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Supporting Information

Microscopic Properties of Na and Li—A First Principle Study of Metal Battery Anode Materials

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SUPPORTING INFORMATION

Table of contents

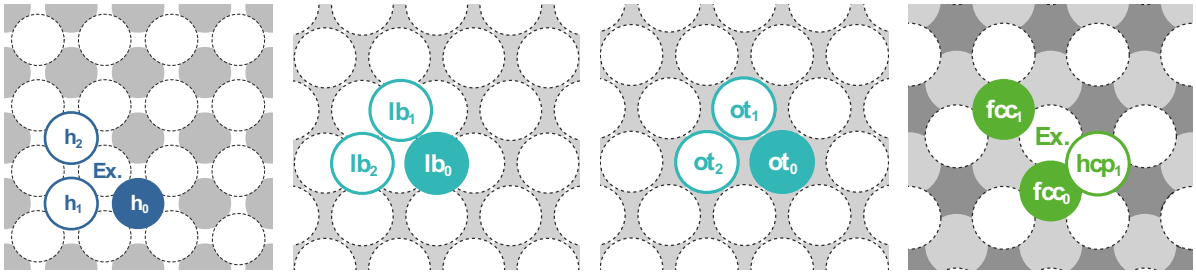
I. BULK PROPERTIES

Table 1. Calculated (PBE, BEEF-vdW) and experimental (Expt.) physical constants for the various bulk phases of sodium and lithium. Lattice constant a_0 and c_0 are given in Å, cohesive energies E_{coh} are given in eV/atom, and bulk moduli B_0 are given in GPa. All experimental results were taken from Ref. 1. For BEEF-vdW the calculated standard deviation of the cohesive energy is given in parentheses. For the experimental data of a_0, E_{coh} and B_0 the values of $\Delta a_0/a_0$, E_{ZPVE} and $\Delta B_0/B_0$ are given in parentheses, respectively.

		Sodium			Lithium		
		PBE	BEEF-vdW	Expt.	PBE	BEEF-vdW	Expt.
bcc	a_0	4.19	4.18	4.21 (0.02)	3.44[2]	3.40	3.45 (0.03)
	E_{coh}	1.09	1.15 s(0.25)	1.13 (0.02)	1.61[2]	1.66 (0.16)	1.67 (0.03)
	B_0	7.96	8.48	7.73 (-0.03)	13.92[2]	15.43	13.90 (-0.05)
fcc	a_0	5.29	5.27	-	4.33[2]	4.28	-
	E_{coh}	1.09	1.14 (0.25)	-	1.61[2]	1.66 (0.16)	-
	B_0	7.87	8.43	-	13.86[2]	15.50	-
hcp	a_0	3.74	3.73	-	3.06[2]	3.03	-
	c_0	6.11	6.09	-	5.00[2]	4.95	-
	E_{coh}	1.09	1.14 (0.25)	-	1.61[2]	1.65 (0.16)	-
	B_0	7.91	8.38	-	13.87[2]	15.21	-
hR9	a_0	3.72	3.71	-	3.07	3.04	-
	c_0	27.80	27.71	-	22.33	22.09	-
	E_{coh}	1.09	1.14 (0.25)	-	1.61	1.66 (0.16)	-
	B_0	7.84	8.43	-	13.97	15.47	-
a15	a_0	6.68	6.66	-	5.46	5.41	-
	E_{coh}	1.08	1.13 (0.25)	-	1.60	1.64 (0.16)	-
	B_0	7.65	8.20	-	13.61	15.16	-
dia	a_0	7.59	7.79	-	5.91[2]	5.80	-
	E_{coh}	0.75	0.81 (0.25)	-	1.09[2]	1.13 (0.16)	-
	B_0	2.81	2.03	-	5.30[2]	6.00	-
sc	a_0	3.41	3.40	-	2.73[2]	2.71	-
	E_{coh}	0.97	1.02 (0.25)	-	1.49[2]	1.54 (0.16)	-
	B_0	6.22	6.39	-	12.48[2]	13.38	-

II. DIFFUSION PROPERTIES

A. Terrace self-diffusion on the low-index surfaces of Na and Li



(a) (100) (b) Na(110) (c) Li(110) (d) (111)

Fig. 1: Schematic representation of the examined self-diffusion pathways on (a) Na(100) and Li(100), (b) Na(110), (c) Li(110), and (d) Na(111) and Li(111). For the initial positions the most stable adsorption site on the respective surface was chosen, i.e. hollow (h), long-bridge (lb), ontop (ot) and fcc. Here, a filled circle marks the initial position, while a framed circle indicates possible final positions of the diffusion pathway. All circles marked with Ex symbolize atoms participating in the exchange process. The obtained activation energies and reaction rates are given in Table II and Table III.

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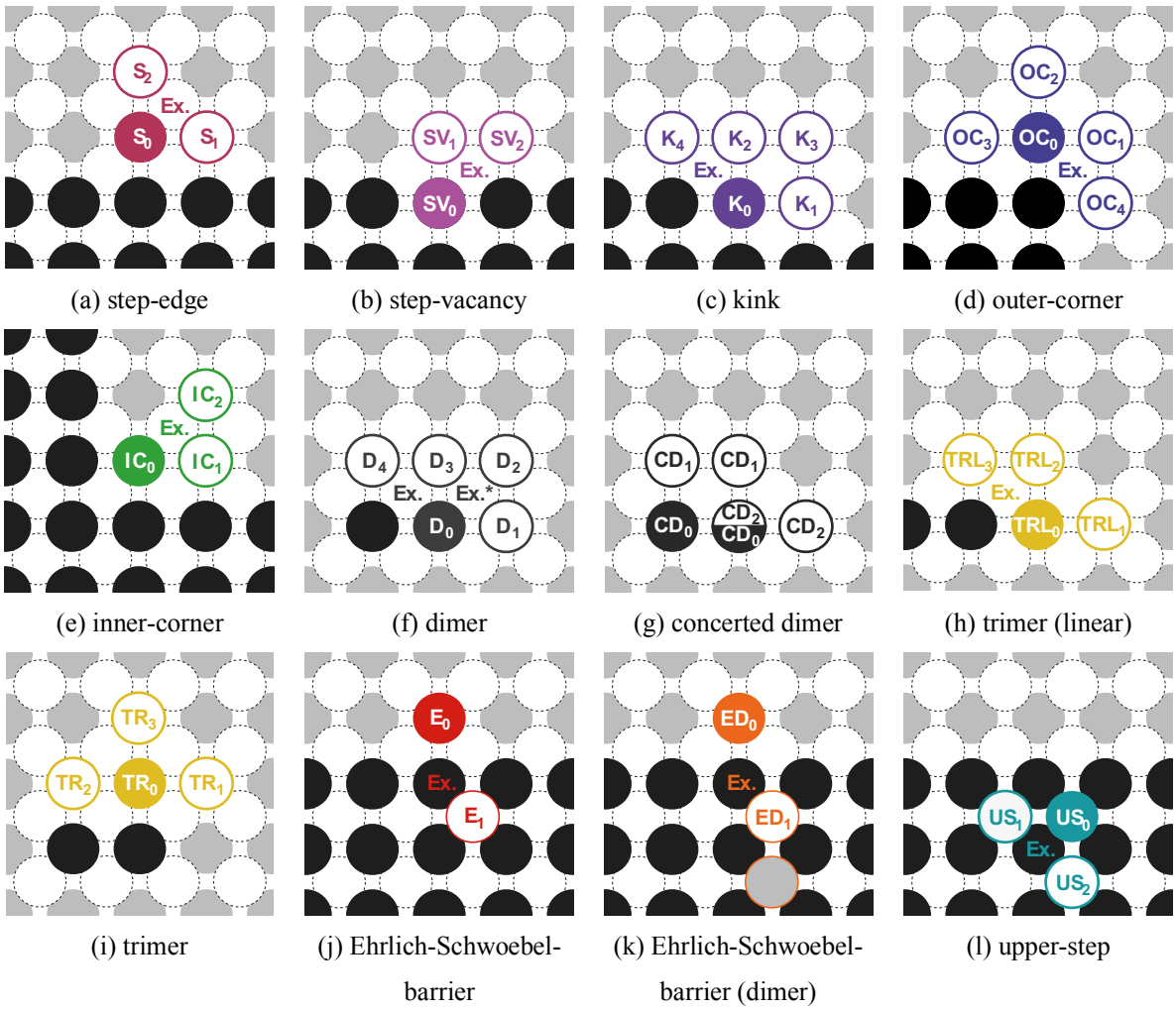
Table II: Calculated terrace self-diffusion barriers of sodium and lithium on its low-index surfaces. For BEEF-vdW, the calculated standard deviation of the forward (for) and reversed (rev) activation energy E_a is given in parentheses. All values are reported in eV.

			PBE		BEEF-vdW	
			E_a^{for}	E_a^{rev}	E_a^{for}	E_a^{rev}
Sodium	(100)	$h_0 \leftrightarrow h_1$	0.09	0.09	0.11 (0.03)	0.11 (0.03)
		$h_0 \leftrightarrow h_2$	0.31	0.31	0.31 (0.09)	0.31 (0.09)
		$h_0 \leftrightarrow h_2$ (Ex.)	0.06	0.06	0.06 (0.03)	0.06 (0.03)
	(110)	$lb_0 \leftrightarrow lb_1$	0.04	0.04	0.04 (0.07)	0.04 (0.07)
		$lb_0 \leftrightarrow lb_2$	0.03	0.03	0.05 (0.04)	0.05 (0.04)
	(111)	$fcc_0 \leftrightarrow fcc_1$ (Ex.)	0.09	0.09	0.08 (0.04)	0.08 (0.04)
		$fcc_0 \leftrightarrow hcp_1$	0.27	0.00	0.25 (0.04)	0.01 (0.02)
		$fcc_1 \leftrightarrow hcp_1$ (Ex.)	0.29	0.03	0.29 (0.05)	0.05 (0.05)
Lithium	(100)	$h_0 \leftrightarrow h_1$	0.04	0.04	0.05 (0.04)	0.05 (0.04)
		$h_0 \leftrightarrow h_2$	0.20	0.20	0.21 (0.07)	0.21 (0.07)
		$h_0 \leftrightarrow h_2$ (Ex.)	0.11	0.11	0.11 (0.03)	0.11 (0.03)
	(110)	$ot_0 \leftrightarrow ot_1$	0.05	0.05	0.05 (0.03)	0.05 (0.03)
		$ot_0 \leftrightarrow ot_2$	0.05	0.05	0.05 (0.02)	0.05 (0.02)
	(111)	$fcc_0 \leftrightarrow fcc_1$ (Ex.)	0.13	0.13	0.12 (0.02)	0.12 (0.02)
		$fcc_0 \leftrightarrow hcp_1$	0.39	0.00	0.40 (0.07)	0.00 (-----)
		$fcc_1 \leftrightarrow hcp_1$ (Ex.)	0.39	0.00	0.40 (0.07)	0.00 (-----)

Table III: Calculated forward (for) and reversed (rev) room-temperature reaction rates ($k_{@\mathrm{RT}}$) of sodium and lithium on its low-index surfaces. The DFT-PBE values for Li(100) have been adapted from Ref 2. For all further values, we assumed a pre-exponential factor of $\nu = 5 \cdot 10^{12}$ Hz. All values are reported in Hz and have been obtained by means of DFT-PBE.

			PBE		BEEF-vdW	
			$k^{\mathrm{for}}_{@\mathrm{RT}}$	$k^{\mathrm{rev}}_{@\mathrm{RT}}$	$k^{\mathrm{for}}_{@\mathrm{RT}}$	$k^{\mathrm{rev}}_{@\mathrm{RT}}$
Sodium	(100)	$h_0 \leftrightarrow h_1$	$1.5 \cdot 10^{11}$	$1.5 \cdot 10^{11}$	$6.9 \cdot 10^{10}$	$6.9 \cdot 10^{10}$
		$h_0 \leftrightarrow h_2$	$2.9 \cdot 10^{07}$	$2.9 \cdot 10^{07}$	$2.9 \cdot 10^{07}$	$2.9 \cdot 10^{07}$
		$h_0 \leftrightarrow h_2$ (Ex.)	$4.8 \cdot 10^{11}$	$4.8 \cdot 10^{11}$	$4.8 \cdot 10^{11}$	$4.8 \cdot 10^{11}$
	(110)	$lb_0 \leftrightarrow lb_1$	$1.1 \cdot 10^{12}$	$1.1 \cdot 10^{12}$	$1.1 \cdot 10^{12}$	$1.1 \cdot 10^{12}$
		$lb_0 \leftrightarrow lb_2$	$1.6 \cdot 10^{12}$	$1.6 \cdot 10^{12}$	$7.1 \cdot 10^{11}$	$7.1 \cdot 10^{11}$
	(111)	$fcc_0 \leftrightarrow fcc_1$ (Ex.)	$1.5 \cdot 10^{11}$	$1.5 \cdot 10^{11}$	$2.2 \cdot 10^{11}$	$2.2 \cdot 10^{11}$
		$fcc_0 \leftrightarrow hcp_1$	$1.4 \cdot 10^{08}$	---	$3.0 \cdot 10^{08}$	$3.4 \cdot 10^{12}$
		$fcc_1 \leftrightarrow hcp_1$ (Ex.)	$6.3 \cdot 10^{07}$	$1.6 \cdot 10^{12}$	$6.3 \cdot 10^{07}$	$7.1 \cdot 10^{11}$
Lithium	(100)	$h_0 \leftrightarrow h_1$	$6.1 \cdot 10^{11}$	$6.1 \cdot 10^{11}$	$7.1 \cdot 10^{11}$	$7.1 \cdot 10^{11}$
		$h_0 \leftrightarrow h_2$	$1.1 \cdot 10^{09}$	$1.1 \cdot 10^{09}$	$1.4 \cdot 10^{09}$	$1.4 \cdot 10^{09}$
		$h_0 \leftrightarrow h_2$ (Ex.)	$5.5 \cdot 10^{10}$	$5.5 \cdot 10^{10}$	$6.9 \cdot 10^{10}$	$6.9 \cdot 10^{10}$
	(110)	$ot_0 \leftrightarrow ot_1$	$7.1 \cdot 10^{11}$	$7.1 \cdot 10^{11}$	$7.1 \cdot 10^{11}$	$7.1 \cdot 10^{11}$
		$ot_0 \leftrightarrow ot_2$	$7.1 \cdot 10^{11}$	$7.1 \cdot 10^{11}$	$7.1 \cdot 10^{11}$	$7.1 \cdot 10^{11}$
	(111)	$fcc_0 \leftrightarrow fcc_1$ (Ex.)	$3.2 \cdot 10^{10}$	$3.2 \cdot 10^{10}$	$4.7 \cdot 10^{10}$	$4.7 \cdot 10^{10}$
		$fcc_0 \leftrightarrow hcp_1$	$1.3 \cdot 10^{06}$	---	$8.7 \cdot 10^{05}$	---
		$fcc_1 \leftrightarrow hcp_1$ (Ex.)	$1.3 \cdot 10^{06}$	---	$8.7 \cdot 10^{05}$	---

B. Diffusion properties on Na(100) and Li(100)



(a) step-edge (b) step-vacancy (c) kink (d) outer-corner

(e) inner-corner (f) dimer (g) concerted dimer (h) trimer (linear)

(i) trimer (j) Ehrlich-Schwoebel-barrier (k) Ehrlich-Schwoebel-barrier (dimer) (l) upper-step

Fig. 2: Schematic representation of the investigated self-diffusion on Na(100). Here, a filled circle marks the initial position, while a framed circle indicates possible final positions of the diffusion pathway. Circles labeled by Ex mark atoms participating in the exchange process. For all illustrated processes, the characteristic values are listed in Table IV and Table V.

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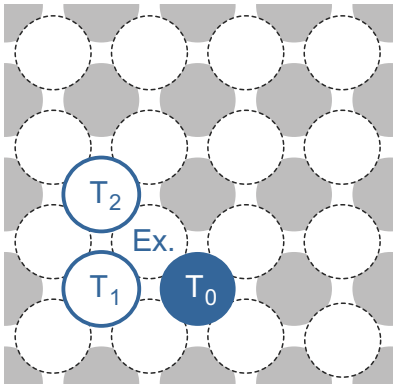
Table IV: Calculated forward (for) and reversed (rev) activation energies (E_a) for the various diffusion pathways on Na(100) and Li(100). The values for lithium have been adapted from Ref. 2. All values are reported in eV and have been calculated by means of DFT-PBE.

		Na(100)		Li(100)	
System	Pathway	E_a^{for}	E_a^{rev}	E_a^{for}	E_a^{rev}
Step-edge	$S_0 \leftrightarrow S_1$	0.13	0.13	0.09	0.09
	$S_0 \leftrightarrow S_2$	0.15	0.05	0.19	0.01
	$S_1 \leftrightarrow S_2$ (Ex.)	0.15	0.06	0.24	0.06
Step-vacancy	$SV_0 \leftrightarrow SV_1$	0.32	0.06	0.47	0.00
	$SV_0 \leftrightarrow SV_2$ (Ex.)	0.20	0.04	0.39	0.07
Kink	$K_0 \leftrightarrow K_1$	0.21	0.11	0.20	0.06
	$K_0 \leftrightarrow K_2$	0.26	0.06	0.34	0.01
	$K_1 \leftrightarrow K_3$	0.13	0.05	0.24	0.04
	$K_0 \leftrightarrow K_4$ (Ex.)	0.18	0.08	0.26	0.09
Inner-corner	$IC_0 \leftrightarrow IC_1$	0.19	0.10	0.20	0.05
	$IC_1 \leftrightarrow IC_2$	0.18	0.08	0.25	0.04
Outer-corner	$OC_0 \leftrightarrow OC_1$	0.19	0.09	0.21	0.02
	$OC_0 \leftrightarrow OC_2$	0.17	0.06	0.19	0.01
	$OC_0 \leftrightarrow OC_3$	0.13	0.12	0.06	0.07
	$OC_0 \leftrightarrow OC_4$ (Ex.)	0.04	0.04	0.11	0.12
Dimer	$D_0 \leftrightarrow D_1$	0.21	0.07	0.21	0.01
	$D_0 \leftrightarrow D_2$ (Ex.*)	0.20	0.06	0.26	0.06
	$D_0 \leftrightarrow D_3$	0.18	0.04	0.14	0.00
	$D_0 \leftrightarrow D_4$ (Ex.)	0.05	0.05	0.08	0.08
Concerted dimer	$CD_0 \leftrightarrow CD_1$	0.29	0.29	0.14	0.14
	$CD_0 \leftrightarrow CD_2$	0.24	0.24	0.21	0.21
Trimer	$TRL_0 \leftrightarrow TRL_1$	0.20	0.08	0.19	0.01
	$TRL_0 \leftrightarrow TRL_2$	0.19	0.07	0.17	0.00
	$TRL_0 \leftrightarrow TRL_3$ (Ex.)	0.06	0.05	0.10	0.13
	$TR_0 \leftrightarrow TR_1$	0.18	0.06	0.20	0.00
	$TR_0 \leftrightarrow TR_2$	0.13	0.13	0.03	0.03
	$TR_0 \leftrightarrow TR_3$	0.18	0.06	0.24	0.02
Ehrlich-Schwoebel-barrier	$E_0 \leftrightarrow E_1$	0.26	0.17	0.39	0.22
	$E_0 \leftrightarrow E_1$ (Ex.)	0.23	0.14	0.28	0.11
Ehrlich-Schwoebel-barrier (dimer)	$ED_0 \leftrightarrow ED_1$	0.26	0.31	0.38	0.41
	$ED_0 \leftrightarrow ED_1$ (Ex.)	0.23	0.28	0.22	0.24
Upper step	$US_0 \leftrightarrow US_1$	0.12	0.12	0.08	0.08
	$US_0 \leftrightarrow US_2$	0.07	0.06	0.02	0.01
	$US_1 \leftrightarrow US_2$ (Ex.)	0.06	0.05	0.06	0.05

Table V: Calculated forward (for) and reversed (rev) room-temperature reaction rates ($k_{@\mathrm{RT}}$) for the various diffusion pathways on Na(100) and Li(100). For Sodium, we assumed a pre-exponential factor of $\nu = 5 \cdot 10^{12}$ Hz. The values for lithium have been adapted from Ref 2. All values are reported in Hz and have been obtained by means of DFT-PBE.

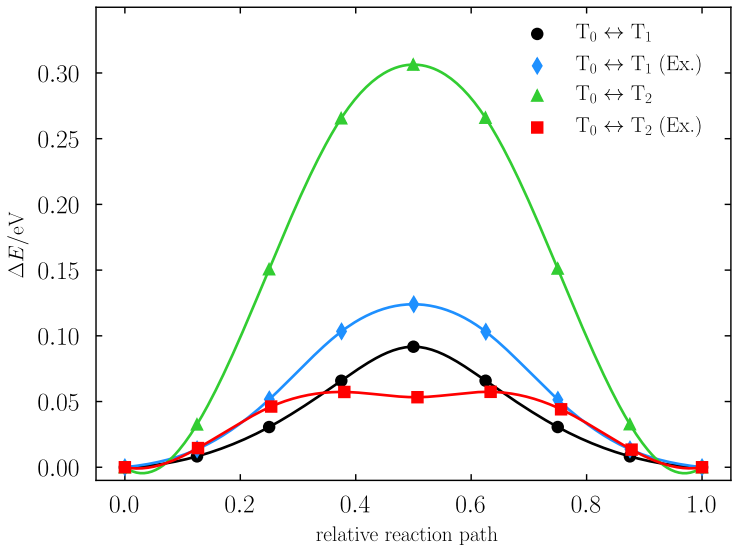
		Na(100)		Li(100)	
System	Pathway	$k^{\mathrm{for}}_{@\mathrm{RT}}$	$k^{\mathrm{rev}}_{@\mathrm{RT}}$	$k^{\mathrm{for}}_{@\mathrm{RT}}$	$k^{\mathrm{rev}}_{@\mathrm{RT}}$
Step-edge	$S_0 \leftrightarrow S_1$	$3.2 \cdot 10^{10}$	$3.2 \cdot 10^{10}$	$1.4 \cdot 10^{11}$	$1.4 \cdot 10^{11}$
	$S_0 \leftrightarrow S_2$	$1.5 \cdot 10^{10}$	$7.1 \cdot 10^{11}$	$1.4 \cdot 10^{09}$	$4.5 \cdot 10^{12}$
	$S_{1a} \leftrightarrow S_2$ (Ex.)	$1.5 \cdot 10^{10}$	$4.8 \cdot 10^{11}$	$4.4 \cdot 10^{08}$	$4.8 \cdot 10^{11}$
Step-vacancy	$SV_0 \leftrightarrow SV_1$	$1.9 \cdot 10^{07}$	$4.8 \cdot 10^{11}$	$5.7 \cdot 10^{04}$	---
	$SV_0 \leftrightarrow SV_2$ (Ex.)	$2.1 \cdot 10^{09}$	$1.1 \cdot 10^{12}$	$1.6 \cdot 10^{06}$	$2.6 \cdot 10^{11}$
Kink	$K_0 \leftrightarrow K_1$	$1.4 \cdot 10^{09}$	$6.9 \cdot 10^{10}$	$3.0 \cdot 10^{09}$	$3.8 \cdot 10^{11}$
	$K_0 \leftrightarrow K_2$	$2.0 \cdot 10^{08}$	$4.8 \cdot 10^{11}$	$1.7 \cdot 10^{07}$	$9.5 \cdot 10^{11}$
	$K_1 \leftrightarrow K_3$	$3.2 \cdot 10^{10}$	$7.1 \cdot 10^{11}$	$2.8 \cdot 10^{08}$	$6.3 \cdot 10^{11}$
	$K_0 \leftrightarrow K_4$ (Ex.)	$4.5 \cdot 10^{09}$	$2.2 \cdot 10^{11}$	$2.2 \cdot 10^{08}$	$1.1 \cdot 10^{11}$
Inner-corner	$IC_0 \leftrightarrow IC_1$	$3.1 \cdot 10^{09}$	$1.0 \cdot 10^{11}$	$2.1 \cdot 10^{09}$	$4.1 \cdot 10^{11}$
	$IC_1 \leftrightarrow IC_2$	$4.5 \cdot 10^{09}$	$2.2 \cdot 10^{11}$	$2.1 \cdot 10^{08}$	$6.1 \cdot 10^{12}$
Outer-corner	$OC_0 \leftrightarrow OC_1$	$3.1 \cdot 10^{09}$	$1.5 \cdot 10^{11}$	$1.2 \cdot 10^{09}$	$1.5 \cdot 10^{12}$
	$OC_0 \leftrightarrow OC_2$	$6.7 \cdot 10^{09}$	$4.8 \cdot 10^{11}$	$2.3 \cdot 10^{09}$	$2.2 \cdot 10^{12}$
	$OC_0 \leftrightarrow OC_3$	$3.2 \cdot 10^{10}$	$4.7 \cdot 10^{10}$	$3.1 \cdot 10^{11}$	$2.1 \cdot 10^{11}$
	$OC_0 \leftrightarrow OC_4$ (Ex.)	$1.1 \cdot 10^{12}$	$1.1 \cdot 10^{12}$	$3.7 \cdot 10^{10}$	$2.5 \cdot 10^{10}$
Dimer	$D_0 \leftrightarrow D_1$	$1.4 \cdot 10^{09}$	$3.3 \cdot 10^{11}$	$1.0 \cdot 10^{09}$	$3.4 \cdot 10^{12}$
	$D_0 \leftrightarrow D_2$ (Ex.*)	$2.1 \cdot 10^{09}$	$4.8 \cdot 10^{11}$	$2.0 \cdot 10^{08}$	$4.8 \cdot 10^{11}$
	$D_0 \leftrightarrow D_3$	$4.5 \cdot 10^{09}$	$1.1 \cdot 10^{12}$	$2.1 \cdot 10^{10}$	---
	$D_0 \leftrightarrow D_4$ (Ex.)	$7.1 \cdot 10^{11}$	$7.1 \cdot 10^{11}$	$9.3 \cdot 10^{10}$	$9.3 \cdot 10^{10}$
Concerted dimer	$CD_0 \leftrightarrow CD_1$	$6.3 \cdot 10^{07}$	$6.3 \cdot 10^{07}$	$3.4 \cdot 10^{10}$	$3.4 \cdot 10^{10}$
	$CD_0 \leftrightarrow CD_2$	$4.4 \cdot 10^{08}$	$4.4 \cdot 10^{08}$	$9.9 \cdot 10^{08}$	$9.9 \cdot 10^{08}$
Trimer	$TRL_0 \leftrightarrow TRL_1$	$2.1 \cdot 10^{09}$	$2.2 \cdot 10^{11}$	$2.6 \cdot 10^{09}$	$2.2 \cdot 10^{12}$
	$TRL_0 \leftrightarrow TRL_2$	$3.1 \cdot 10^{09}$	$3.3 \cdot 10^{11}$	$6.7 \cdot 10^{09}$	---
	$TRL_0 \leftrightarrow TRL_3$ (Ex.)	$4.8 \cdot 10^{11}$	$7.1 \cdot 10^{11}$	$5.1 \cdot 10^{10}$	$1.5 \cdot 10^{10}$
	$TR_0 \leftrightarrow TR_1$	$4.5 \cdot 10^{09}$	$4.8 \cdot 10^{11}$	$2.1 \cdot 10^{09}$	---
	$TR_0 \leftrightarrow TR_2$	$3.2 \cdot 10^{10}$	$3.2 \cdot 10^{10}$	$3.1 \cdot 10^{11}$	$3.1 \cdot 10^{11}$
	$TR_0 \leftrightarrow TR_3$	$4.5 \cdot 10^{09}$	$4.8 \cdot 10^{11}$	$1.8 \cdot 10^{08}$	$8.3 \cdot 10^{11}$
Ehrlich-Schwöbel-barrier	$E_0 \leftrightarrow E_1$	$2.0 \cdot 10^{08}$	$6.7 \cdot 10^{09}$	$1.9 \cdot 10^{06}$	$1.9 \cdot 10^{09}$
	$E_0 \leftrightarrow E_1$ (Ex.)	$6.5 \cdot 10^{08}$	$2.2 \cdot 10^{10}$	$1.6 \cdot 10^{08}$	$1.5 \cdot 10^{11}$
Ehrlich-Schwöbel-barrier (dimer)	$ED_0 \leftrightarrow ED_1$	$2.0 \cdot 10^{08}$	$2.9 \cdot 10^{07}$	$3.6 \cdot 10^{06}$	$3.4 \cdot 10^{05}$
	$ED_0 \leftrightarrow ED_1$ (Ex.)	$6.5 \cdot 10^{08}$	$9.2 \cdot 10^{07}$	$1.7 \cdot 10^{09}$	$6.1 \cdot 10^{08}$
Upper step	$US_0 \leftrightarrow US_1$	$4.7 \cdot 10^{10}$	$4.7 \cdot 10^{10}$	$2.2 \cdot 10^{11}$	$2.2 \cdot 10^{11}$
	$US_0 \leftrightarrow US_2$	$3.3 \cdot 10^{11}$	$4.8 \cdot 10^{11}$	$9.6 \cdot 10^{11}$	$8.8 \cdot 10^{11}$
	$US_1 \leftrightarrow US_2$ (Ex.)	$4.8 \cdot 10^{11}$	$7.1 \cdot 10^{11}$	$4.8 \cdot 10^{11}$	$7.1 \cdot 10^{11}$

Terrace

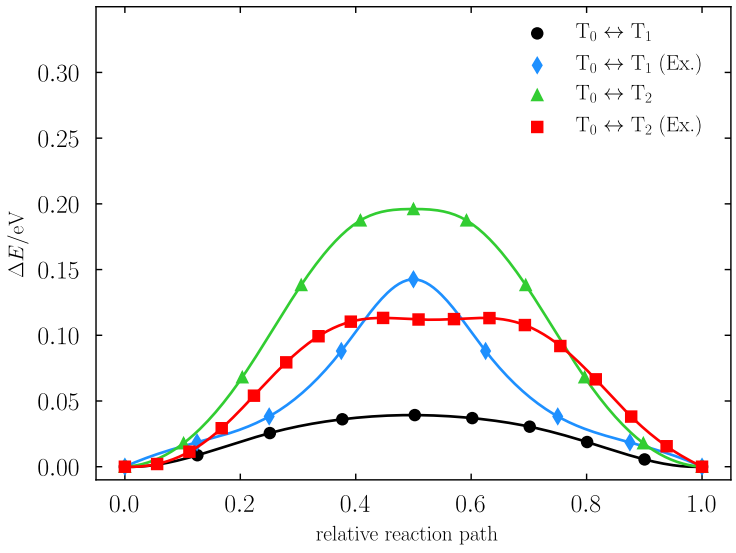


Pathway	Na(100)		Li(100)	
	E_a^{for}	E_a^{rev}	E_a^{for}	E_a^{rev}
$T_0 \leftrightarrow T_1$	0.09	0.09	0.04	0.04
$T_0 \leftrightarrow T_1$ (Ex.)	0.12	0.12	0.14	0.14
$T_0 \leftrightarrow T_2$	0.31	0.31	0.20	0.20
$T_0 \leftrightarrow T_2$ (Ex.)	0.06	0.06	0.11	0.11

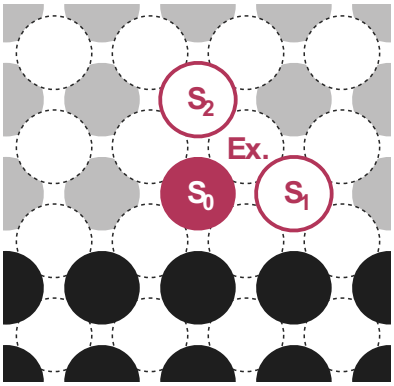
Sodium



Lithium

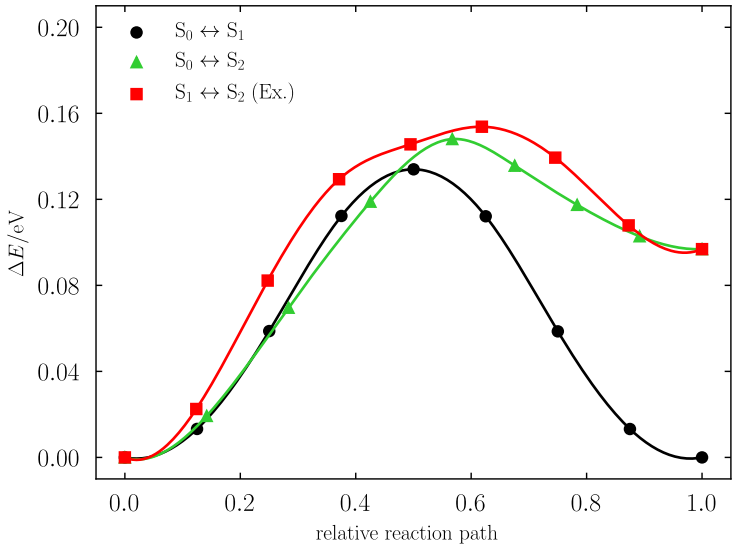


Step-edge

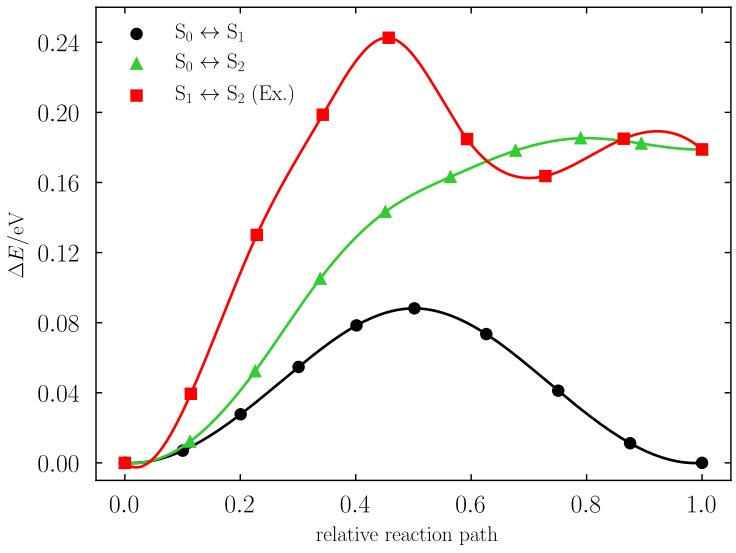


	Na(100)		Li(100)	
Pathway	E_a^{for}	E_a^{rev}	E_a^{for}	E_a^{rev}
$S_0 \leftrightarrow S_1$	0.13	0.13	0.09	0.09
$S_0 \leftrightarrow S_2$	0.15	0.05	0.19	0.01
$S_1 \leftrightarrow S_2$ (Ex.)	0.15	0.06	0.24	0.06

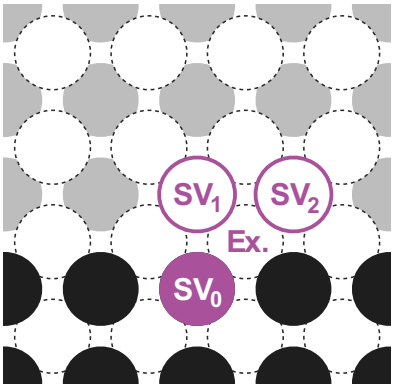
Sodium



Lithium

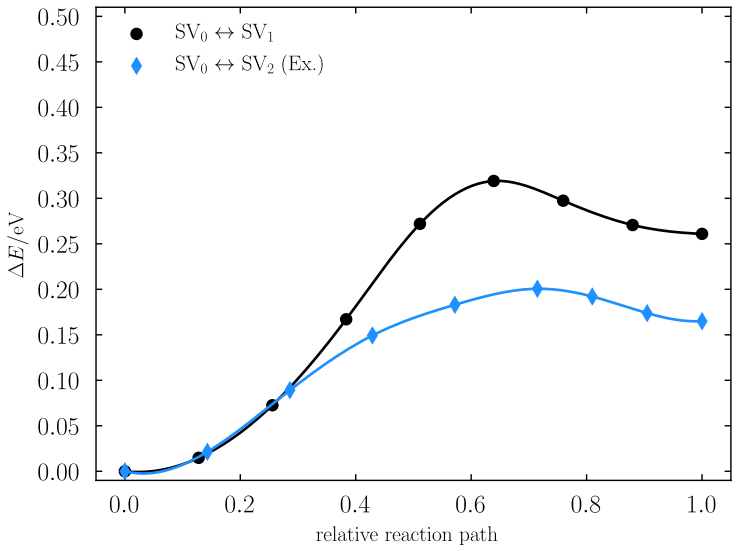


Step-vacancy



	Na(100)		Li(100)	
Pathway	E_a^{for}	E_a^{rev}	E_a^{for}	E_a^{rev}
$SV_0 \leftrightarrow SV_1$	0.32	0.06	0.47	0.00
$SV_0 \leftrightarrow SV_2$ (Ex.)	0.20	0.04	0.39	0.07

Sodium



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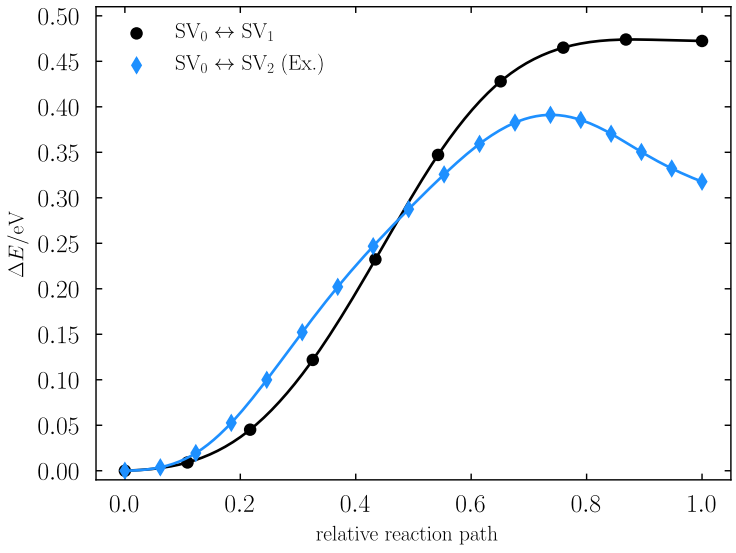
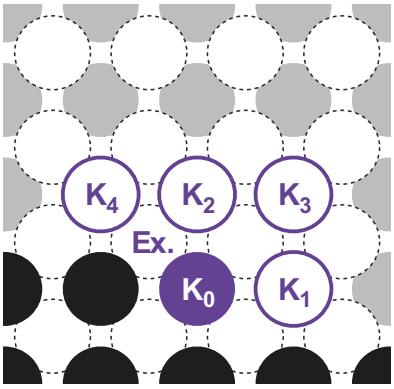
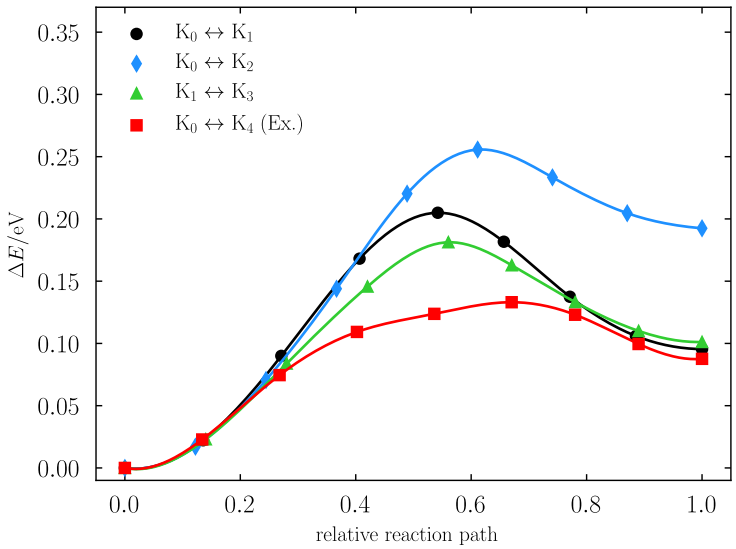


Kink

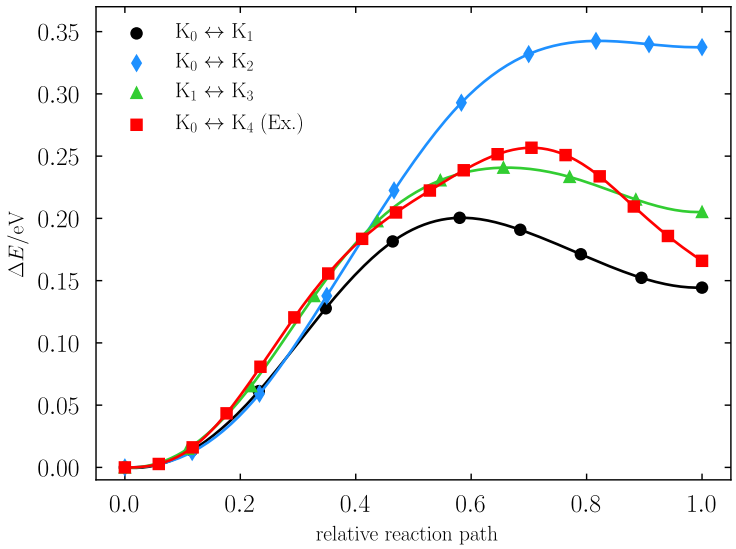


	Na(100)		Li(100)	
Pathway	E_a^{for}	E_a^{rev}	E_a^{for}	E_a^{rev}
$K_0 \leftrightarrow K_1$	0.21	0.11	0.20	0.06
$K_0 \leftrightarrow K_2$	0.26	0.06	0.34	0.01
$K_1 \leftrightarrow K_3$	0.13	0.05	0.24	0.04
$K_0 \leftrightarrow K_4$ (Ex.)	0.18	0.08	0.26	0.09

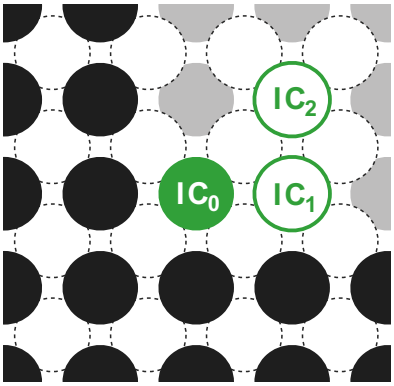
Sodium



Lithium

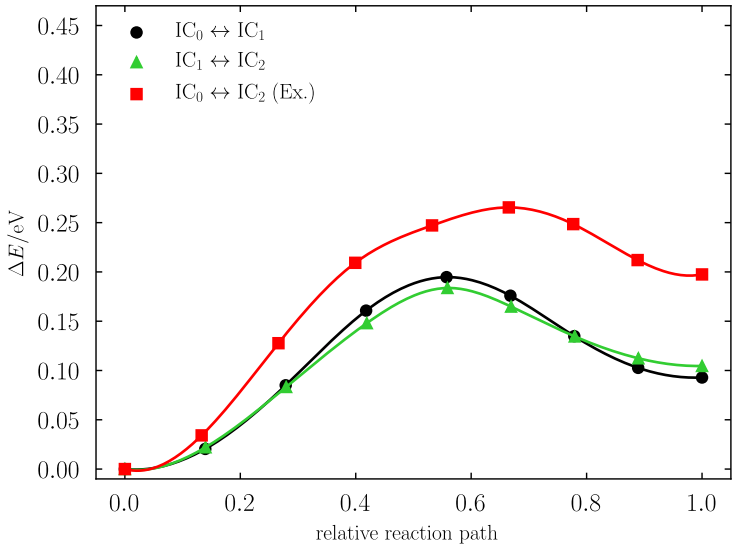


Inner-corner

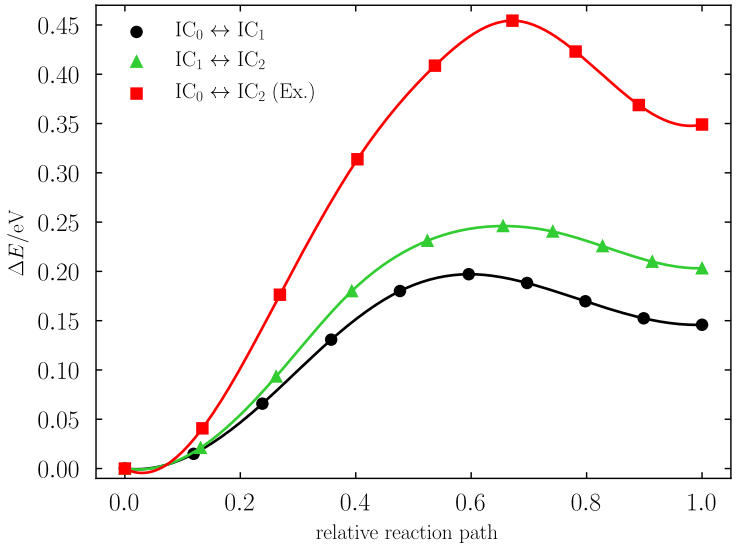


	Na(100)		Li(100)	
Pathway	E_a^{for}	E_a^{rev}	E_a^{for}	E_a^{rev}
$IC_0 \leftrightarrow IC_1$	0.19	0.10	0.20	0.05
$IC_1 \leftrightarrow IC_2$	0.18	0.08	0.25	0.04
$IC_0 \leftrightarrow IC_2$ (Ex.)	0.27	0.07	0.45	0.11

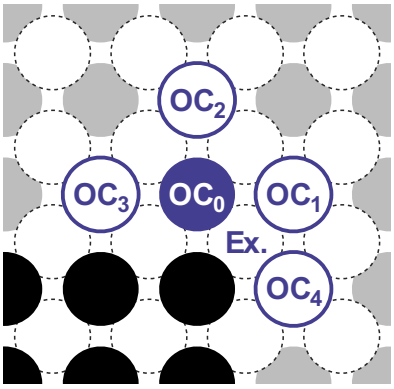
Sodium



Lithium

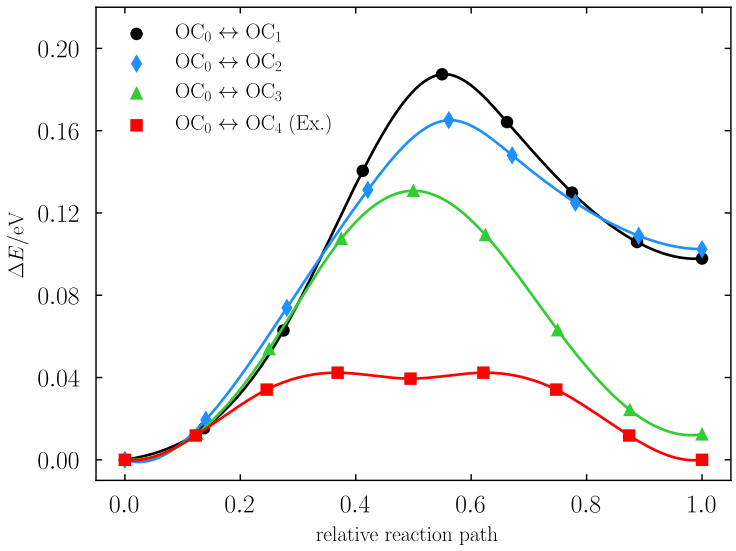


Outer-corner

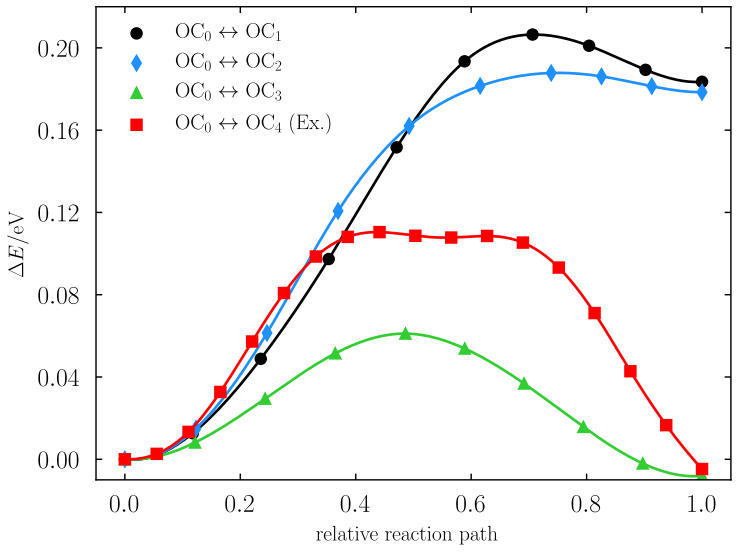


Pathway	Na(100)		Li(100)	
	E_a^{for}	E_a^{rev}	E_a^{for}	E_a^{rev}
OC0↔OC1	0.19	0.09	0.21	0.02
OC0↔OC2	0.17	0.06	0.19	0.01
OC0↔OC3	0.13	0.12	0.06	0.07
OC0↔OC4 (Ex.)	0.04	0.04	0.11	0.12

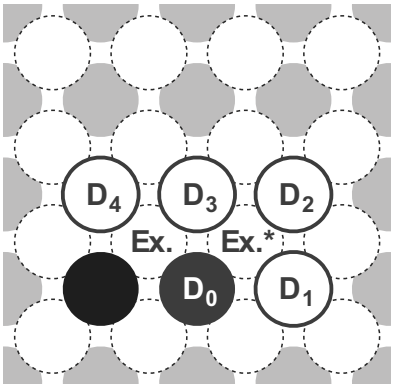
Sodium



Lithium

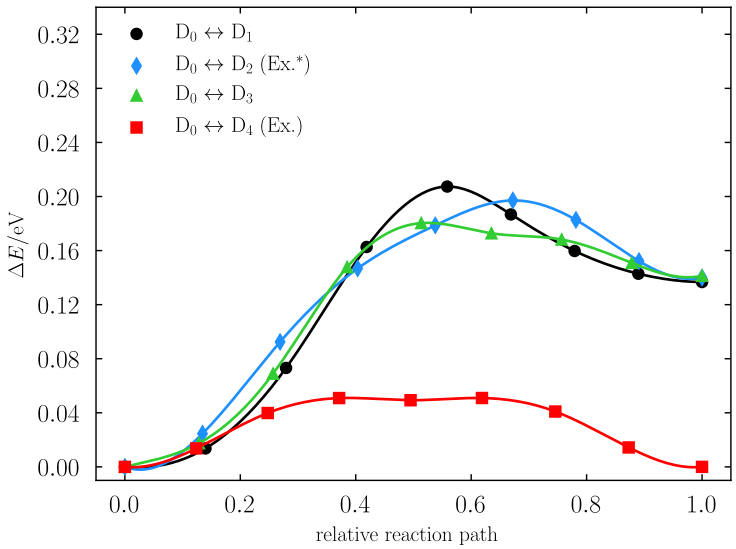


Dimer

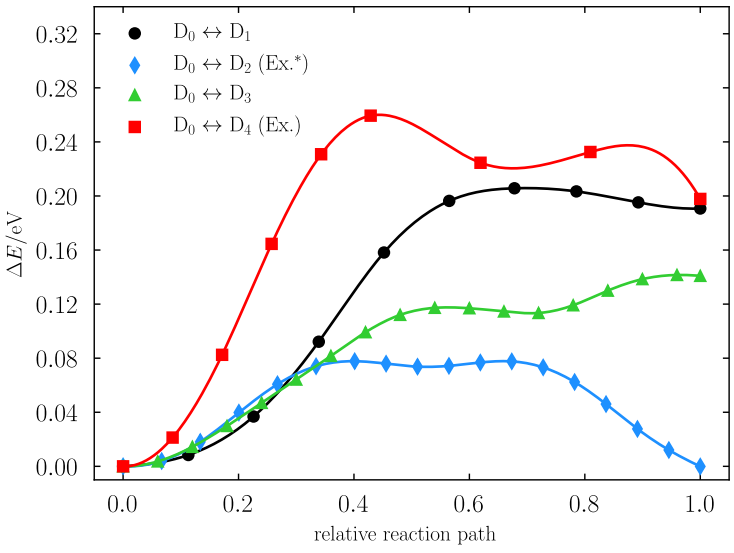


Pathway	Na(100) E_a^{for}	Na(100) E_a^{rev}	Li(100) E_a^{for}	Li(100) E_a^{rev}
$D_0 \leftrightarrow D_1$	0.21	0.07	0.21	0.01
$D_0 \leftrightarrow D_2$ (Ex.*)	0.20	0.06	0.26	0.06
$D_0 \leftrightarrow D_3$	0.18	0.04	0.14	0.00
$D_0 \leftrightarrow D_4$ (Ex.)	0.05	0.05	0.08	0.08

Sodium

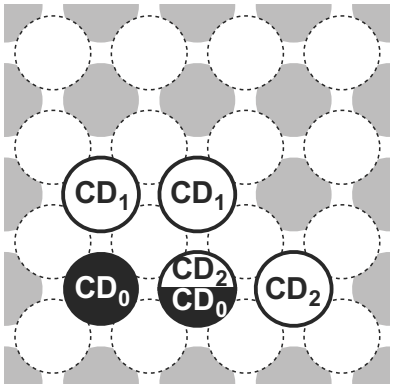


Lithium



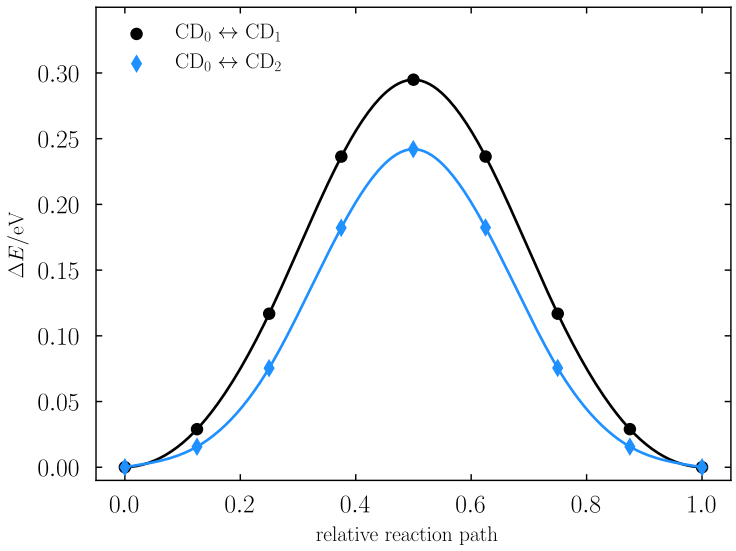
s

Concerted dimer

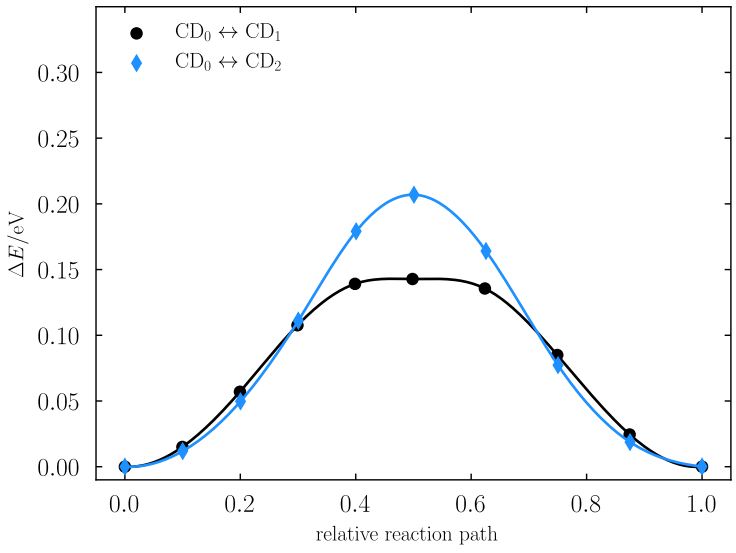


	Na(100)		Li(100)	
Pathway	E_a^{for}	E_a^{rev}	E_a^{for}	E_a^{rev}
$CD_0 \leftrightarrow CD_1$	0.29	0.29	0.14	0.14
$CD_0 \leftrightarrow CD_2$	0.24	0.24	0.21	0.21

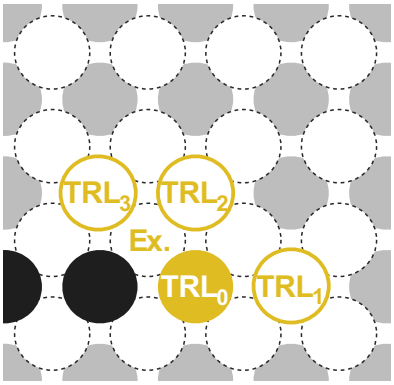
Sodium



Lithium

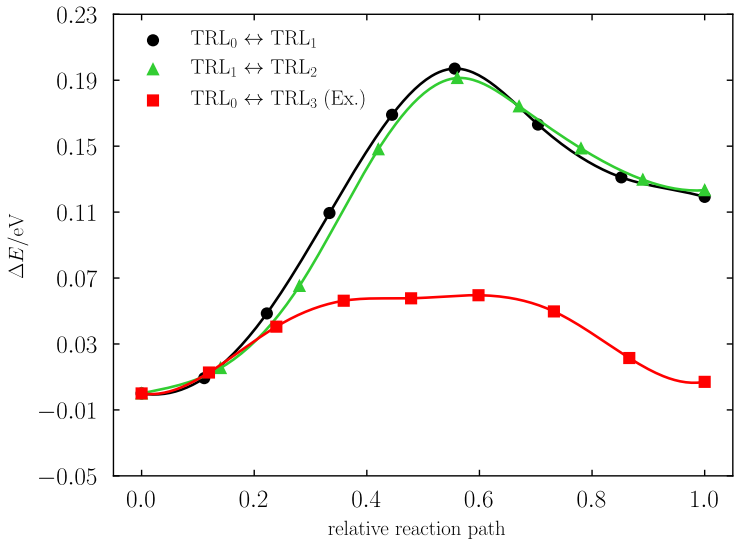


Trimer (linear)

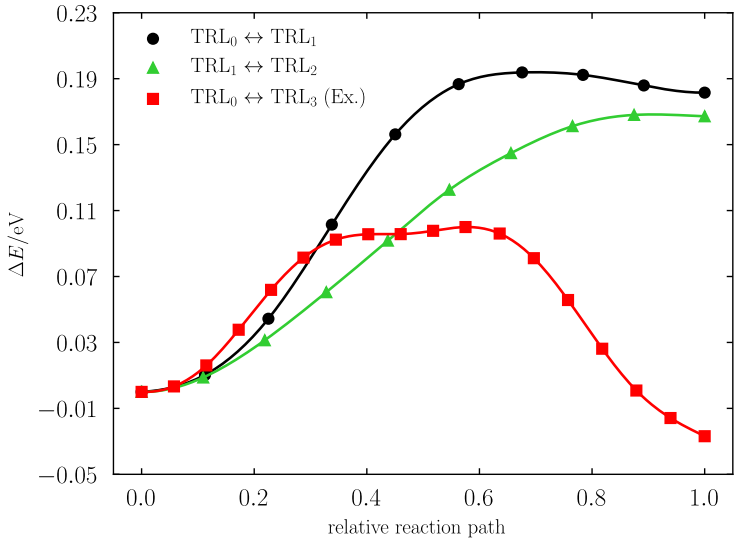


	Na(100)		Li(100)	
Pathway	E_a^{for}	E_a^{rev}	E_a^{for}	E_a^{rev}
TRL$_0$↔ TRL$_1$	0.20	0.08	0.19	0.01
TRL$_0$↔ TRL$_2$	0.19	0.07	0.17	0.00
TRL$_0$↔ TRL$_3$ (Ex.)	0.06	0.05	0.10	0.13

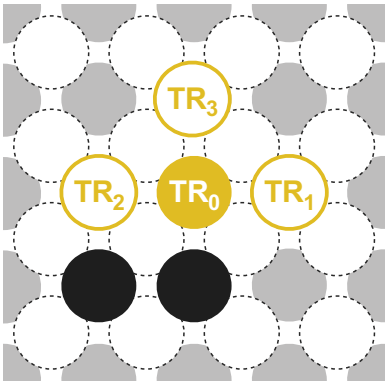
Sodium



Lithium

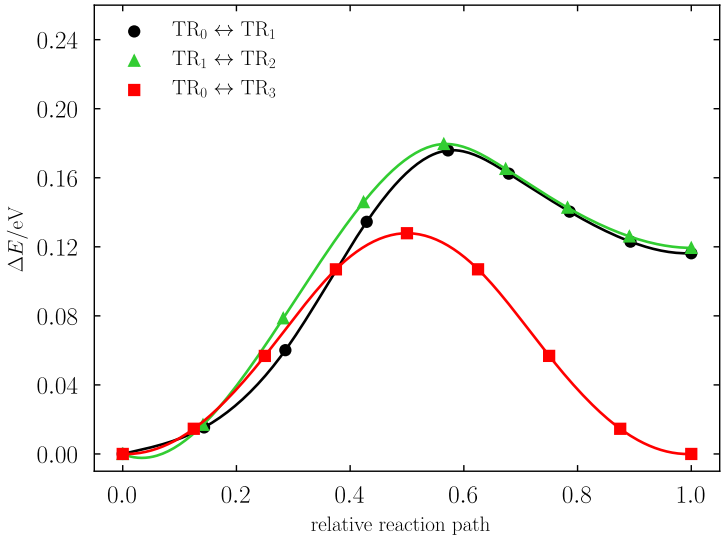


Trimer (linear)

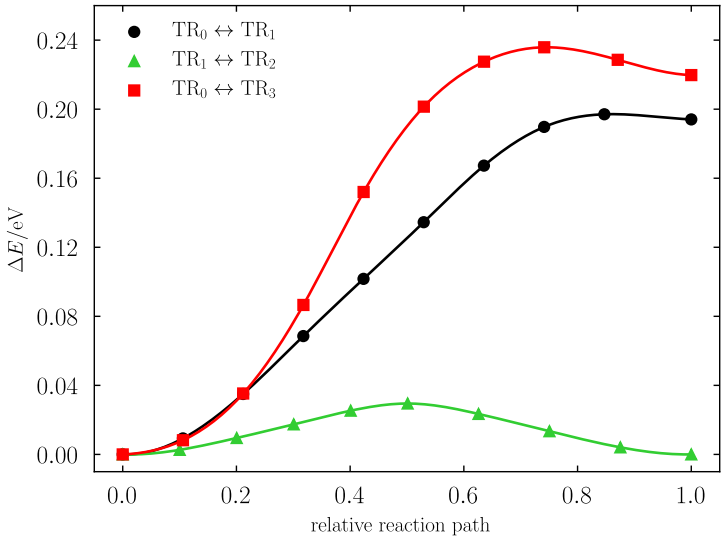


	Na(100)		Li(100)	
Pathway	E_a^{for}	E_a^{rev}	E_a^{for}	E_a^{rev}
$TRL_0 \leftrightarrow TRL_1$	0.20	0.08	0.19	0.01
$TRL_0 \leftrightarrow TRL_2$	0.19	0.07	0.17	0.00
$TRL_0 \leftrightarrow TRL_3$ (Ex.)	0.06	0.05	0.10	0.13

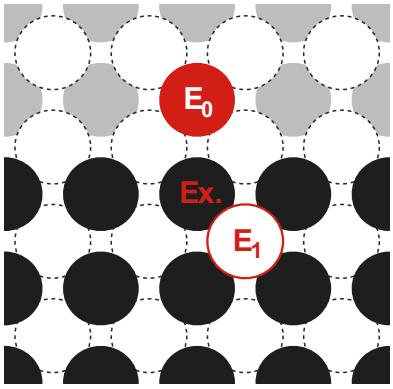
Sodium



Lithium

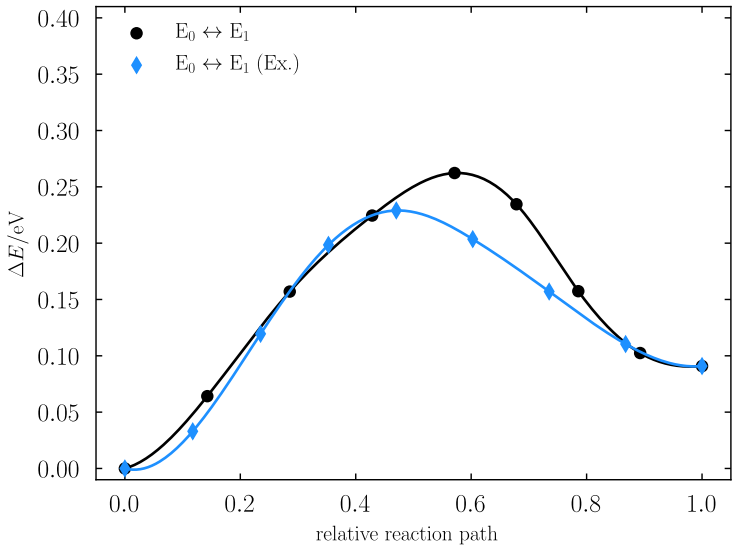


Ehrlich-Schwoebel-barrier

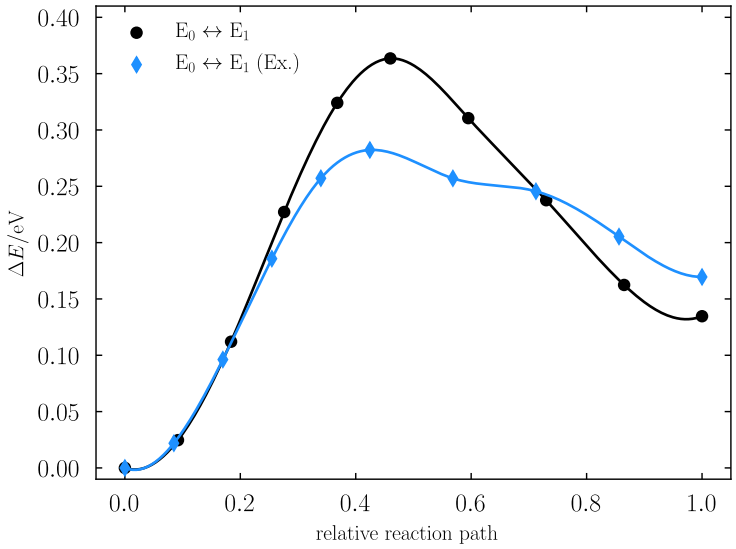


	Na(100)		Li(100)	
Pathway	E_a^{for}	E_a^{rev}	E_a^{for}	E_a^{rev}
$E_0 \leftrightarrow E_1$	0.26	0.17	0.39	0.22
$E_0 \leftrightarrow E_1$ (Ex.)	0.23	0.14	0.28	0.11

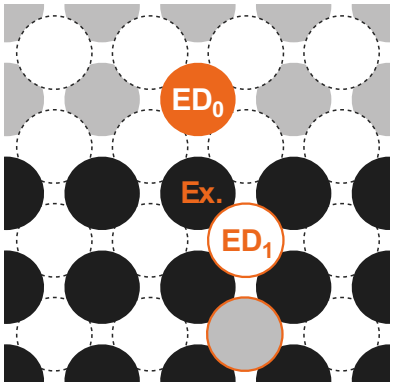
Sodium



Lithium

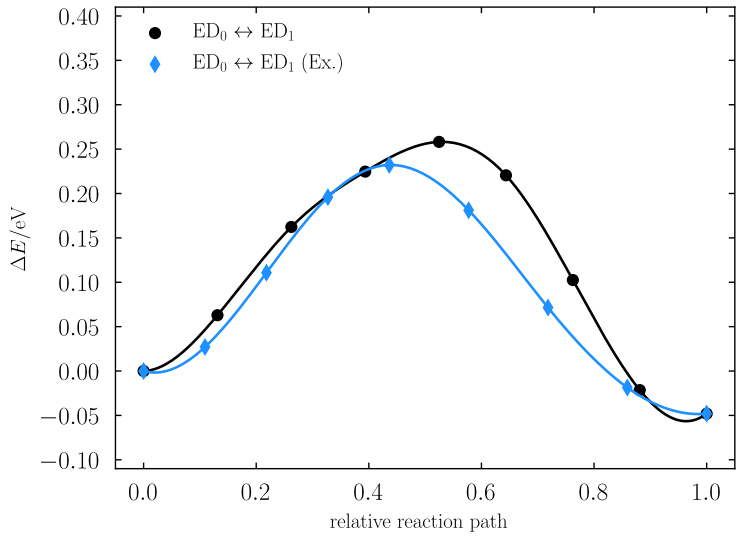


Ehrlich-Schwoebel-barrier (dimer)

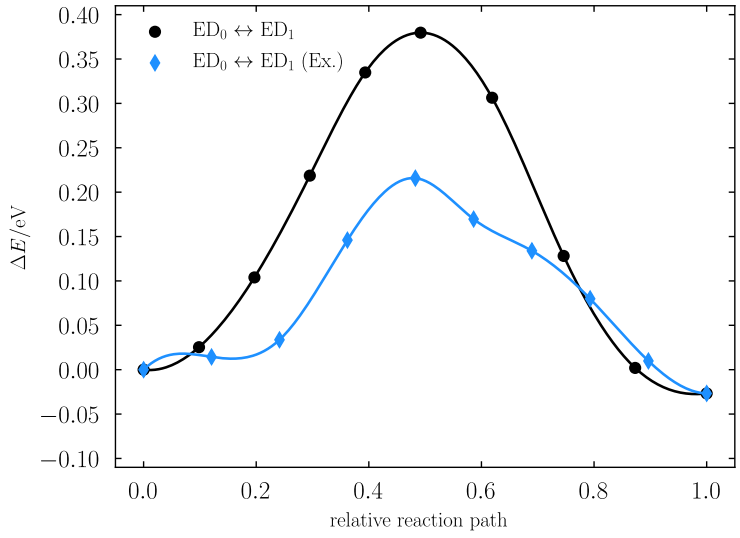


	Na(100)		Li(100)	
Pathway	E_a^{for}	E_a^{rev}	E_a^{for}	E_a^{rev}
$ED_0 \leftrightarrow ED_1$	0.26	0.31	0.38	0.41
$ED_0 \leftrightarrow ED_1$ (Ex.)	0.23	0.28	0.22	0.24

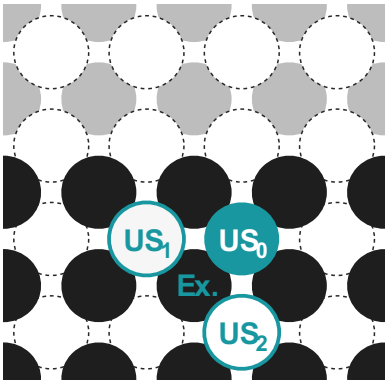
Sodium



Lithium

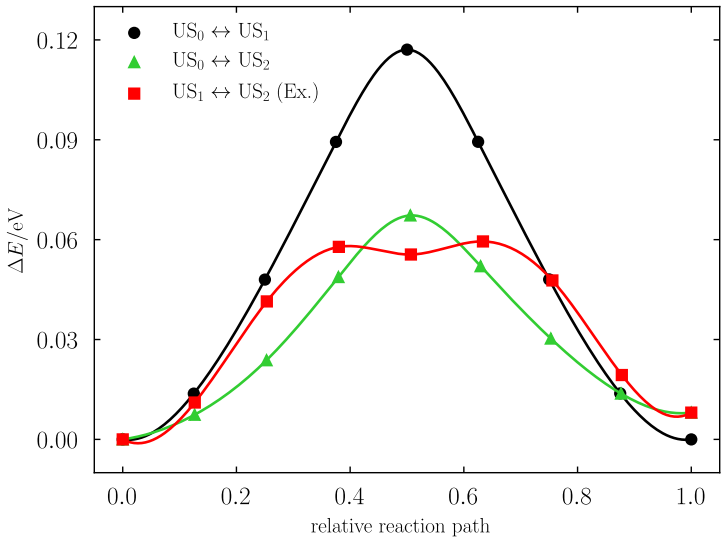


Upper step

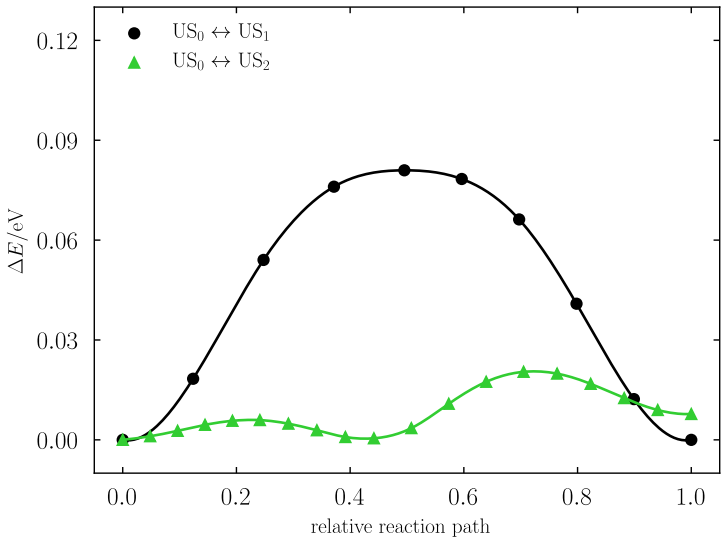


	Na(100)		Li(100)	
Pathway	E_a^{for}	E_a^{rev}	E_a^{for}	E_a^{rev}
$US_0 \leftrightarrow US_1$	0.12	0.12	0.08	0.08
$US_0 \leftrightarrow US_2$	0.07	0.06	0.02	0.01
$US_1 \leftrightarrow US_2$ (Ex.)	0.06	0.05	0.06	0.05

Sodium



Lithium



C. Diffusion properties on Na(110)

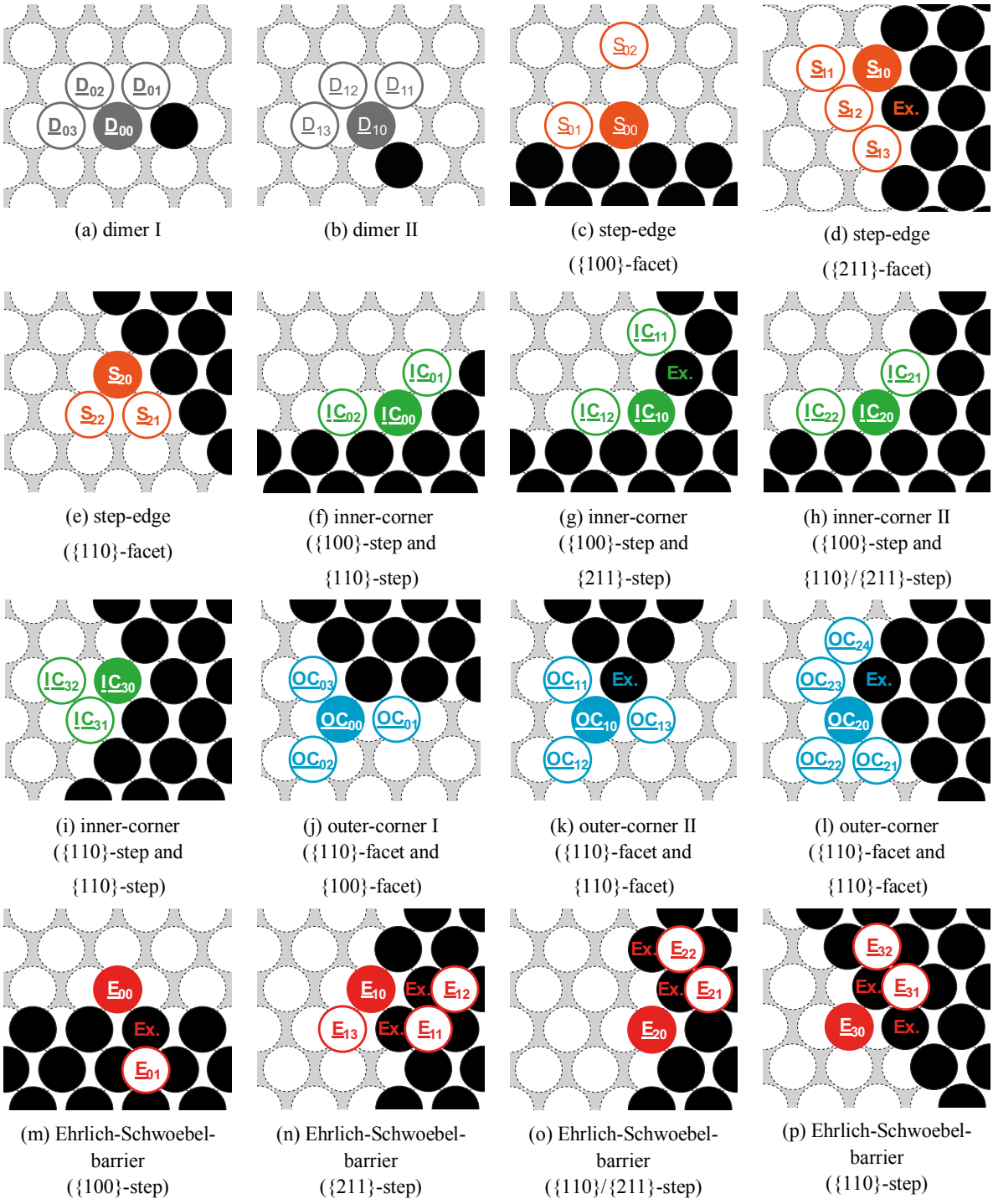


Fig. 3: Schematic representation of the investigated self-diffusion on Na(110). Filled circle marks the initial position, while a framed circle indicates possible final positions of the diffusion pathway. Circles labeled by Ex. mark atoms participating in the exchange process. For all illustrated processes, the characteristic values are listed in Table VI and Table VII.

Gelösch
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Table VI: Calculated forward (for) and reversed (rev) activation energies (E_a) as well as forward (for) and reversed (rev) rate constants ($k_{@RT}$) for the various diffusion pathways on Na(110). For the pre-exponential factor we assumed a value of $\nu = 5 \cdot 10^{12}$ Hz. All activation energies are reported in eV as well as the reaction rates in Hz. All values have been obtained by means of DFT-PBE.

System	Pathway	E_a^{for}	E_a^{rev}	$k_{@RT}^{for}$	$k_{@RT}^{rev}$
Dimer	$\underline{D}_{00} \leftrightarrow \underline{D}_{01}$	0.03	0.02	$1.6 \cdot 10^{12}$	$2.3 \cdot 10^{12}$
	$\underline{D}_{00} \leftrightarrow \underline{D}_{02}$	0.15	0.01	$1.5 \cdot 10^{10}$	$3.4 \cdot 10^{12}$
	$\underline{D}_{00} \leftrightarrow \underline{D}_{03}$	0.13	0.00	$3.2 \cdot 10^{10}$	$5.0 \cdot 10^{12}$
	$\underline{D}_{10} \leftrightarrow \underline{D}_{11}$	0.04	0.00	$1.1 \cdot 10^{12}$	$5.0 \cdot 10^{12}$
	$\underline{D}_{10} \leftrightarrow \underline{D}_{12}$	0.10	0.02	$1.0 \cdot 10^{11}$	$2.3 \cdot 10^{12}$
	$\underline{D}_{10} \leftrightarrow \underline{D}_{13}$	0.14	0.01	$2.2 \cdot 10^{10}$	$3.4 \cdot 10^{12}$
Step-edge	$\underline{S}_{00} \leftrightarrow \underline{S}_{01}$	0.12	0.12	$4.7 \cdot 10^{10}$	$4.7 \cdot 10^{10}$
	$\underline{S}_{00} \leftrightarrow \underline{S}_{02}$	0.23	0.04	$6.5 \cdot 10^{08}$	$1.1 \cdot 10^{12}$
	$\underline{S}_{10} \leftrightarrow \underline{S}_{11}$	0.27	0.00	$1.4 \cdot 10^{08}$	$5.0 \cdot 10^{12}$
	$\underline{S}_{10} \leftrightarrow \underline{S}_{12}$	0.16	0.01	$9.9 \cdot 10^{09}$	$3.4 \cdot 10^{12}$
	$\underline{S}_{10} \leftrightarrow \underline{S}_{13}$ (Ex.)	0.08	0.08	$2.2 \cdot 10^{11}$	$2.2 \cdot 10^{11}$
	$\underline{S}_{20} \leftrightarrow \underline{S}_{21}$	0.03	0.03	$1.6 \cdot 10^{12}$	$1.6 \cdot 10^{12}$
	$\underline{S}_{20} \leftrightarrow \underline{S}_{22}$	0.19	0.00	$3.1 \cdot 10^{09}$	$5.0 \cdot 10^{12}$
Inner-corner	$\underline{IC}_{00} \leftrightarrow \underline{IC}_{01}$	0.09	0.02	$1.5 \cdot 10^{11}$	$2.3 \cdot 10^{12}$
	$\underline{IC}_{00} \leftrightarrow \underline{IC}_{02}$	0.18	0.10	$4.5 \cdot 10^{09}$	$1.0 \cdot 10^{11}$
	$\underline{IC}_{10} \leftrightarrow \underline{IC}_{11}$ (Ex.)	0.11	0.05	$6.9 \cdot 10^{10}$	$7.1 \cdot 10^{11}$
	$\underline{IC}_{10} \leftrightarrow \underline{IC}_{12}$	0.21	0.06	$1.4 \cdot 10^{09}$	$4.8 \cdot 10^{11}$
	$\underline{IC}_{20} \leftrightarrow \underline{IC}_{21}$	0.07	0.07	$3.3 \cdot 10^{11}$	$3.3 \cdot 10^{11}$
	$\underline{IC}_{20} \leftrightarrow \underline{IC}_{22}$	0.19	0.10	$3.1 \cdot 10^{09}$	$1.0 \cdot 10^{11}$
	$\underline{IC}_{30} \leftrightarrow \underline{IC}_{31}$	0.07	0.02	$3.3 \cdot 10^{11}$	$2.3 \cdot 10^{12}$
Outer-corner	$\underline{OC}_{00} \leftrightarrow \underline{OC}_{01}$	0.05	0.10	$7.1 \cdot 10^{11}$	$1.0 \cdot 10^{11}$
	$\underline{OC}_{00} \leftrightarrow \underline{OC}_{02}$	0.14	0.02	$2.2 \cdot 10^{10}$	$2.3 \cdot 10^{12}$
	$\underline{OC}_{00} \leftrightarrow \underline{OC}_{03}$	0.05	0.12	$7.1 \cdot 10^{11}$	$4.7 \cdot 10^{10}$
	$\underline{OC}_{10} \leftrightarrow \underline{OC}_{11}$	0.00	0.07	$5.0 \cdot 10^{12}$	$3.3 \cdot 10^{11}$
	$\underline{OC}_{10} \leftrightarrow \underline{OC}_{12}$	0.13	0.02	$3.2 \cdot 10^{10}$	$2.3 \cdot 10^{12}$
	$\underline{OC}_{10} \leftrightarrow \underline{OC}_{13}$	0.04	0.04	$1.1 \cdot 10^{12}$	$1.1 \cdot 10^{12}$
	$\underline{OC}_{10} \leftrightarrow \underline{OC}_{13}$ (Ex.)	0.06	0.06	$4.8 \cdot 10^{11}$	$4.8 \cdot 10^{11}$
	$\underline{OC}_{20} \leftrightarrow \underline{OC}_{21}$	0.05	0.04	$7.1 \cdot 10^{11}$	$1.1 \cdot 10^{12}$
	$\underline{OC}_{20} \leftrightarrow \underline{OC}_{22}$	0.20	0.00	$2.1 \cdot 10^{09}$	$5.0 \cdot 10^{12}$
	$\underline{OC}_{20} \leftrightarrow \underline{OC}_{23}$	0.11	0.01	$6.9 \cdot 10^{10}$	$3.4 \cdot 10^{12}$
	$\underline{OC}_{20} \leftrightarrow \underline{OC}_{24}$ (Ex.)	0.16	0.16	$9.9 \cdot 10^{09}$	$9.9 \cdot 10^{09}$

Table VII: Calculated forward (for) and reversed (rev) activation energies (E_a) as well as forward (for) and reversed (rev) room-temperature rate constants ($k_{@RT}$) for the various diffusion pathways on Na(110). For the pre-exponential factor we assumed a value of $\nu = 5 \cdot 10^{12}$ Hz. All activation energies are reported in eV as well as the reaction rates in Hz.All values have been obtained by means of DFT-PBE.

System	Pathway	E_a^{for}	E_a^{rev}	$k_{@RT}^{for}$	$k_{@RT}^{rev}$
Ehrlich-Schwoebel-barrier	$\underline{E}_{00} \leftrightarrow \underline{E}_{01}$	0.29	0.10	$6.3 \cdot 10^{07}$	$1.0 \cdot 10^{11}$
	$\underline{E}_{00} \leftrightarrow \underline{E}_{01}$ (Ex.)	0.28	0.09	$9.2 \cdot 10^{07}$	$1.5 \cdot 10^{11}$
	$\underline{E}_{10} \leftrightarrow \underline{E}_{11}$ (Ex.)	0.31	0.04	$2.9 \cdot 10^{07}$	$1.1 \cdot 10^{12}$
	$\underline{E}_{10} \leftrightarrow \underline{E}_{12}$	0.36	0.09	$4.1 \cdot 10^{06}$	$1.5 \cdot 10^{11}$
	$\underline{E}_{10} \leftrightarrow \underline{E}_{12}$ (Ex.)	0.37	0.10	$2.8 \cdot 10^{06}$	$1.0 \cdot 10^{11}$
	$\underline{E}_{20} \leftrightarrow \underline{E}_{21}$	0.35	0.09	$6.1 \cdot 10^{06}$	$1.5 \cdot 10^{11}$
	$\underline{E}_{20} \leftrightarrow \underline{E}_{21}$ (Ex.)	0.27	0.00	$1.4 \cdot 10^{08}$	$5.0 \cdot 10^{12}$
	$\underline{E}_{20} \leftrightarrow \underline{E}_{22}$ (Ex.)	0.30	0.03	$4.2 \cdot 10^{07}$	$1.6 \cdot 10^{12}$
	$\underline{E}_{30} \leftrightarrow \underline{E}_{31}$ (Ex.)	0.19	0.08	$3.1 \cdot 10^{09}$	$2.2 \cdot 10^{11}$

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