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ELECTRONIC SUPPLEMENTARY INFORMATION

Predicting pressure-dependent unimolecular rate constants using variational transition state theory with multidimensional tunneling combined with system-specific quantum RRK theory: A definitive test for fluoroform dissociation

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Table S1. Classical (ZPE-excluded) forward and reverse barriers and energy of reaction (kcal/mol) computed based on CCSD(T)-F12a/jun-cc-pVTZ optimized geometries; mean unsigned errors (MUEs, in kcal/mol) are computed based on coupled cluster results as reference.

Model chemistries	$V_f^{\ddagger}$	$V_r^{\ddagger}$	ΔE_{rxn}	MUE
M08-HX/aug-cc-pVTZ	77.93	18.67	59.25	0.15
M08-HX/jul-cc-pVTZ	77.93	18.74	59.19	0.19
M08-HX/jun-cc-pVTZ	77.94	18.88	59.06	0.28
M08-HX/MG3S	78.84	19.06	59.78	0.72
M08-SO/MG3S	78.86	19.70	59.16	0.83
M08-SO/aug-cc-pVTZ	78.52	19.77	58.75	0.88
M08-SO/jul-cc-pVTZ	78.50	19.82	58.68	0.91
MN15/MG3S	76.42	16.99	59.43	0.98
M08-SO/jun-cc-pVTZ	78.43	19.94	58.49	0.99
MN15/jun-cc-pVTZ	76.03	16.84	59.19	1.15
MN15/jul-cc-pVTZ	76.16	16.66	59.49	1.20
MN15/aug-cc-pVTZ	76.18	16.60	59.58	1.24
M06-2X/aug-cc-pVTZ	81.01	18.67	62.33	2.17
M06-2X/jul-cc-pVTZ	81.02	18.73	62.29	2.18
M06-2X/jun-cc-pVTZ	81.04	18.87	62.17	2.19
MN15-L/aug-cc-pVTZ	74.31	15.72	58.59	2.30
MN15-L/jul-cc-pVTZ	74.27	15.74	58.52	2.33
MN15-L/MG3S	74.12	16.05	58.07	2.42
MN15-L/jun-cc-pVTZ	74.10	15.92	58.18	2.44
ωB97X-D/jun-cc-pVTZ	75.08	14.71	60.36	2.50
ωB97X-D/MG3S	75.57	14.66	60.91	2.53
ωB97X-D/jul-cc-pVTZ	75.18	14.64	60.54	2.55
ωB97X-D/aug-cc-pVTZ	75.20	14.62	60.58	2.56
M06-2X/MG3S	82.02	19.08	62.94	2.84
B3LYP/MG3S	71.86	12.95	58.90	3.93
MPW1K/jun-cc-pVTZ	81.59	16.29	65.30	4.00
MPW1K/jul-cc-pVTZ	81.65	16.19	65.46	4.11
MPW1K/aug-cc-pVTZ	81.67	16.18	65.49	4.13
B3LYP/aug-cc-pVTZ	71.52	12.98	58.54	4.16
B3LYP/jul-cc-pVTZ	71.51	12.97	58.54	4.16
B3LYP/jun-cc-pVTZ	71.42	13.05	58.38	4.22
MPW1K/MG3S	82.07	16.13	65.93	4.42
CCSD(T)-F12a/jun-cc-pVTZ	77.75	18.46	59.30	0.00

Table S2. High-pressure-limit CVT/SCT dissociation rate constants (s^{-1}), Arrhenius activation energies $E_a(T)$, and frequency factors $A_{uni}^{\infty}(T)$ at various temperatures (K).

T/K	$k^{CVT/SCT}$	$E_a(T)$	$A_{uni}^{\infty}(T)$
298	1.9362E-39	67.62	7.54754E+10
400	3.2986E-26	72.58	1.49104E+14
600	6.7740E-13	74.30	7.83640E+14
800	3.9540E-06	74.20	7.36499E+14
1000	4.8664E-02	74.21	8.04455E+14
1200	2.6690E+01	74.53	9.99706E+14
1400	2.4474E+03	75.11	1.29925E+15
1600	7.3004E+04	75.90	1.70067E+15
1800	1.0272E+06	76.85	2.19956E+15
2000	8.5274E+06	77.93	2.79550E+15
2200	4.8180E+07	79.10	3.47205E+15
2400	2.0392E+08	80.34	4.21973E+15

Table S3. Vibrational frequencies and geometric mean frequency (cm^{-1}) of CHF_3, computed at M08-HX/aug-cc-pVTZ level and scaled by a factor of 0.975.

Mode	Vibrational frequency (cm^{-1})
1	3056.49
2	1354.31
3	1353.55
4	1142.14
5	1141.97
6	1119.18
7	685.13
8	496.84
9	496.77
Zero-point vibrational energy (kcal/mol)	15.51
Geometric mean frequency (cm^{-1})	1036.688

Table S4. High-pressure-limit CVT/SCT dissociation rate constants (s^{-1}), Arrhenius activation energies $E_a(T)$ and frequency factors $A_{uni}^{\infty}(T)$ at temperatures from 1490 K–1960 K.

T/K	$k^{CVT/SCT}$	$E_a(T)$	$A_{uni}^{\infty}(T)$
1490	1.2618E+04	75.44	1.4661E+15
1505	1.6273E+04	75.50	1.4965E+15
1530	2.4594E+04	75.60	1.5473E+15
1555	3.6682E+04	75.71	1.6034E+15
1600	7.3004E+04	75.90	1.7007E+15
1635	1.2148E+05	76.06	1.7834E+15
1645	1.3995E+05	76.10	1.8040E+15
1650	1.5012E+05	76.13	1.8198E+15
1660	1.7250E+05	76.17	1.8403E+15
1670	1.9789E+05	76.22	1.8665E+15
1685	2.4242E+05	76.29	1.9030E+15
1710	3.3732E+05	76.41	1.9661E+15
1720	3.8394E+05	76.46	1.9925E+15
1730	4.3636E+05	76.51	2.0190E+15
1760	6.3502E+05	76.65	2.0927E+15
1770	7.1760E+05	76.70	2.1194E+15
1820	1.2961E+06	76.96	2.2594E+15
1830	1.4531E+06	77.01	2.2863E+15
1840	1.6271E+06	77.06	2.3133E+15
1850	1.8198E+06	77.11	2.3402E+15
1870	2.2682E+06	77.22	2.4007E+15
1900	3.1288E+06	77.38	2.4886E+15
1910	3.4750E+06	77.43	2.5156E+15
1940	4.7308E+06	77.60	2.6108E+15
1960	5.7804E+06	77.71	2.6721E+15

Table S5. Computed dissociation rate constants (s^{-1}) at various temperatures (K) and pressures (bar), and the ratio of calculated rate constant to experimental value (k_{calc}/k_{exptl}). Average energy transfer parameter $|\langle \Delta E \rangle|$ is 58 cm^{-1}.

T/K	[Ar]/(mol cm^{-3})	p/bar	k_{calc}	k_{calc}/k_{exptl}
1490	1.30E-04	16.0965	1.65E+03	0.61
1505	1.20E-04	15.0079	1.94E+03	0.74
1505	2.50E-05	3.1266	7.17E+02	0.51
1530	2.40E-05	3.0514	9.60E+02	0.64
1555	1.20E-04	15.5065	3.73E+03	0.75
1600	1.80E-05	2.3933	1.78E+03	0.66
1600	1.10E-04	14.6256	6.10E+03	0.76
1635	1.30E-04	17.6629	1.01E+04	0.84
1645	2.30E-05	3.1441	3.46E+03	0.74
1645	1.30E-04	17.7709	1.12E+04	0.62
1650	1.10E-04	15.0827	1.07E+04	0.76
1660	2.10E-05	2.8969	3.77E+03	0.97
1670	1.80E-05	2.4980	3.71E+03	0.66
1670	1.30E-04	18.0410	1.47E+04	0.86
1685	1.00E-04	14.0024	1.45E+04	0.76
1645	1.00E-04	13.6700	9.52E+03	0.73
1710	1.90E-05	2.6999	5.68E+03	1.67
1710	1.60E-05	2.2736	4.97E+03	0.76
1720	1.20E-04	17.1518	2.31E+04	0.86
1730	1.20E-04	17.2516	2.54E+04	0.91
1760	1.80E-05	2.6326	8.53E+03	0.71
1770	1.20E-04	17.6504	3.69E+04	0.97
1820	1.10E-04	16.6366	5.36E+04	0.54
1820	1.40E-05	2.1174	1.14E+04	0.64
1830	1.00E-04	15.2073	5.45E+04	0.94
1830	1.90E-05	2.8894	1.58E+04	0.72
1840	1.40E-05	2.1407	1.34E+04	0.70
1850	1.10E-04	16.9109	6.85E+04	0.82
1870	1.90E-05	2.9525	2.14E+04	0.74
1900	9.70E-05	15.3153	9.20E+04	0.92
1910	2.00E-05	3.1744	2.97E+04	0.58
1940	1.80E-05	2.9019	3.34E+04	0.70
1960	1.90E-05	3.0946	3.98E+04	0.67
1960	1.80E-05	2.9318	3.81E+04	0.54

Average k_{calc}/k_{exptl} = 0.76, with a standard deviation of 0.20.

Table S6. Computed dissociation rate constants (s^{-1}) at various temperatures (K) and pressures (bar), and the ratios of the calculated rate constants to the experimental values (k_{calc}/k_{exptl}). The average energy transfer parameter (cm^{-1}) used in each test is given in column headings.

		$\lvert\langle\Delta E\rangle\rvert$	29 cm^{-1}	116 cm^{-1}	232 cm^{-1}	464 cm^{-1}
T/K	[Ar]/(mol cm^{-3})	p/bar	k_{calc}/k_{exptl}	k_{calc}/k_{exptl}	k_{calc}/k_{exptl}	k_{calc}/k_{exptl}
1490	1.30E-04	16.0965	0.42	0.85	1.13	1.43
1505	1.20E-04	15.0079	0.51	1.04	1.40	1.78
1505	2.50E-05	3.1266	0.33	0.77	1.10	1.50
1530	2.40E-05	3.0514	0.41	0.97	1.40	1.92
1555	1.20E-04	15.5065	0.50	1.06	1.44	1.86
1600	1.80E-05	2.3933	0.41	1.02	1.52	2.15
1600	1.10E-04	14.6256	0.51	1.10	1.51	1.99
1635	1.30E-04	17.6629	0.56	1.21	1.67	2.20
1645	2.30E-05	3.1441	0.45	1.14	1.70	2.40
1645	1.30E-04	17.7709	0.41	0.90	1.25	1.65
1650	1.10E-04	15.0827	0.45	1.11	1.55	2.06
1660	2.10E-05	2.8969	0.59	1.51	2.26	3.21
1670	1.80E-05	2.4980	0.41	1.04	1.57	2.25
1670	1.30E-04	18.0410	0.13	1.26	1.75	2.32
1685	1.00E-04	14.0024	0.51	1.13	1.59	2.14
1645	1.00E-04	13.6700	0.72	1.07	1.50	2.00
1710	1.90E-05	2.6999	1.01	2.64	4.00	5.77
1710	1.60E-05	2.2736	0.46	1.22	1.86	2.69
1720	1.20E-04	17.1518	0.56	1.26	1.79	2.41
1730	1.20E-04	17.2516	0.59	1.34	1.90	2.57
1760	1.80E-05	2.6326	0.43	1.14	1.74	2.54
1770	1.20E-04	17.6504	0.62	1.45	2.07	2.82
1820	1.10E-04	16.6366	0.34	0.81	1.18	1.62
1820	1.40E-05	2.1174	0.37	1.04	1.62	2.41
1830	1.00E-04	15.2073	0.59	1.43	2.08	2.90
1830	1.90E-05	2.8894	0.43	1.16	1.80	2.65
1840	1.40E-05	2.1407	0.41	1.15	1.80	2.69
1850	1.10E-04	16.9109	0.52	1.24	1.81	2.52
1870	1.90E-05	2.9525	0.43	1.20	1.87	2.77
1900	9.70E-05	15.3153	0.57	1.42	2.10	2.97
1910	2.00E-05	3.1744	0.34	0.95	1.49	2.22
1940	1.80E-05	2.9019	0.40	1.15	1.81	2.72
1960	1.90E-05	3.0946	0.39	1.11	1.76	2.65
1960	1.80E-05	2.9318	0.31	0.89	1.40	2.11
Average k_{calc}/k_{exptl}			0.47	1.17	1.72	2.41
Standard deviation			0.14	0.31	0.48	0.73

Table S7. Computed dissociation rate constants (s^{-1}) at various temperatures (K) and pressures (bar). Average energy transfer parameter $\left|\langle \Delta E \rangle\right|$ is 58 cm^{-1}.

T/K \ *p*/bar	0.01	1	100
250	5.5374E-49	5.5374E-49	5.5374E-49
300	4.1886E-39	4.1943E-39	4.1944E-39
400	1.0840E-26	3.1639E-26	3.2811E-26
600	2.1925E-14	4.0505E-13	6.6338E-13
1000	1.6050E-04	7.2687E-03	3.7184E-02
1500	2.7240E+00	2.1284E+02	3.9110E+03
2400	7.1084E+02	6.8469E+04	3.5989E+06