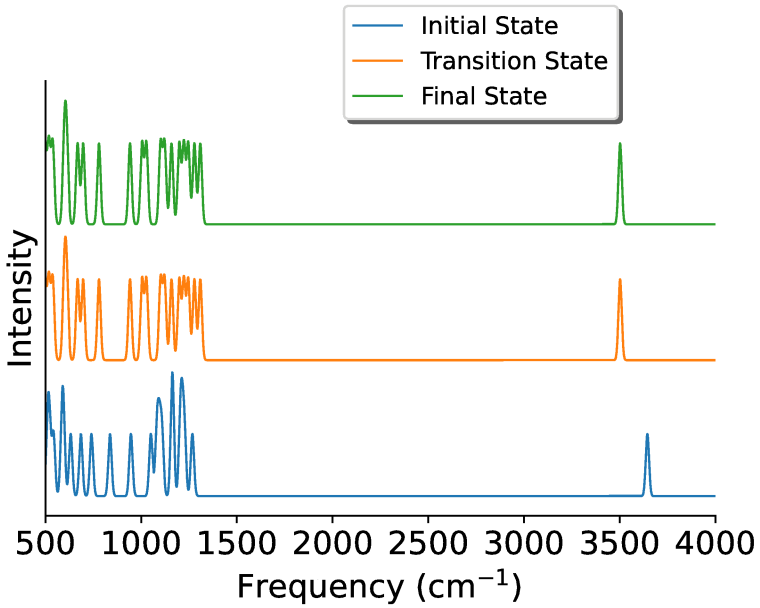

Figure S3: Vibrational spectra of the initial, transition, and final state for reaction **R5** in the carbo binding mode.

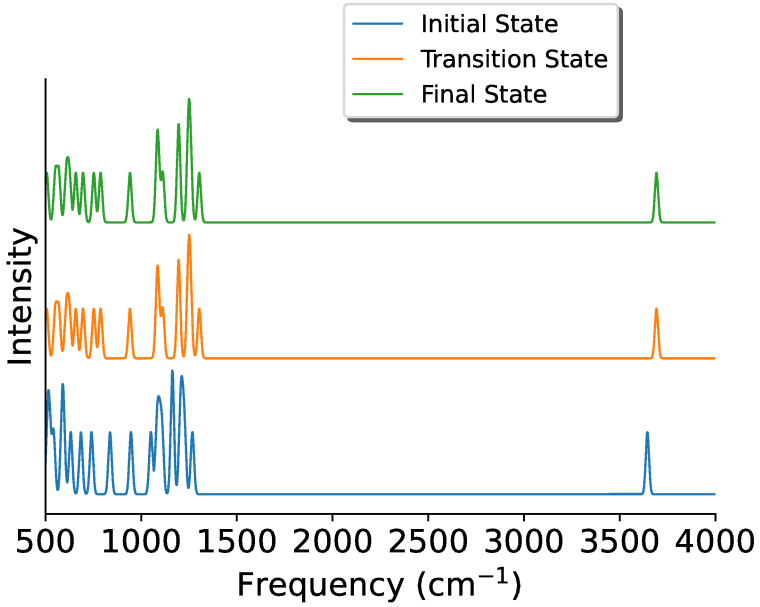

Figure S4: Vibrational spectra of the initial, transition, and final state for reaction **R6** in the carbo binding mode.

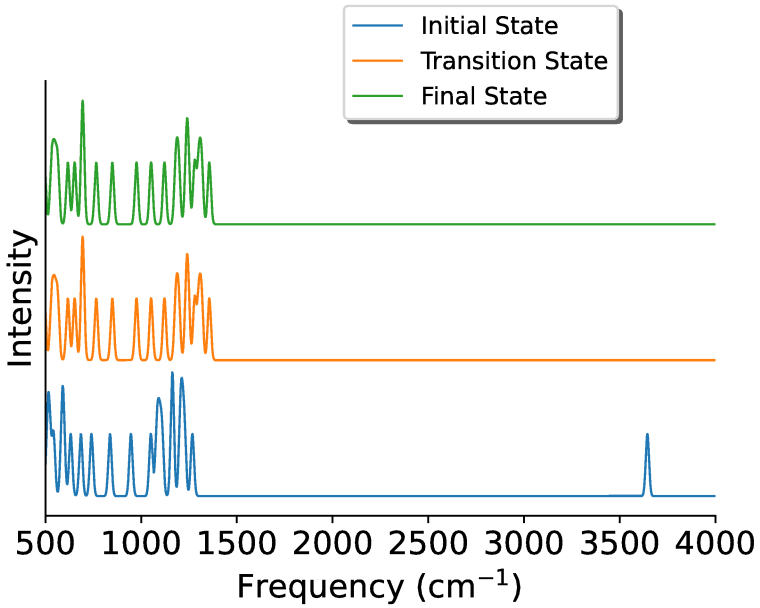

Figure S5: Vibrational spectra of the initial, transition, and final state for reaction **R8** in the carbo binding mode.

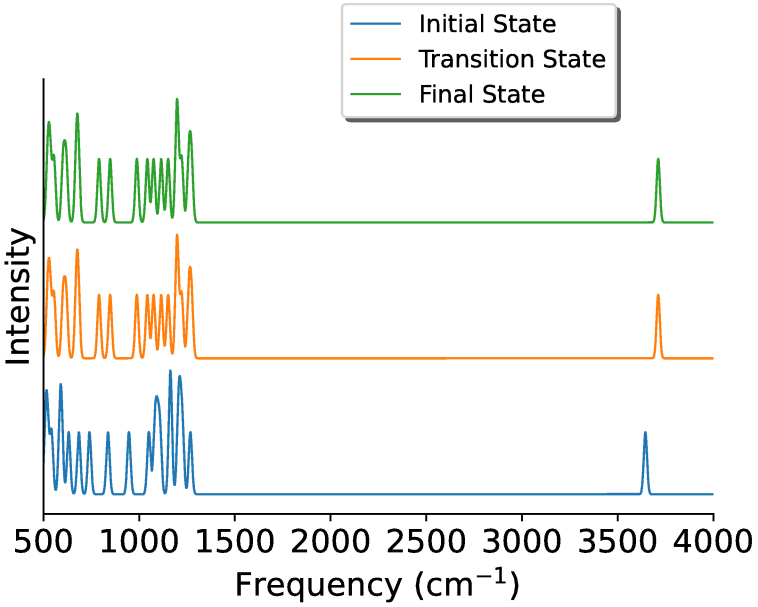

Figure S6: Vibrational spectra of the initial, transition, and final state for reaction **R9** in the carbo binding mode.

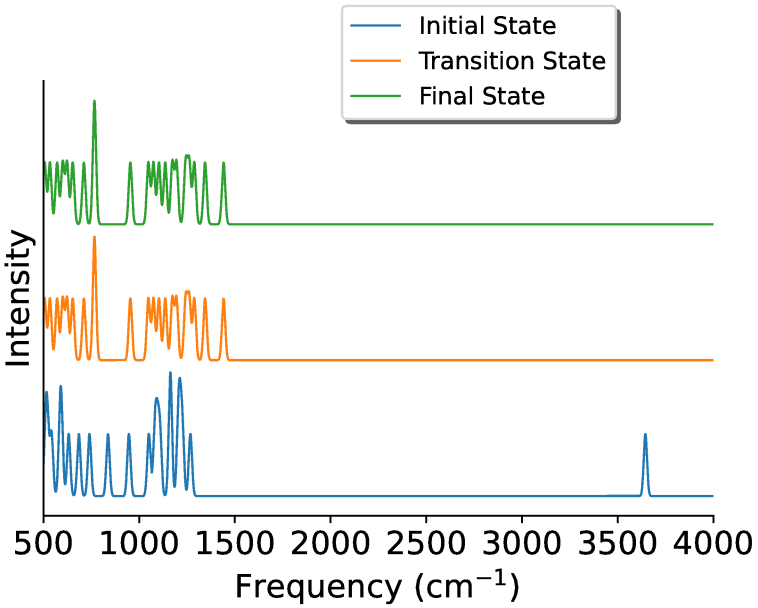

Figure S7: Vibrational spectra of the initial, transition, and final state for reaction **R10** in the carbo binding mode.

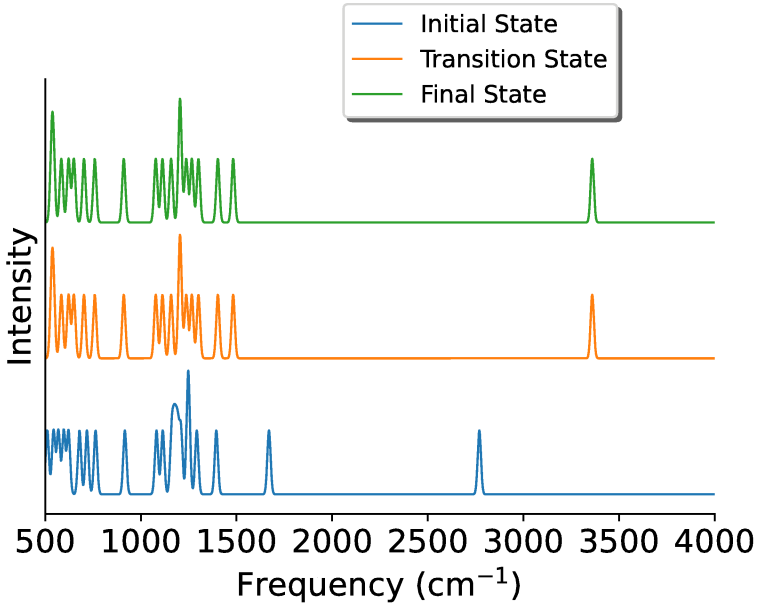

Figure S8: Vibrational spectra of the initial, transition, and final state for reaction **R2** in the flat binding mode.

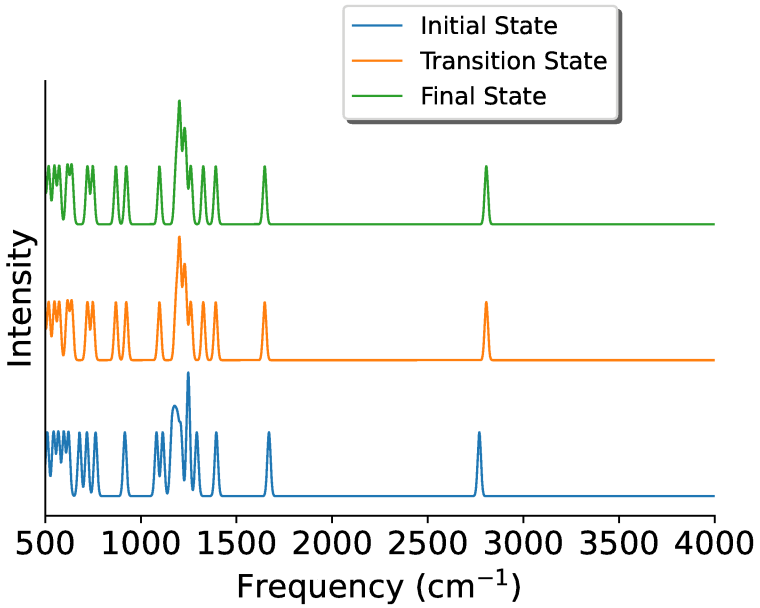

Figure S9: Vibrational spectra of the initial, transition, and final state for reaction **R3** in the flat binding mode.

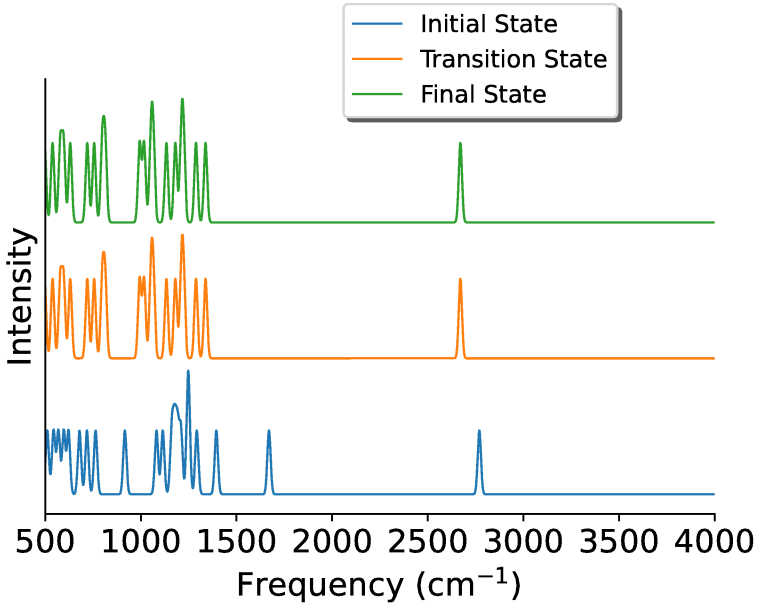

Figure S10: Vibrational spectra of the initial, transition, and final state for reaction **R4** in the flat binding mode.

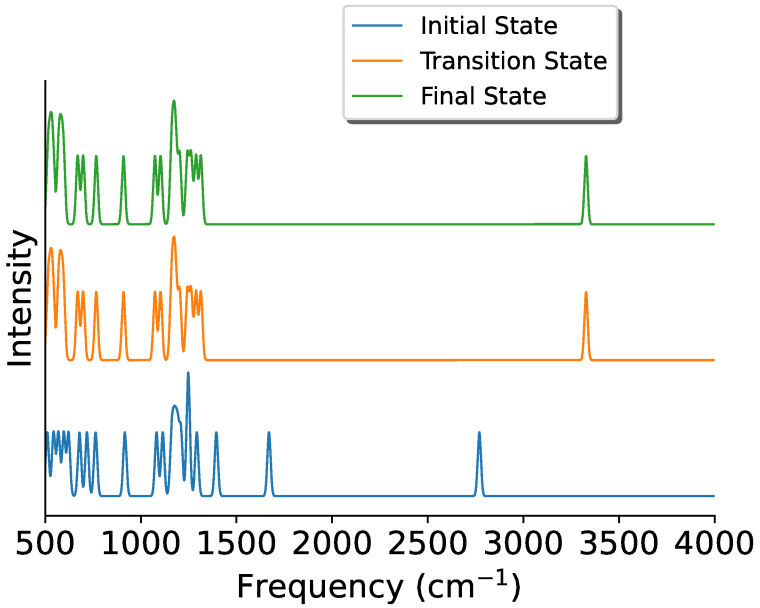

Figure S11: Vibrational spectra of the initial, transition, and final state for reaction **R5** in the flat binding mode.

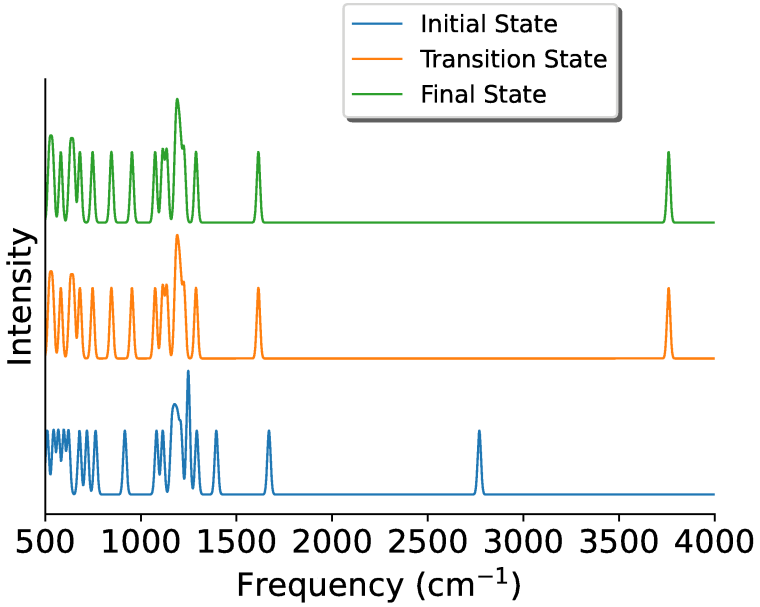

Figure S12: Vibrational spectra of the initial, transition, and final state for reaction **R6** in the flat binding mode.

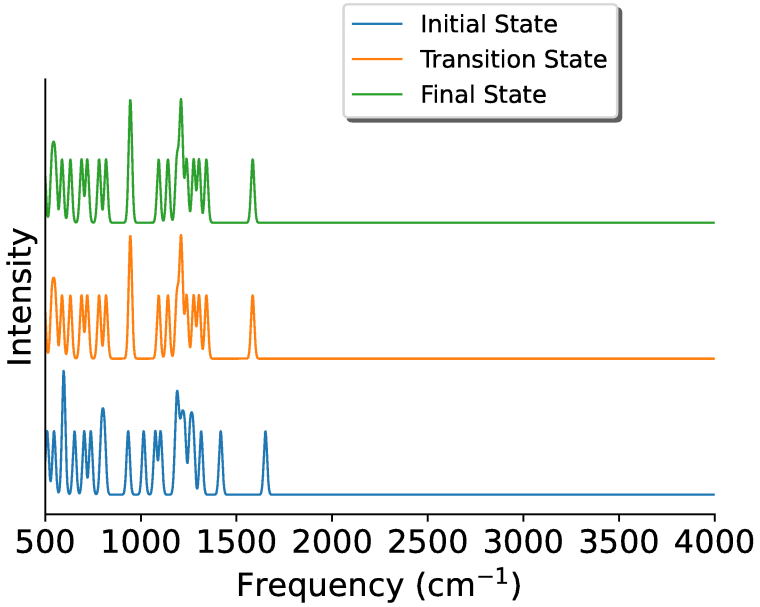

Figure S13: Vibrational spectra of the initial, transition, and final state for reaction **R8** in the flat binding mode.

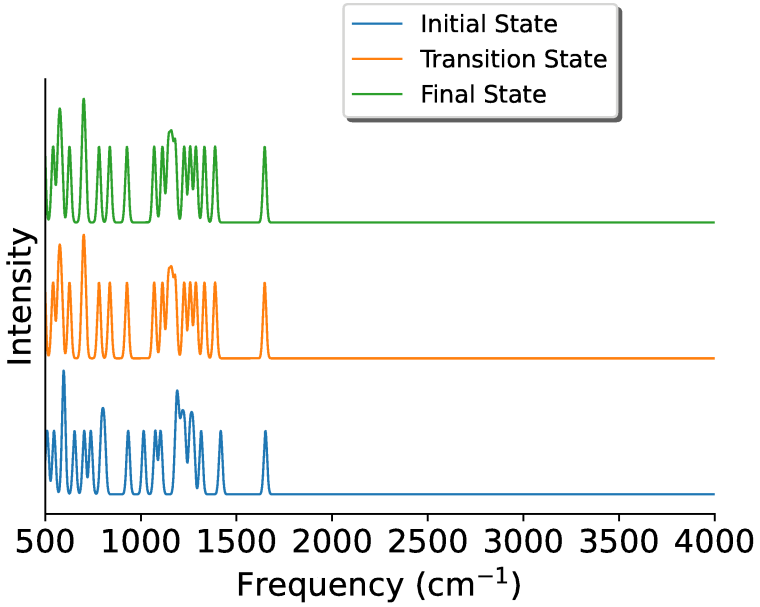

Figure S14: Vibrational spectra of the initial, transition, and final state for reaction **R8** in the flat binding mode.

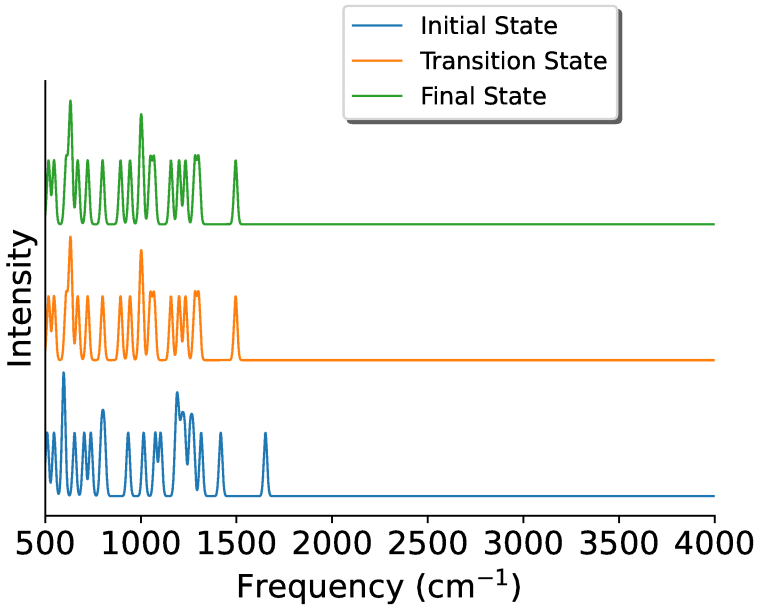

Figure S15: Vibrational spectra of the initial, transition, and final state for reaction **R9** in the flat binding mode.

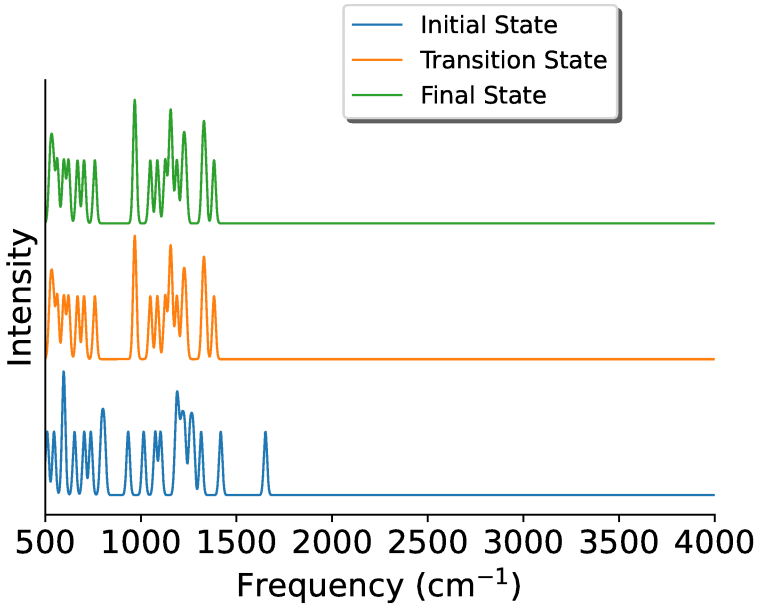

Figure S16: Vibrational spectra of the initial, transition, and final state for reaction **R10** in the flat binding mode.

3 XAS Spectra

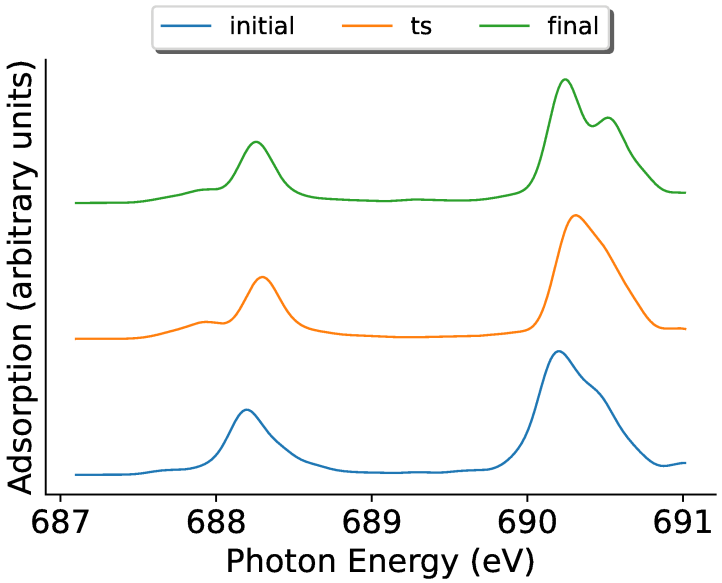

Figure S17: Fluorine *K*-edge XAS of the initial, transition, and final state for reaction **R1** in the carbo binding mode.

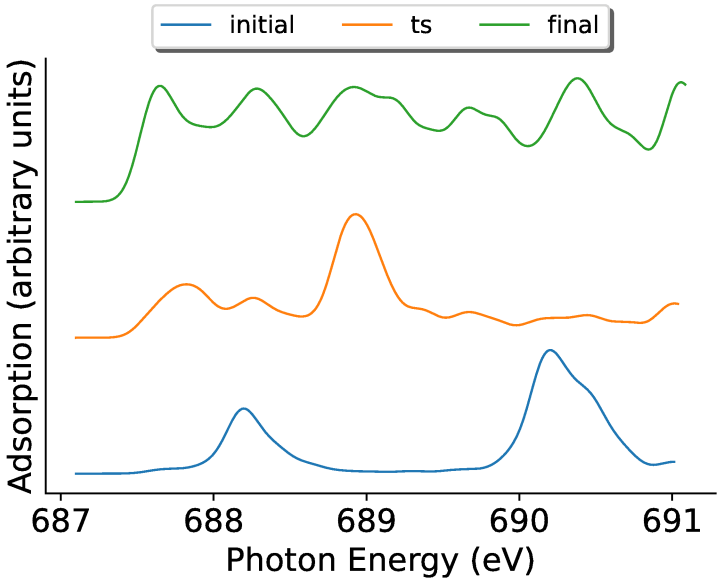

Figure S18: Fluorine *K*-edge XAS of the initial, transition, and final state for reaction **R2** in the carbo binding mode.

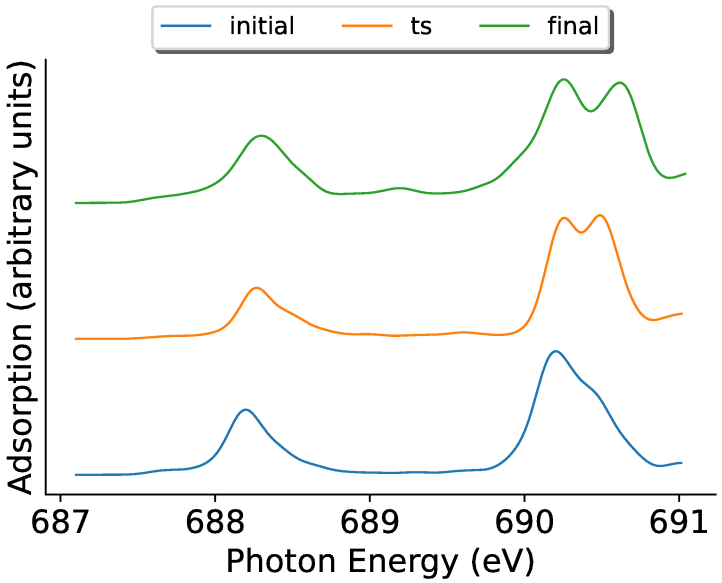

Figure S19: Fluorine *K*-edge XAS of the initial, transition, and final state for reaction **R4** in the carbo binding mode.

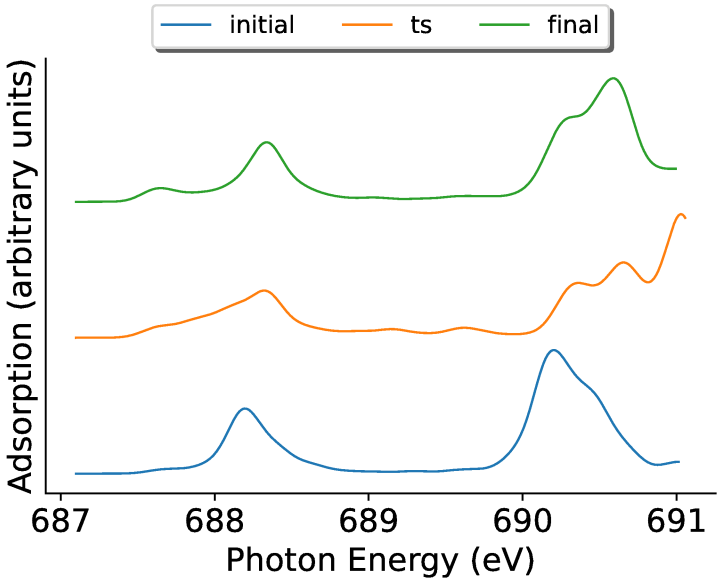

Figure S20: Fluorine *K*-edge XAS of the initial, transition, and final state for reaction **R5** in the carbo binding mode.

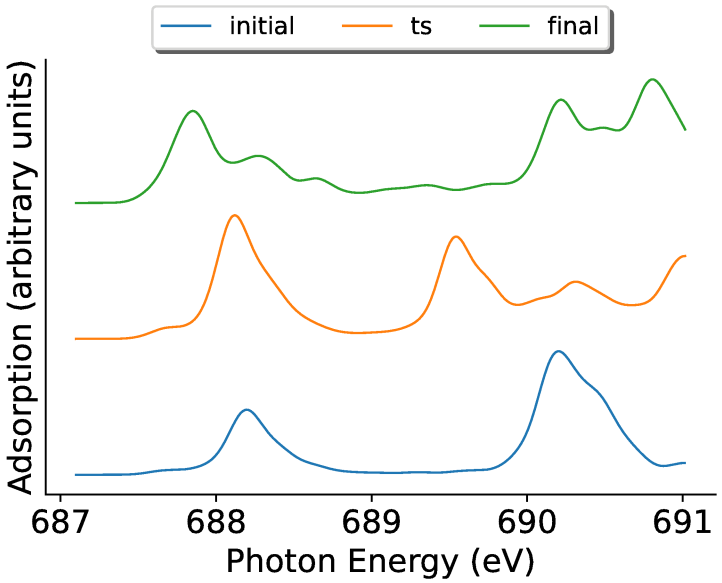

Figure S21: Fluorine *K*-edge XAS of the initial, transition, and final state for reaction **R6** in the carbo binding mode.

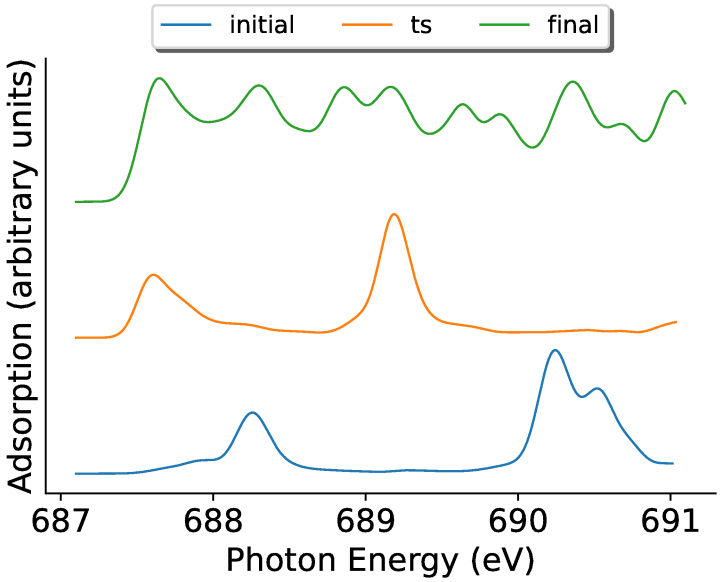

Figure S22: Fluorine *K*-edge XAS of the initial, transition, and final state for reaction **R7** in the carbo binding mode.

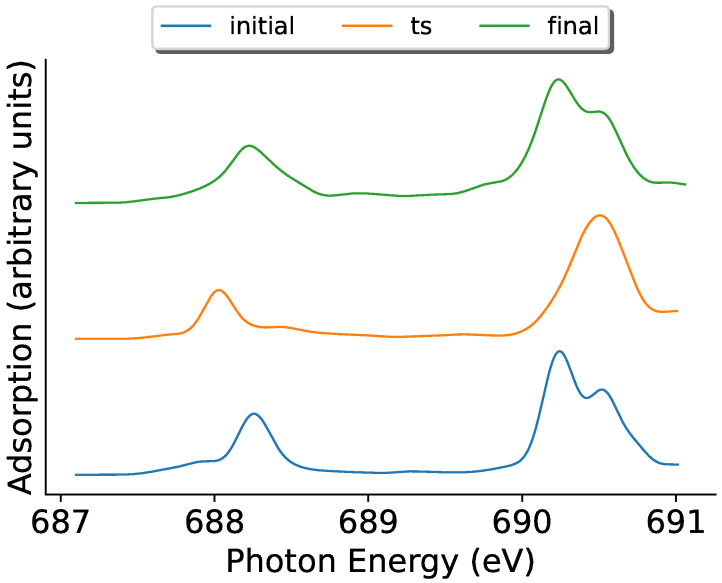

Figure S23: Fluorine *K*-edge XAS of the initial, transition, and final state for reaction **R9** in the carbo binding mode.

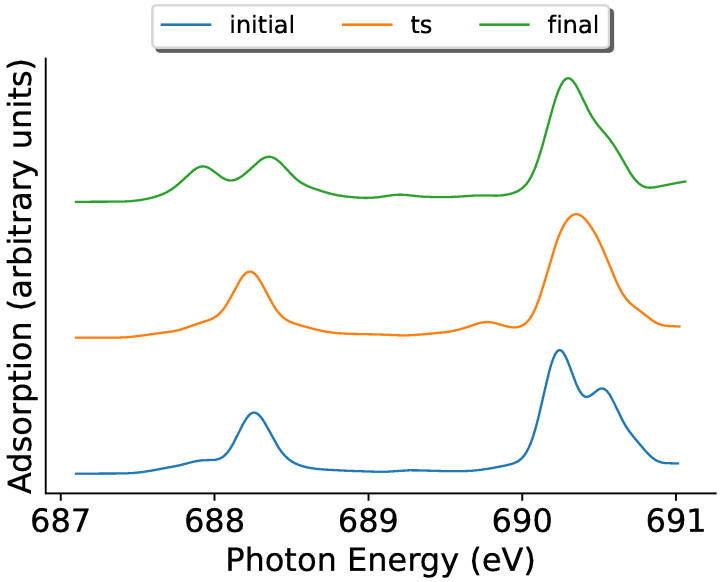

Figure S24: Fluorine *K*-edge XAS of the initial, transition, and final state for reaction **R10** in the carbo binding mode.

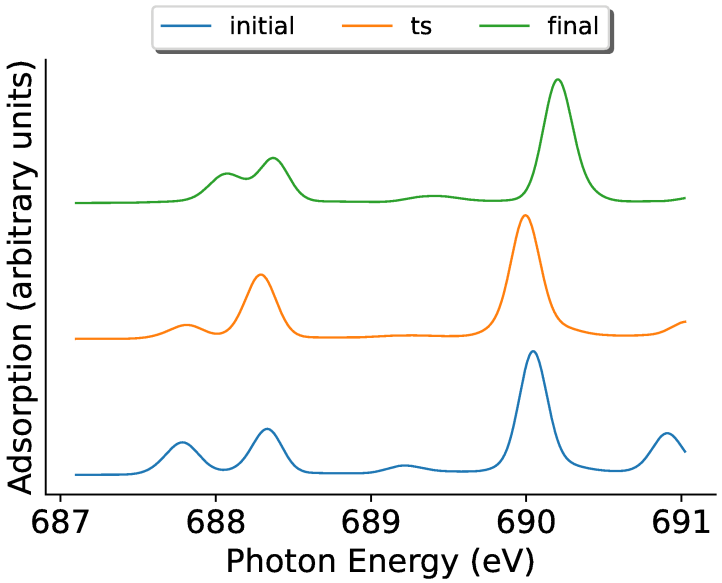

Figure S25: Fluorine *K*-edge XAS of the initial, transition, and final state for reaction **R1** in the flat binding mode.

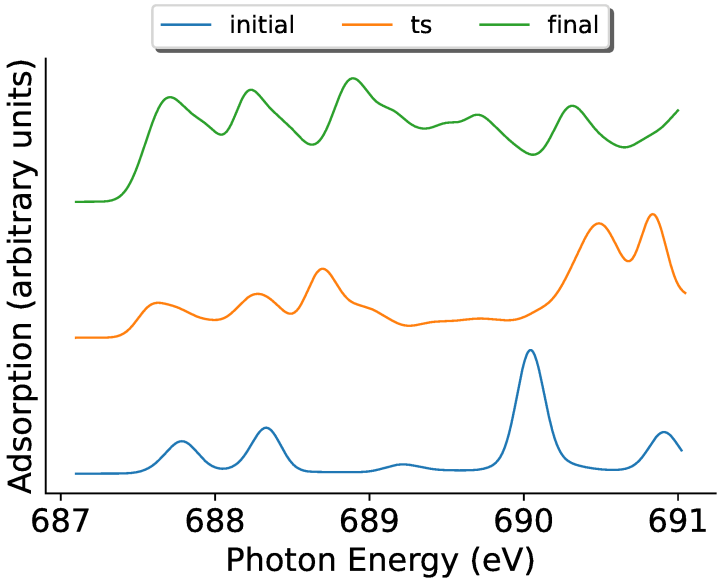

Figure S26: Fluorine *K*-edge XAS of the initial, transition, and final state for reaction **R2** in the flat binding mode.

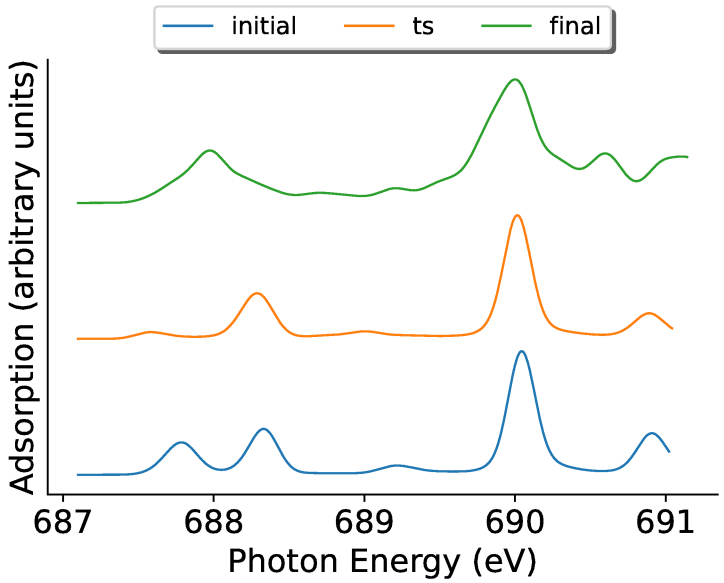

Figure S27: Fluorine *K*-edge XAS of the initial, transition, and final state for reaction **R3** in the flat binding mode.

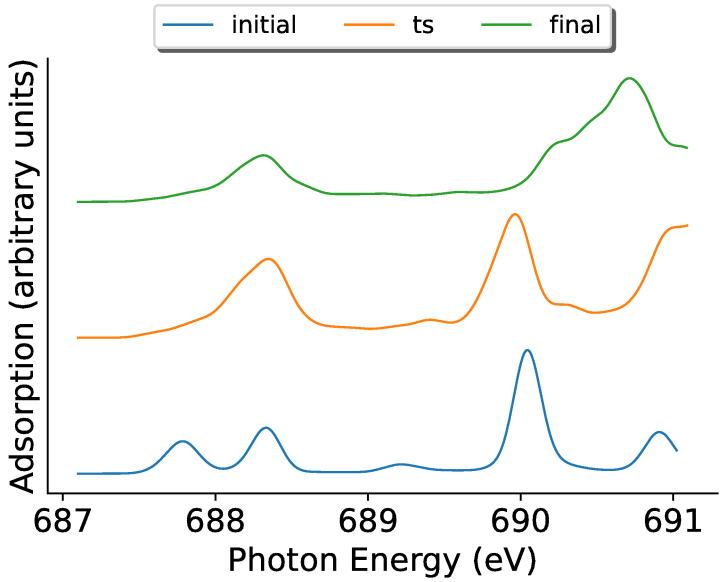

Figure S28: Fluorine *K*-edge XAS of the initial, transition, and final state for reaction **R4** in the flat binding mode.

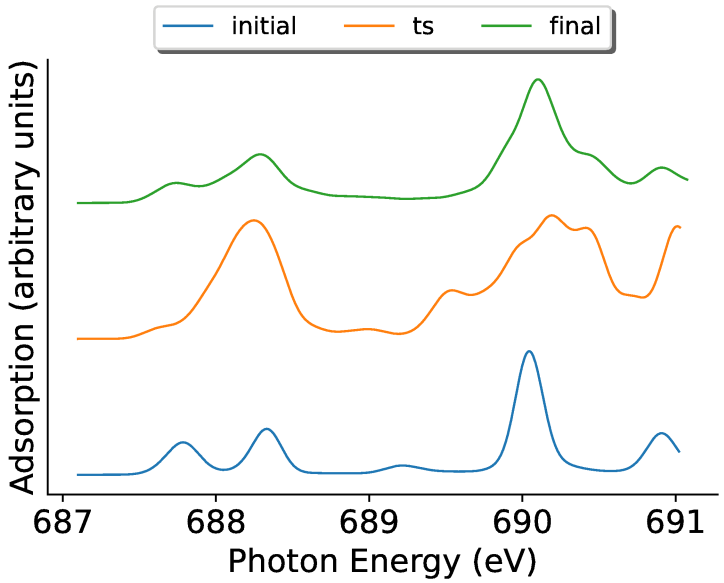

Figure S29: Fluorine *K*-edge XAS of the initial, transition, and final state for reaction **R5** in the flat binding mode.

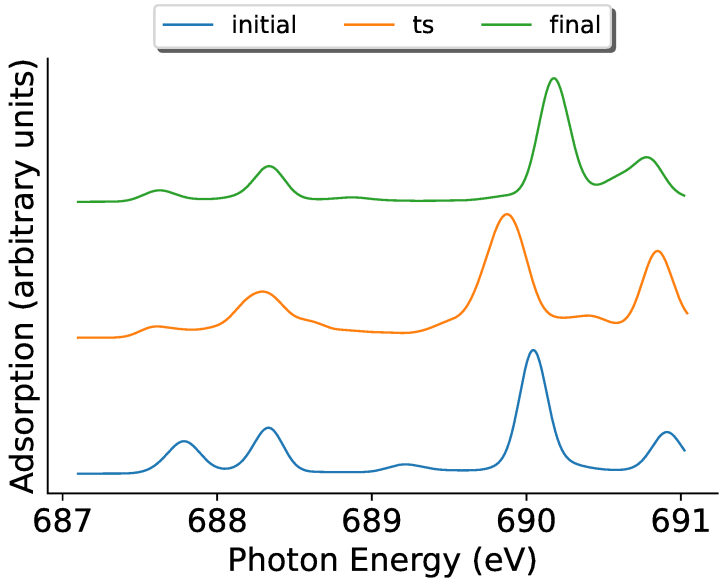

Figure S30: Fluorine *K*-edge XAS of the initial, transition, and final state for reaction **R6** in the flat binding mode.

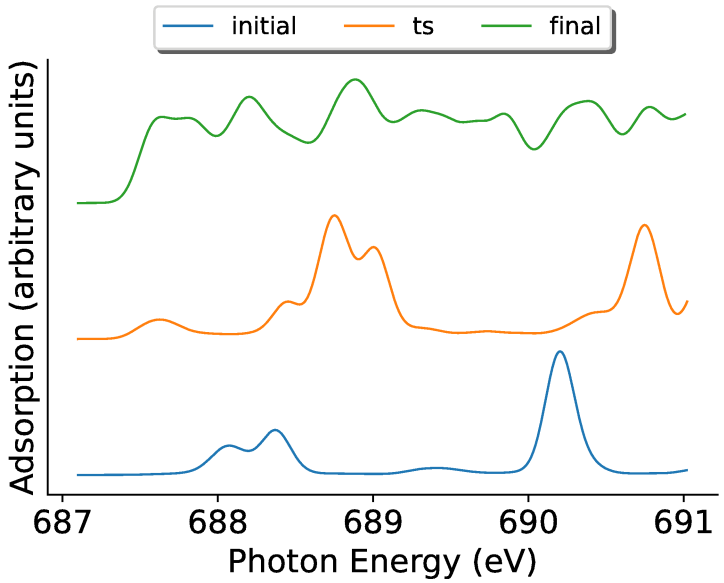

Figure S31: Fluorine *K*-edge XAS of the initial, transition, and final state for reaction **R7** in the flat binding mode.

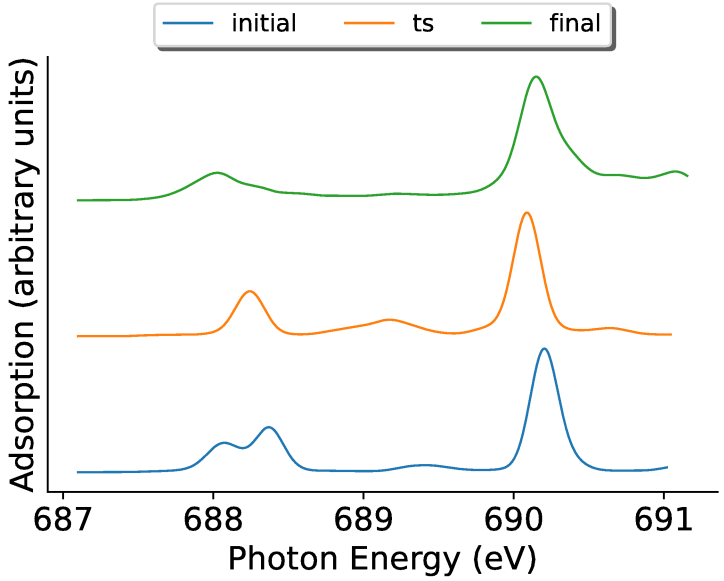

Figure S32: Fluorine *K*-edge XAS of the initial, transition, and final state for reaction **R8** in the flat binding mode.

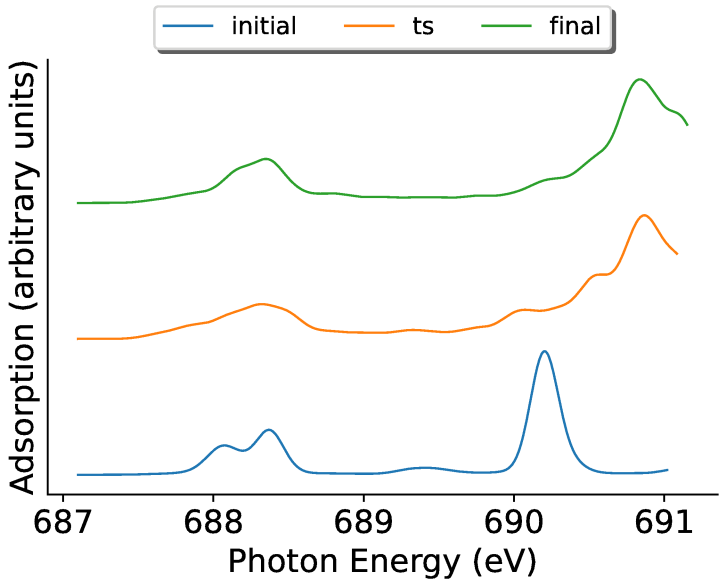

Figure S33: Fluorine *K*-edge XAS of the initial, transition, and final state for reaction **R9** in the flat binding mode.

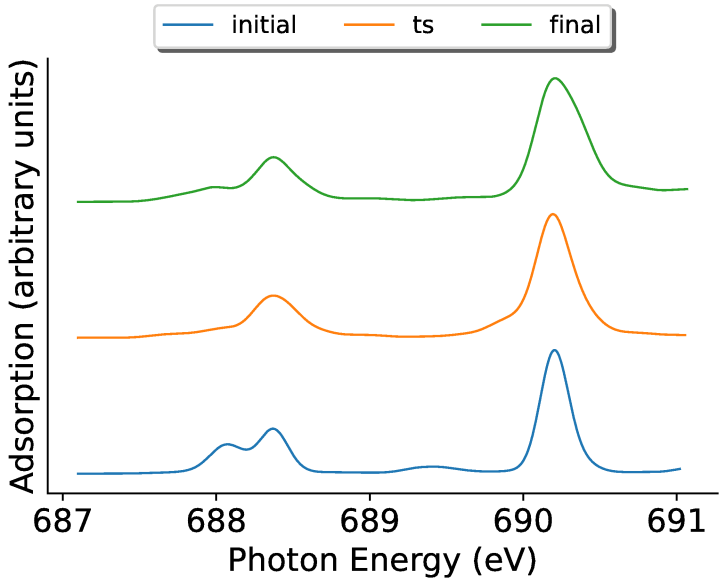

Figure S34: Fluorine *K*-edge XAS of the initial, transition, and final state for reaction **R10** in the flat binding mode.