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On the Mechanism of Spontaneous Thiol–Disulfide Exchange in Proteins. Electronic Supplementary Information

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FIG. 1. Additional representations of free energy surfaces for the dimethyldisulfide–methylthiolate system.



FIG. 2. Additional representations of free energy surfaces for all of the small peptides considered.

Peptide	Min1		Min2		Min3	
	Popul.	$\Delta G$	Popul.	$\Delta G$	Popul.	$\Delta G$
		$\rm kcal/mol$		$\rm kcal/mol$		$\rm kcal/mol$
ACACACA	0.005	3.13	0.008	2.85	0.987	0
ACAACAACA	0.056	0	0.001	3.85	0.342	0.39
ACAAACAAACA	0.072	1.50	0.021	2.23	0.907	0

TABLE I. Populations of energy minima for the disulfide exchange in peptides  $ACA_nCA_nCA$ .

Peptide	TS12	TS23	TS13
	$\operatorname{deg}$	$\operatorname{deg}$	$\operatorname{deg}$
ACACACA	159	160	151
ACAACAACA	157	154	160
ACAAACAAACA	156	164	156

TABLE II. Geometry of transition states for the disulfide exchange in peptides  $ACA_nCA_nCA$ .



FIG. 3. Alternative representations of the free energy surfaces presented in Figs. 5, 6, 7, 9 and 10 in the main text. Free energy is given as a function of  $r_1 - r_2$  and  $r_3$  while  $r_1 + r_2$  is integrated out.