Multi-Structural Kinetics Study on H-atom Abstraction from Fuel Molecules by $\dot{N}H_2$ Radicals with Anharmonicity, Recrossing and Tunneling Effects

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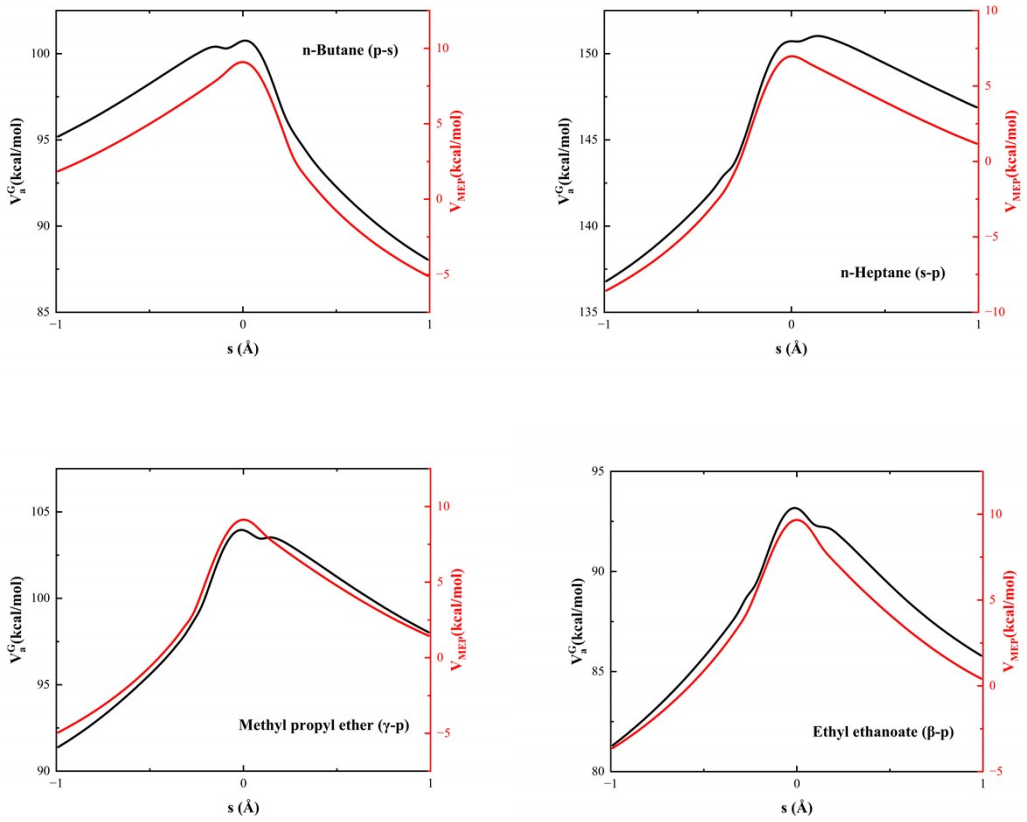


Fig S1: The potential energy (V_{MEP}) and vibrationally adiabatic ground energy (V_a^G) with respect to the reaction coordinate (s).

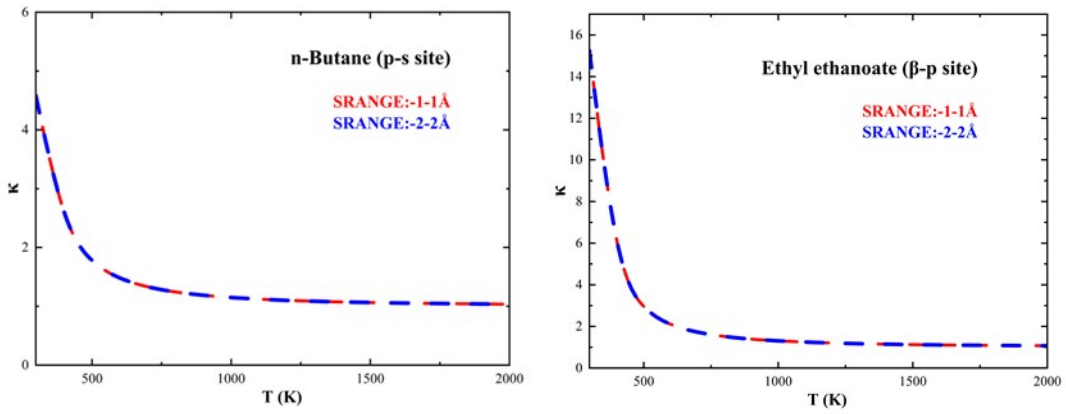
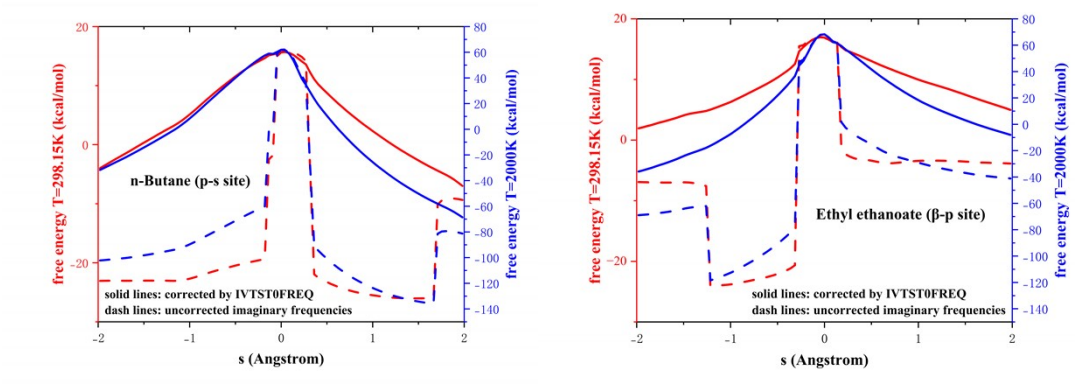
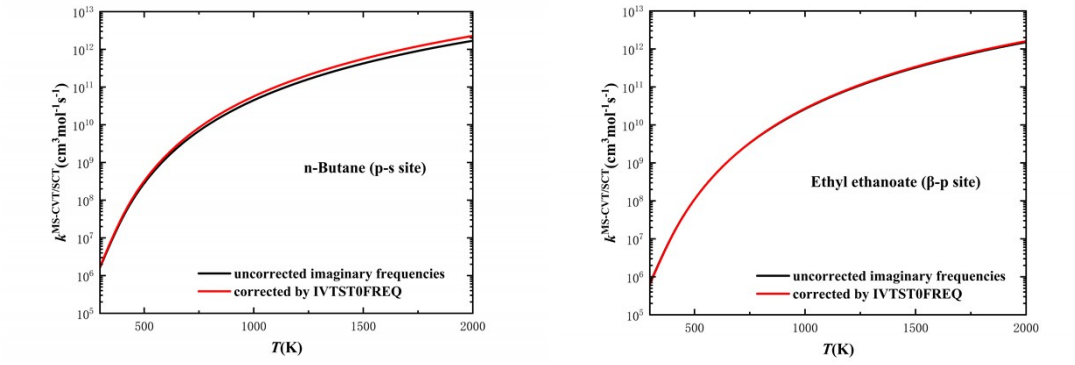


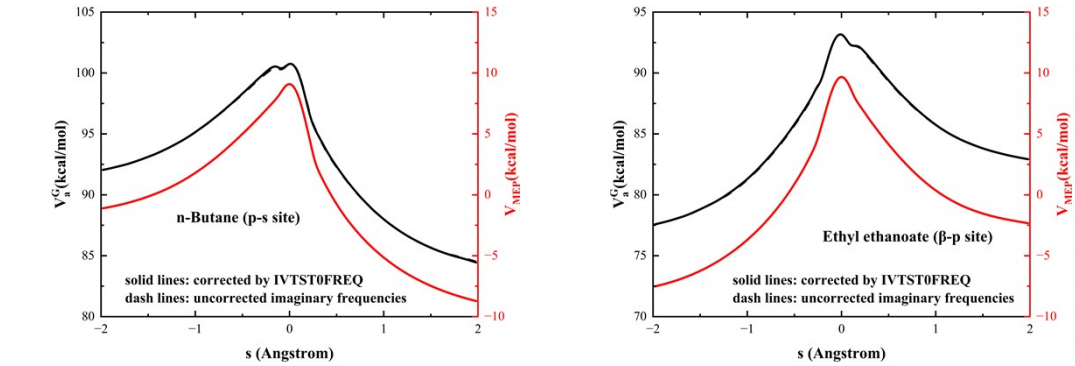
Fig S2: Multi-dimensional SCT tunneling transmission coefficients along different reaction coordinate range for MEP calculation.



(a)



(b)



(c)

Fig S3: Comparison of (a) free energy profiles, (b) rate constants and (c) vibrationally adiabatic potentials before and after transverse imaginary frequency correction.

Table S1
Comparison of thermochemical data for different species calculated in this work and from database. [1]1-D hindered treatment, [2]MS-T method, [a]ATcT database, [b]Burcat's database.

Species	$\Delta H_{f,298}$ (kJ mol^{-1})		S_{298} (J mol^{-1} K^{-1})	
	this work	Literature	this work	Literature
n-Butane C_4H_{10}_1	-126.91[1] -126.46[2]	-125.60±0.67 [53] -127.10±0.67 [54] -125.53±0.19[a] [55] -125.79±0.38[b] [50]	+313.43[1] +312.19[2]	+309.88[b] [50]
iso-Butane C_4H_{10}_2	-135.97[1] -134.65[2]	-134.20±0.63 [53] -135.60±0.54 [54] -134.47±0.27[a] [55] -134.99±0.40[b] [50]	+296.67[1] +296.20[2]	+295.49[b] [50]
n-Pentane C_5H_{12}_1	-147.31[1] -147.36[2]	-146.80±0.59 [56] -147.10±1.00 [57] -146.40±0.67 [54] -146.04±0.29[a] [55] -152.31±8[b] [50]	+355.59[1] +350.78[2]	+349.82±0.84 [58] +348.29[b] [50]
iso-Pentane C_5H_{12}_2	-154.69[1] -153.21[2]	-153.70±0.59 [56] -154.10±0.96 [57] -154.50±0.84 [54] -152.95±0.39[a] [55] -153.70[b] [50]	+347.56[1] +345.48[2]	+343.74[b] [50]
Neopentane C_5H_{12}_3	-171.04[1] -167.19[2]	-167.90±0.63 [56] -168.50±1.00 [57] -166.00±1.00 [54] -167.12±0.38[a] [55] -168.26±8[b] [50]	+309.75[1] +308.92[2]	+309.57[b] [50]
n-Heptane C_7H_{16}	-189.63[1] -188.77[2]	-187.53±0.48 [59] -187.78±0.74 [60] -187.80±0.79 [61] -189.30 [62] -187.26±0.44[a] [55] -187.78±0.74[b] [50]	+432.88[1] +428.42[2]	+428.10 [60] +428.10[b] [50]
iso-Octane C_8H_{18}	-229.06[1] -226.47[2]	-223.70±1.50 [59] -224.01±1.50 [60] -224.10±1.30 [61] -223.50±1.50[a] [55] -224.01±1.50[b] [50]	+432.35[1] +422.78[2]	+423.09 [60] +423.09[b] [50]
n-Butanol	-276.51[1] -275.40[2]	-277.00±5.00 [63] -274.74±0.24[a] [55] -275.98±8.00[b] [50]	+365.48[1] +362.43[2]	+361.98 [64] +361.70[b] [50]
Ethyl ethanoate	-446.32[2]	-446.90 [65] -444.80±0.40 [66] -443.80 [67] -445.43±0.84 [68] -448.55±8.00[b] [50]	+358.77[2]	+362.75 [69] +377.41[b] [50]
Methyl propyl ether	-237.42[2]	-238.02±0.85 [70] -237.70±1.10 [71]	+350.93[2]	352.00 [72]

Tabel S2
Comparison of C_p J mol^{-1} K^{-1} for different species calculated in this work and from the literature.

	This study							Literature						
Species	300	400	500	600	800	1000	1500	300	400	500	600	800	1000	1500
n-Butane C_4H_{10} 1	96.68[1] 97.00[2]	121.29 122.07	145.12 145.64	166.38 166.17	198.87 199.15	224.08 224.162	263.65 263.80	98.95[76] 98.65[b 50]	124.77	148.66	169.28	202.38	227.36	266.40
iso-Butane C_4H_{10} 2	97.75[1] 97.90[2]	123.60 124.38	147.73 148.40	168.84 168.87	200.83 201.26	225.50 225.69	264.33 264.53	97.15[76] 96.64[b 50]	124.43	149.24	170.37	203.64	228.45	267.02
n-Pentane C_5H_{12} 1	119.46[1] 119.10[2]	149.64 150.71	178.99 180.14	205.13 205.58	244.77 246.14	275.39 276.68	323.12 324.62	120.62[77] 112.15[b 50]	152.55	182.59	208.78	250.62	281.58	330.54
iso-Pentane C_5H_{12} 2	120.40[1] 117.00[2]	151.55 149.90	180.90 178.54	206.73 203.95	246.11 244.30	276.32 274.68	323.58 322.67	119.50[77] 118.87[b 50]	152.88	183.26	210.04	253.13	286.19	338.90
Neopentane C_5H_{12}_3	122.85[1] 122.55[2]	155.91 156.20	186.00 186.36	211.85 211.74	250.34 251.10	279.56 280.19	325.25 325.85	121.55[77] 121.91[b 50]	155.98	186.98	214.64	261.08	297.90	359.82
n-Heptane C_7H_{16}	157.15[1] 163.94[2]	198.34 207.61	239.37 248.32	276.08 283.44	330.78 339.13	372.78 380.71	437.36 445.41	165.98[77] 165.18[60] 165.18[b 50]	210.66	252.09	287.44	342.25	381.58	443.50
iso-Octane C_8H_{18}	188.44[1] 189.13[2]	239.74 241.29	286.99 288.42	327.85 328.33	388.76 390.39	434.55 436.01	504.91 506.51	189.45[77] 188.41[60] 188.41[b 50]	244.60	293.42	335.56	403.34	454.80	539.74
Butanol C_4H_9OH	110.79[1] 111.16[2]	136.49 137.62	161.63 162.56	183.99 184.13	217.49 218.25	243.09 243.70	283.01 283.73	108.58 [63] 108.03[b 50]	138.16	164.42	186.38	220.56	245.93	285.54
Ethyl ethanoate $CH_3COOCH_2CH_3$	109.80[2]	136.25	160.63	181.69	214.90	239.08	274.66	113.97 [69] 107.79 [b 50]	137.40	161.92	182.63	213.43	234.51	
Methyl propyl ether $CH_3OCH_2CH_2CH_3$	113.39[2]	138.40	162.37	183.61	218.07	244.18	285.13							

Table S3

Modified Arrhenius expressions for rate constants (s^{-1}) with temperature range from 298.15 K to 2000 K

HAA site		A(s^{-1})	n	E_a(cal mol^{-1})
n-butane	p-s	42.02	3.39	5183.99
	s-ps	137.17	3.32	3884.01
iso-butane	p-t	24.77	3.48	4939.07
	t-3p	1410.89	2.90	3590.20
n-petane	p-s	7.29	3.64	4865.81
	s-ps	65.90	3.36	3765.15
	s-2s	83.28	3.21	3609.53
iso-petane	p-s	0.58	3.94	4819.77
	p-t	0.61	4.05	4611.56
	s-pt	5.70	3.69	3691.87
	t-s2p	87.02	3.23	2721.80
n-heptane	s-ps	32.93	3.49	3822.13
iso-octane	p-q	0.66	4.05	4233.23
butanol	α-s	1.24	3.77	1387.95
	β-s	0.15	4.17	3667.91
	γ-s	3.77	3.87	5638.41
	oh	0.03	4.16	1705.76
methyl propyl ether	α-p	37.13	3.48	3116.27
	α-s	6.49	3.57	1661.37
	β-s	0.20	4.07	2936.90
	γ-p	0.40	3.96	5948.79
ethyl ethanoate	α'-p	0.38	3.95	4330.68
	α-s	1.36	3.80	2927.46
	β-p	0.03	4.32	4560.22