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Supplementary Material

N_2 binding to the E_0–E_4 states of nitrogenase

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Table S1. Relative energies (in kJ/mol) for the best structures calculated with two basis set, def2-SV(P) (SV) and def2-TZVPD (TZ) (the latter single-point energy calculations on the def2-DSV(P) structures). Energies that change by more than 20 kJ/mol are marked in bold face and the corresponding spin populations are shown in Table S2.

E_n	Structure		TPSS		r^2SCAN	
			SV	TZ	SV	TZ
E_1	Fe2+N2		31.0	39.4	39.1	45.5
	Fe6+N2		0.0	0.0	0.0	0.0
	Fe2-N2		31.1	47.3	42.9	59.5
	Fe6-N2		24.1	29.3	60.3	75.0
E_2	Fe2+N2	H6S	47.8	44.8	11.5	7.6
		C2	191.6	201.8	126.1	128.1
	Fe6+N2	H2F	76.2	71.9	44.8	40.1
	Fe2–N2	H6S	6.2	2.5	0.0	0.0
		C2	184.3	193.8	124.2	134.4
	Fe6–N2	H2F	0.0	0.0	17.8	17.2
E_3	Fe2+N2	S6M	58.6	**91.7**	30.6	27.6
		35_3	110.9	111.3	63.5	57.4
		C3	250.8	261.0	156.2	153.8
	Fe6+N2	S2S	74.1	66.7	98.2	98.4
	Fe2-N2	S6M			0.0	0.0
		35_3	78.4	83.4	47.7	47.5
		C3	227.4	224.5	153.6	142.2
	Fe6-N2	S2S	0.0	0.0	29.4	28.6
E_4	Fe2+N2	S6S	75.7	60.7	47.0	**5.2**
	Fe6+N2	S2S	80.7	77.3	68.5	53.9
	Fe2-N2	S6S	35.1	15.5	0.0	0.0
		3523	32.0	13.6	47.4	64.2
		C3	202.3	**229.6**	67.7	**14.0**
	Fe6-N2	S2S	0.0	0.0	10.7	3.5

Table S2. Mulliken spin populations obtained with the def2-SV(P) (SV) and def2-TZVPD (TZ) basis sets (the latter single-point energy calculations on the def2-DSV(P) structures) for the four structures for which the relative energies change by more than 20 kJ/mol in Table S1. For the E_3 state, the BS state changes from BS14 to BS147. For the other three, several spin populations change by more than 1 *e* (marked in bold face), indicating that the electronic structure has changed extensively.

E_n	Structure		DFT	def2-SV(P)								def2-TZVPD							
				Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7	Mo	Fe1	Fe2	Fe3	Fe4	Fe5	Fe6	Fe7	Mo
E_3	Fe6+N2	S2S	TPSS	-3.2	2.3	2.5	-3.2	2.4	1.2	1.0	0.5	-3.0	**3.5**	2.4	-2.7	2.7	1.5	**-0.5**	-0.7
E_4	Fe2+N2	S6S	r^{2}SCAN	-3.7	2.7	3.2	3.3	-3.2	2.4	-3.1	-0.6	-3.4	**4.4**	2.4	3.5	-3.7	**1.0**	-3.5	**2.5**
	Fe2-N2	C3	TPSS	3.1	-3.0	-3.4	-3.4	2.9	3.1	2.8	-0.8	3.0	-3.0	-3.2	-3.4	2.9	3.7	**0.8**	-1.1
			r^{2}SCAN	3.7	-2.3	-3.1	-3.2	3.3	0.3	3.1	-1.4	3.0	**-4.2**	-2.6	-3.8	3.6	1.0	3.6	**-3.4**

Table S3. N_2-binding energies (ΔE_{N2} in kJ/mol) for the best structures calculated with two basis set, def2-SV(P) (SV) and def2-TZVPD (TZ) (the latter single-point energy calculations on the def2-DSV(P) structures). Binding energies for the other complexes can be obtained by summing ΔE_{N2} in this table with the relative energies in Table S1.

E_n	Structure		TPSS		r2SCAN	
			B1	B2	B1	B2
E_1	Fe6+N2		1.9	12.7	-1.7	7.4
E_2	Fe6–N2	H2F	-10.9	-18.0	34.5	53.2
E_3	Fe2-N2	S6M			9.6	23.0
	Fe6-N2	S2S	-45.5	-34.5		
E_4	Fe2-N2	S6S			-18.5	-7.0
	Fe6-N2	S2S	-50.9	-33.4		