

Supporting Information for

Catalysis for dinitrogen activation and reduction by a single cluster Fe₁₃ and its doping systems

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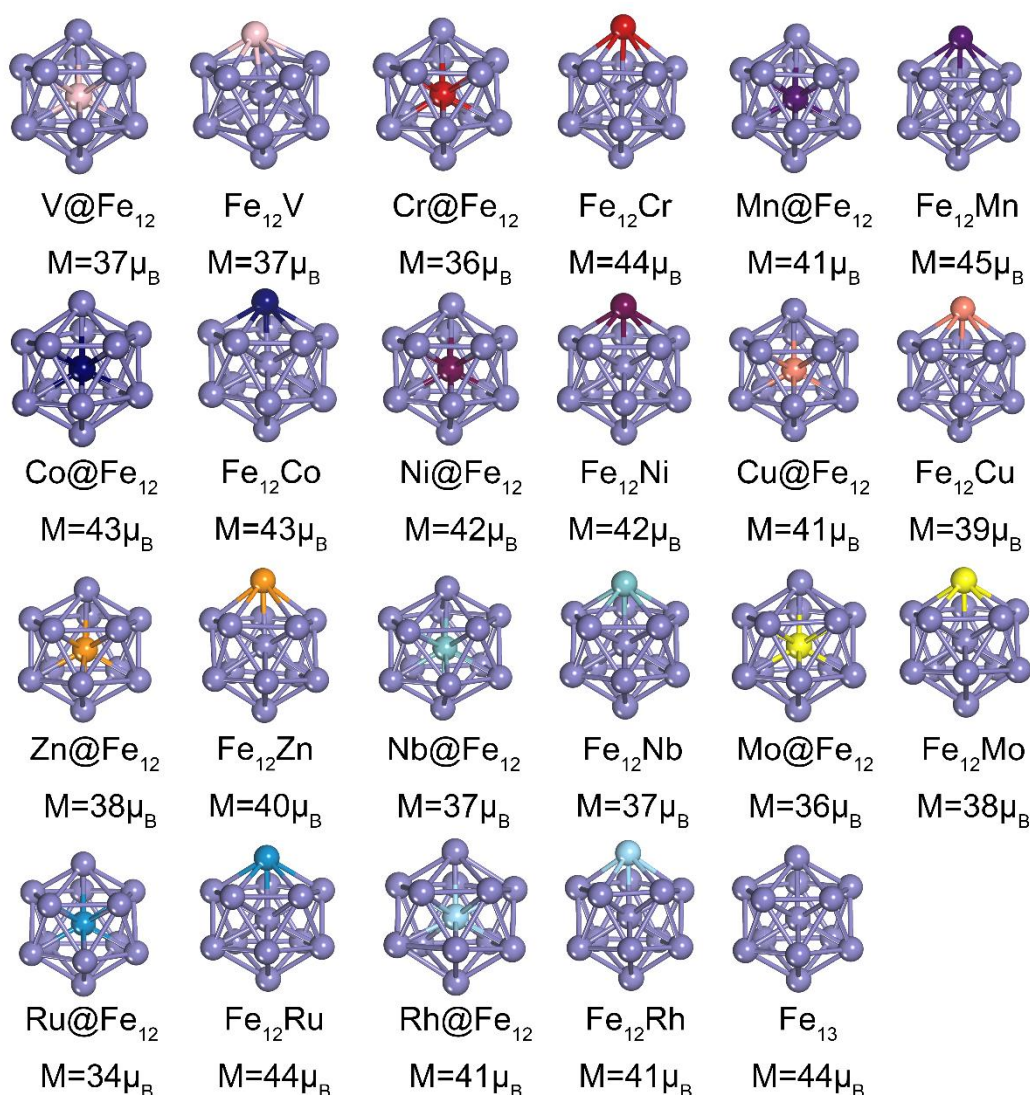


Fig. S1 The optimized geometrical structures of doped Fe_{13} clusters.

Based on the manual of VASP, section 6.13, "If one is searching for a spin polarized (magnetic or antiferromagnetic) solution, it is usually safest to start from larger local magnetic moments, because in some cases, the default values might not be sufficiently big. A safe default is usually the experimental magnetic moment multiplied by 1.2 or 1.5.", therefore, we have compared the energies of five typical clusters by setting with three different magnetic moments (Table S1), and found that the values of magnetic moments for Fe and other doped atoms are reasonable to be set with 5.0 and element-dependent values, respectively.

Table S1 The energies and magnetic moment of selected five clusters with different MAGMOM settings.

Clusters	In the work			MAGMOM=1.0		MAGMOM=20.0	
	Energy	MAGMOM set in the work	Magnetic Moment	Energy	Magnetic Moment	Energy	Magnetic Moment
Fe ₁₃	-86.64 eV	Fe:5.0	44 μ_B	-86.11 eV	36 μ_B	-86.64 eV	44 μ_B
Fe ₁₂ Nb	-87.69 eV	Fe:5, Nb:7.0	37 μ_B	-87.32 eV	29 μ_B	-87.69 eV	37 μ_B
Nb@Fe ₁₂	-87.34 eV	Fe:5, Nb:7.0	37 μ_B	-87.34 eV	37 μ_B	-87.34 eV	37 μ_B
Fe ₁₂ Rh	-85.61 eV	Fe:5.0, Rh:4.0	41 μ_B	-85.31 eV	33 μ_B	-85.70 eV	41 μ_B
Rh@Fe ₁₂	-83.95 eV	Fe:5.0, Rh:4.0	41 μ_B	-83.56 eV	35 μ_B	-83.95 eV	41 μ_B

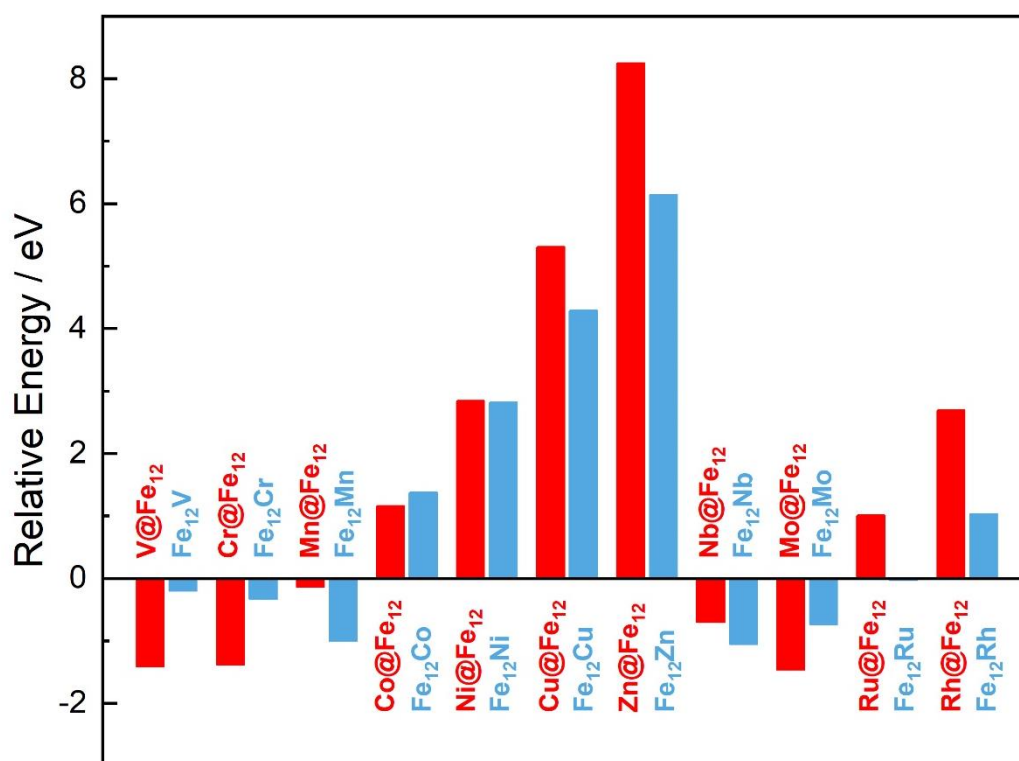


Fig. S2 The relative energy of doped clusters compared to pure Fe₁₃ clusters, in which the negative values indicate that the doped clusters are more stable than Fe₁₃. The relative energy is evaluated according to the equation: $\Delta E = E(\text{Fe}_{12}\text{X}) - E(\text{Fe}_{13})$, where $E(\text{Fe}_{12}\text{X})$ and $E(\text{Fe}_{13})$ present the energy of Fe₁₂X and Fe₁₃ clusters, respectively.

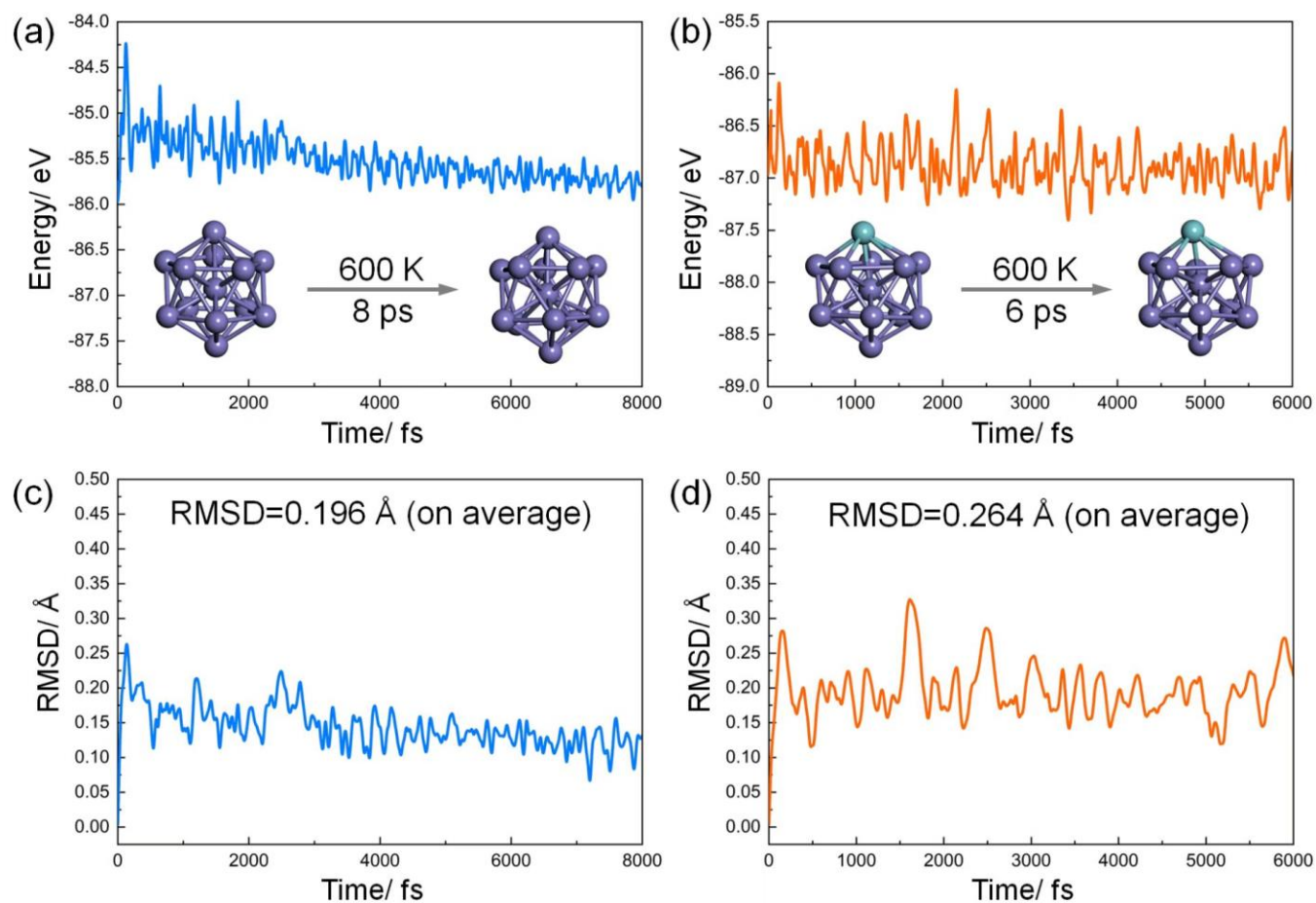


Fig. S3 The energy variations and the root mean square deviation (RMSD) of Fe-Fe and Fe-Nb bond lengths during the AIMD simulations for (a/c) Fe₁₃ and (b/d) Fe₁₂Nb at 600 K (the initial and final structures are shown as insets), respectively. The running time is 8ps and 6 ps respectively, with a time step of 1 fs.

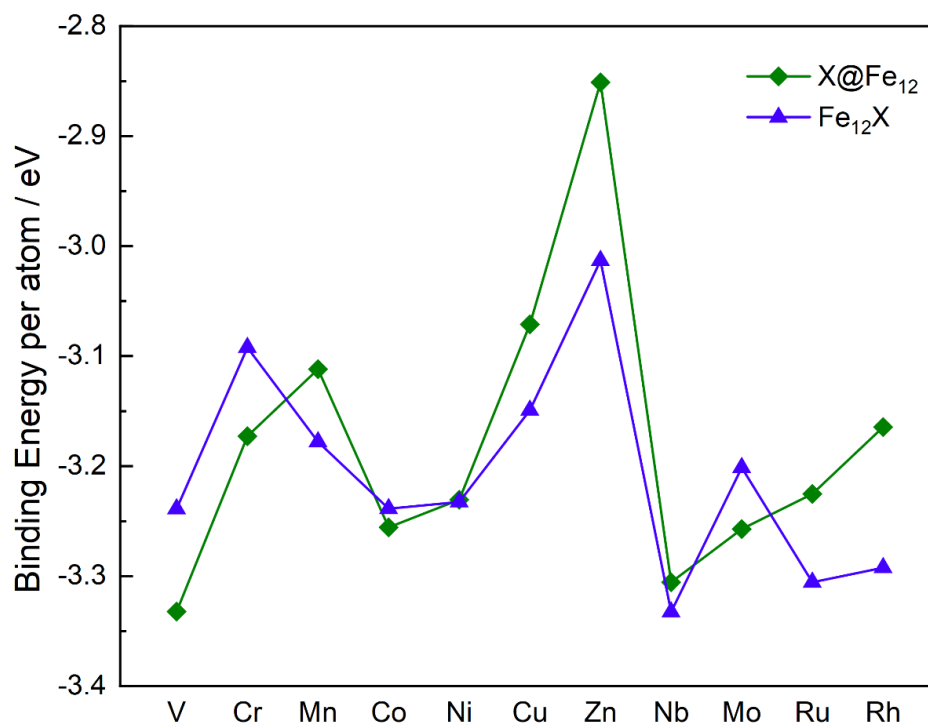


Fig. S4 The average binding energy per atom (E_{ab}) of doped Fe_{13} clusters.

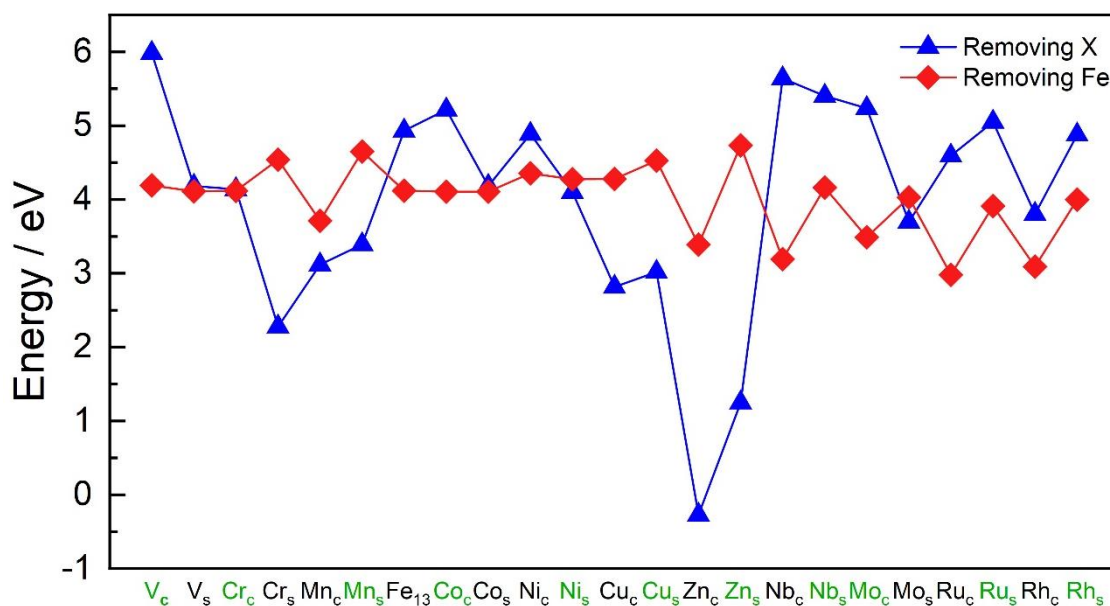


Fig. S5 The energies of removing X or Fe atom of doped Fe_{13} clusters. The “c” and “s” represent the center- and shell- doped clusters, respectively. The green tick labels present the energy favourable structures.

Table S2 The bond length (in Å) between the center-doped atom X and the surrounding Fe atom in X@Fe₁₂ systems.

Doping atom	V	Cr	Mn	Co	Ni	Cu	Zn	Nb	Mo	Ru	Rh
Fe1	2.44	2.40	2.48	2.46	2.38	2.40	2.41	2.51	2.48	2.42	2.50
Fe2	2.44	2.40	2.48	2.37	2.38	2.40	2.44	2.51	2.48	2.45	2.50
Fe3	2.35	2.38	2.34	2.38	2.38	2.39	2.39	2.44	2.39	2.43	2.41
Fe4	2.35	2.35	2.34	2.36	2.38	2.38	2.37	2.44	2.45	2.40	2.41
Fe5	2.35	2.40	2.38	2.40	2.38	2.39	2.39	2.44	2.40	2.41	2.41
Fe6	2.44	2.35	2.33	2.36	2.38	2.38	2.36	2.51	2.49	2.40	2.48
Fe7	2.44	2.40	2.48	2.46	2.38	2.40	2.41	2.51	2.48	2.45	2.50
Fe8	2.34	2.39	2.38	2.40	2.38	2.39	2.39	2.44	2.40	2.43	2.41
Fe9	2.35	2.55	2.34	2.36	2.38	2.38	2.37	2.44	2.45	2.40	2.42
Fe10	2.35	2.38	2.34	2.38	2.38	2.39	2.39	2.44	2.39	2.41	2.42
Fe11	2.44	2.40	2.48	2.37	2.38	2.40	2.44	2.51	2.48	2.42	2.50
Fe12	2.44	2.35	2.33	2.37	2.38	2.38	2.36	2.51	2.49	2.40	2.48

Table S3 The bond length (in Å) between the shell-doped X and the surrounding Fe atom in the doped Fe₁₂X systems.

Doping atom	V	Cr	Mn	Co	Ni	Cu	Zn	Nb	Mo	Ru	Rh
Fe1	2.36	2.67	2.64	2.35	2.41	2.60	2.64	2.48	2.40	2.48	2.57
Fe2	2.36	2.67	2.64	2.35	2.42	2.60	2.61	2.48	2.40	2.49	2.56
Fe3	2.56	2.71	2.64	2.60	2.62	2.63	2.61	2.61	2.63	2.65	2.56
Fe4	2.83	2.69	2.64	2.74	2.79	2.62	2.68	2.83	2.83	2.63	2.64
Fe5	2.53	2.72	2.64	2.58	2.57	2.63	2.81	2.60	2.60	2.64	2.57

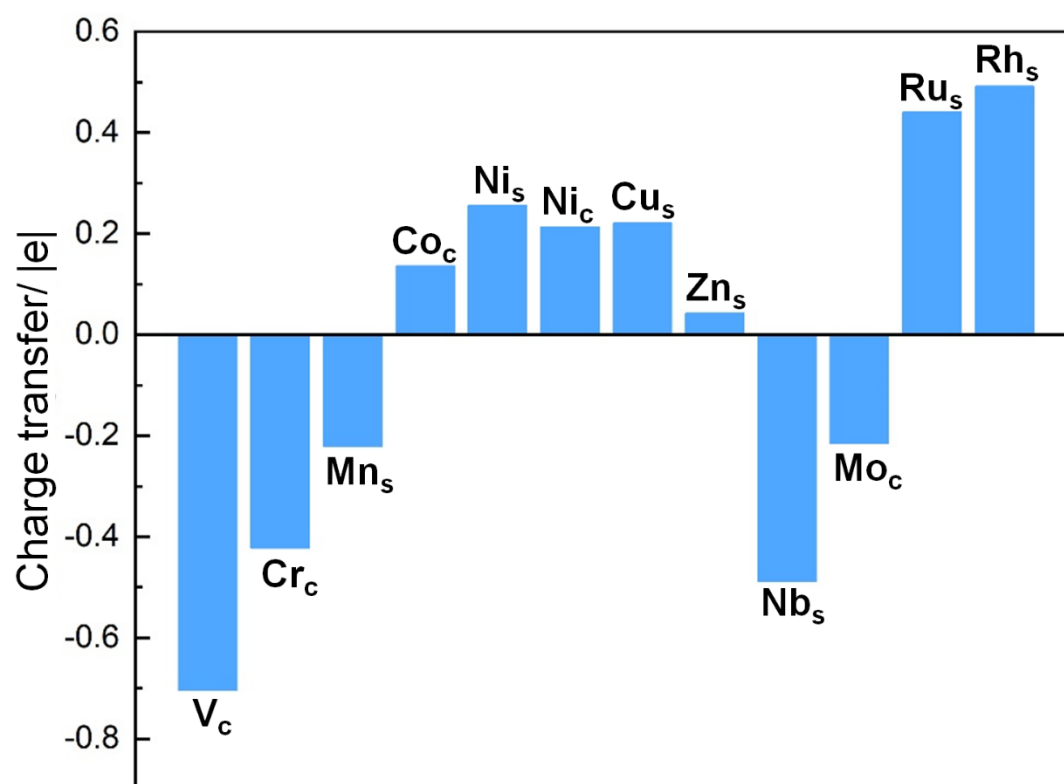
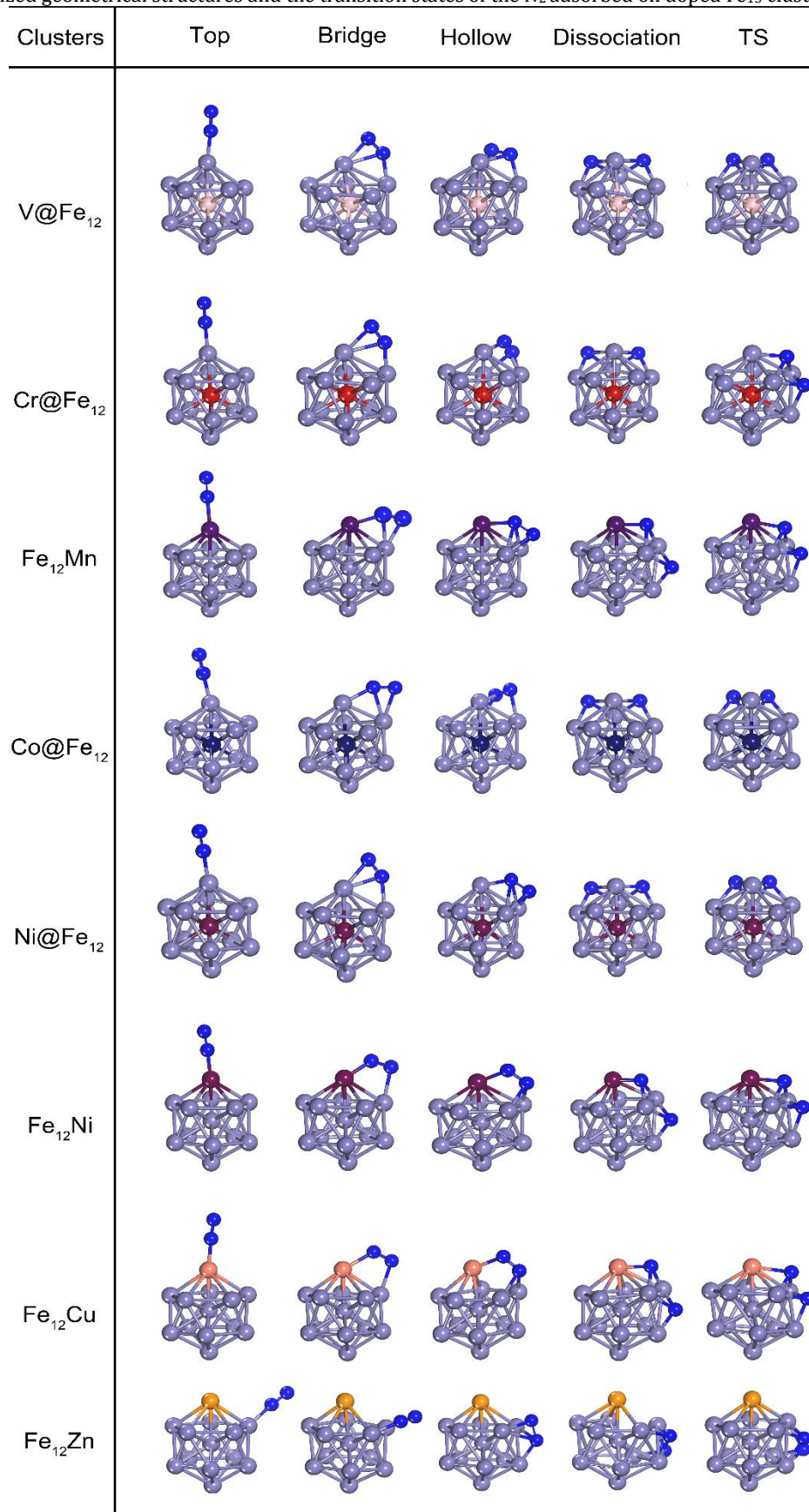
**Fig. S6** The values of Bader charge population on the doped atom. “c” and “s” represent the center- and shell- doped clusters, respectively.

Table S4 The optimized geometrical structures and the transition states of the N₂ adsorbed on doped Fe₁₃ clusters.

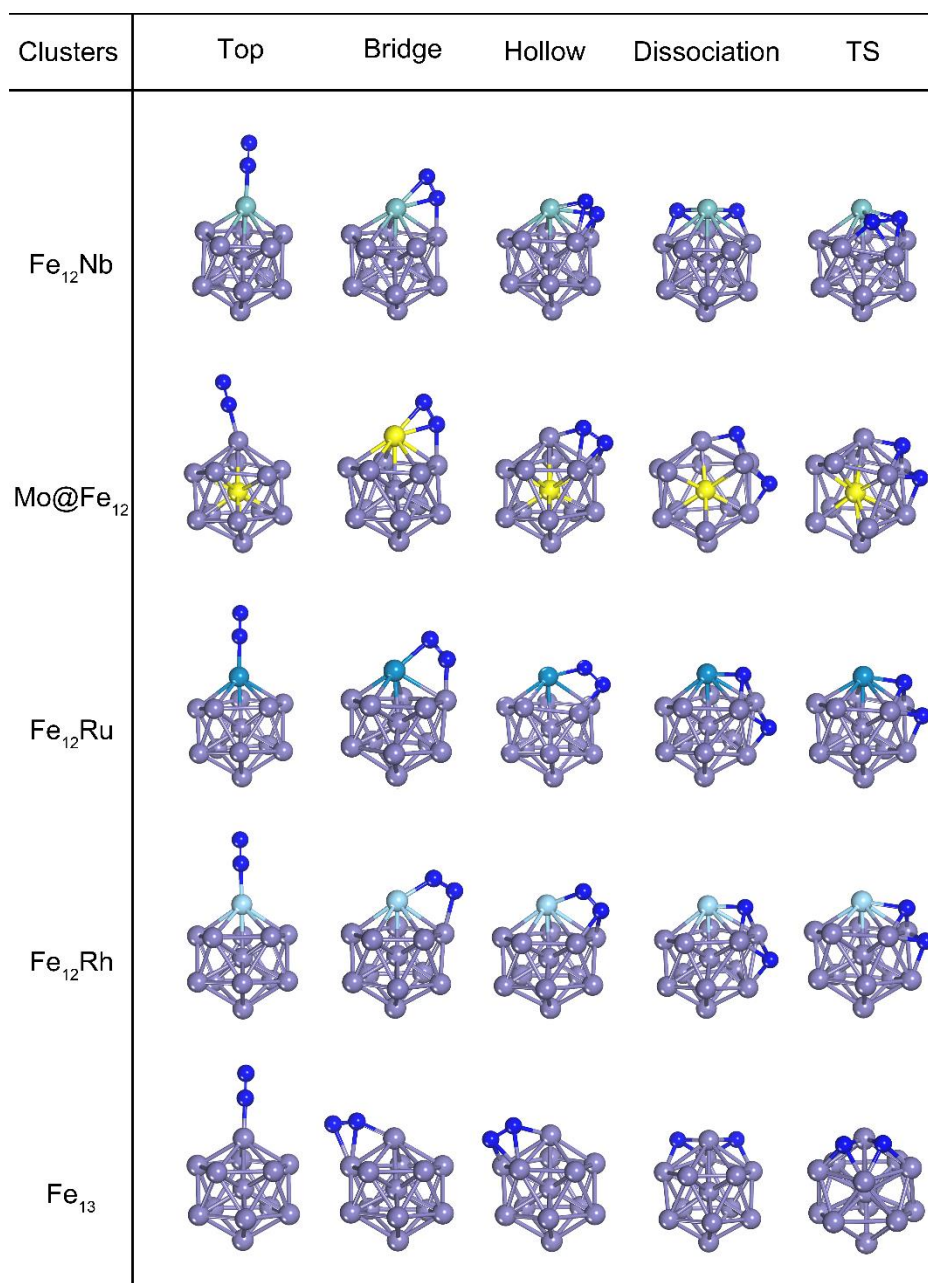
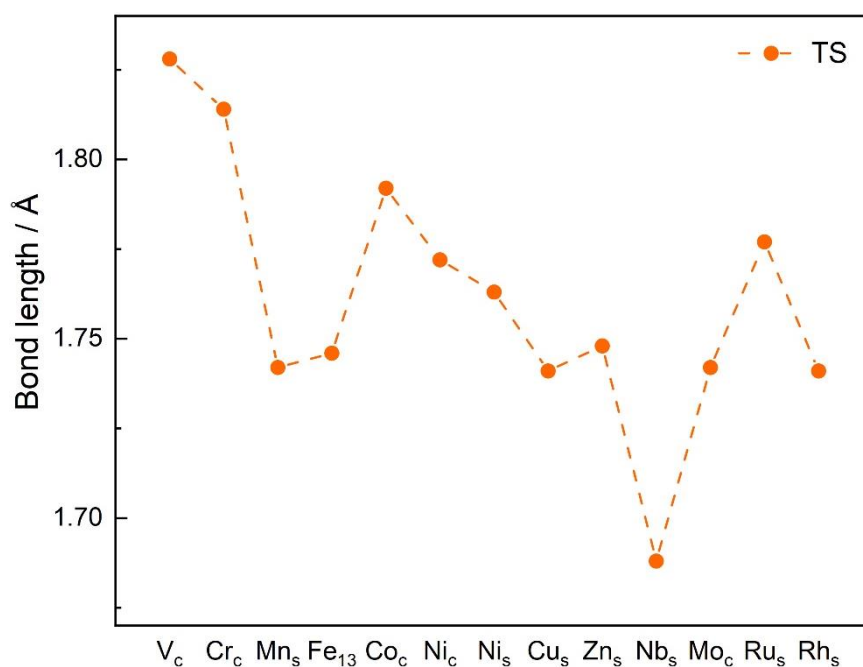


Table S5 The activation energy barriers (ΔE_a / eV) of N_2 dissociation on Fe_{13} and the doped clusters.

Cluster	V@Fe ₁₂	Cr@Fe ₁₂	Fe ₁₂ Mn	Fe ₁₃	Co@Fe ₁₂	Ni@Fe ₁₂	Fe ₁₂ Ni
ΔE_a	1.07	1.18	0.99	0.77	0.79	0.93	1.10
Cluster	Fe ₁₂ Cu	Fe ₁₂ Zn	Fe ₁₂ Nb	Mo@Fe ₁₂	Fe ₁₂ Ru	Fe ₁₂ Rh	
ΔE_a	0.85	0.98	0.56	1.12	1.09	1.25	

**Fig. S7** The bond length of transition state where N_2 dissociation occurs on the doped Fe_{13} clusters. "c" and "s" represent the center- and shell- doped clusters, respectively.

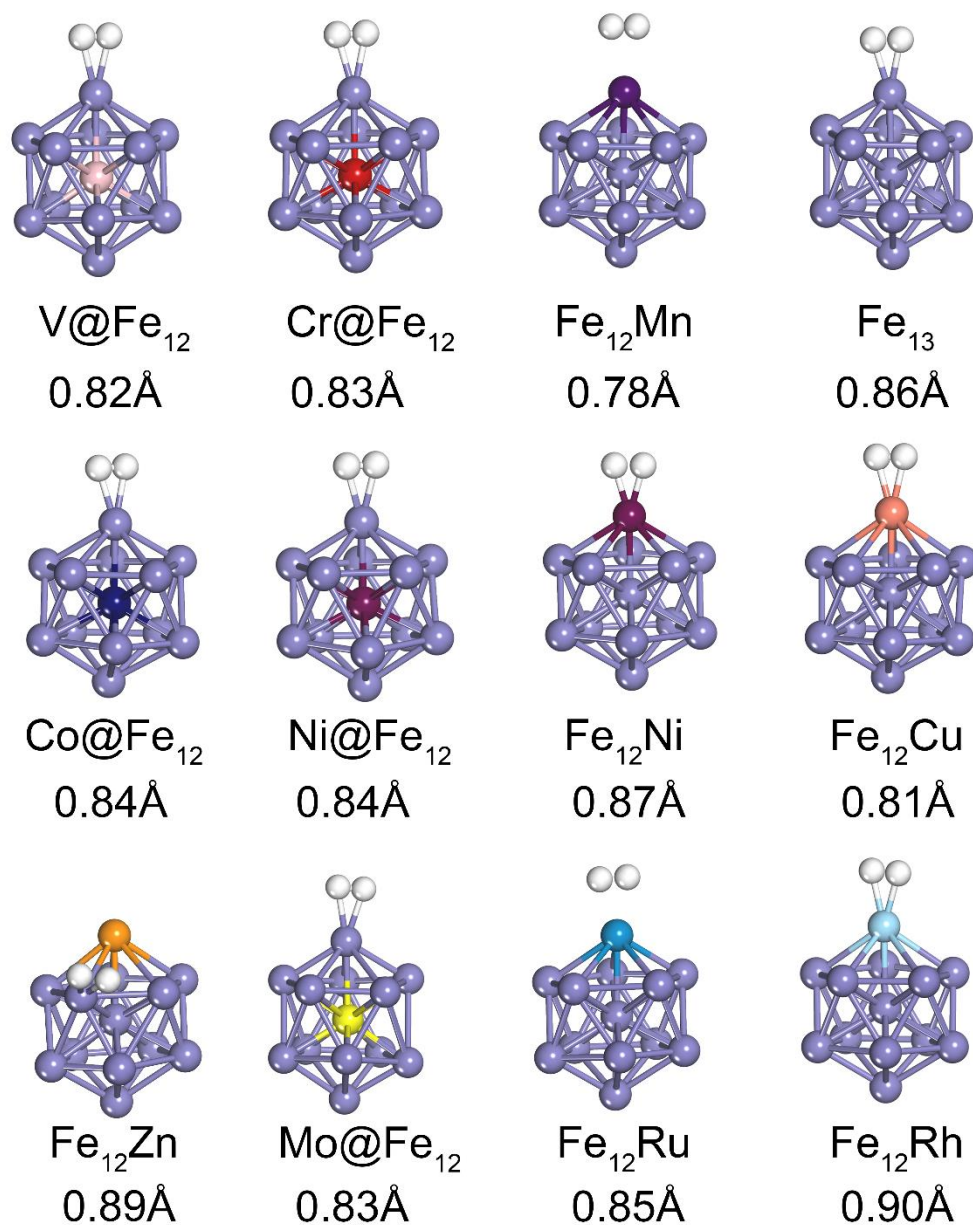


Fig. S8 The optimized geometrical structures and the bond length of the H₂ adsorbed on Fe₁₃ and 12 doped Fe₁₂X clusters.

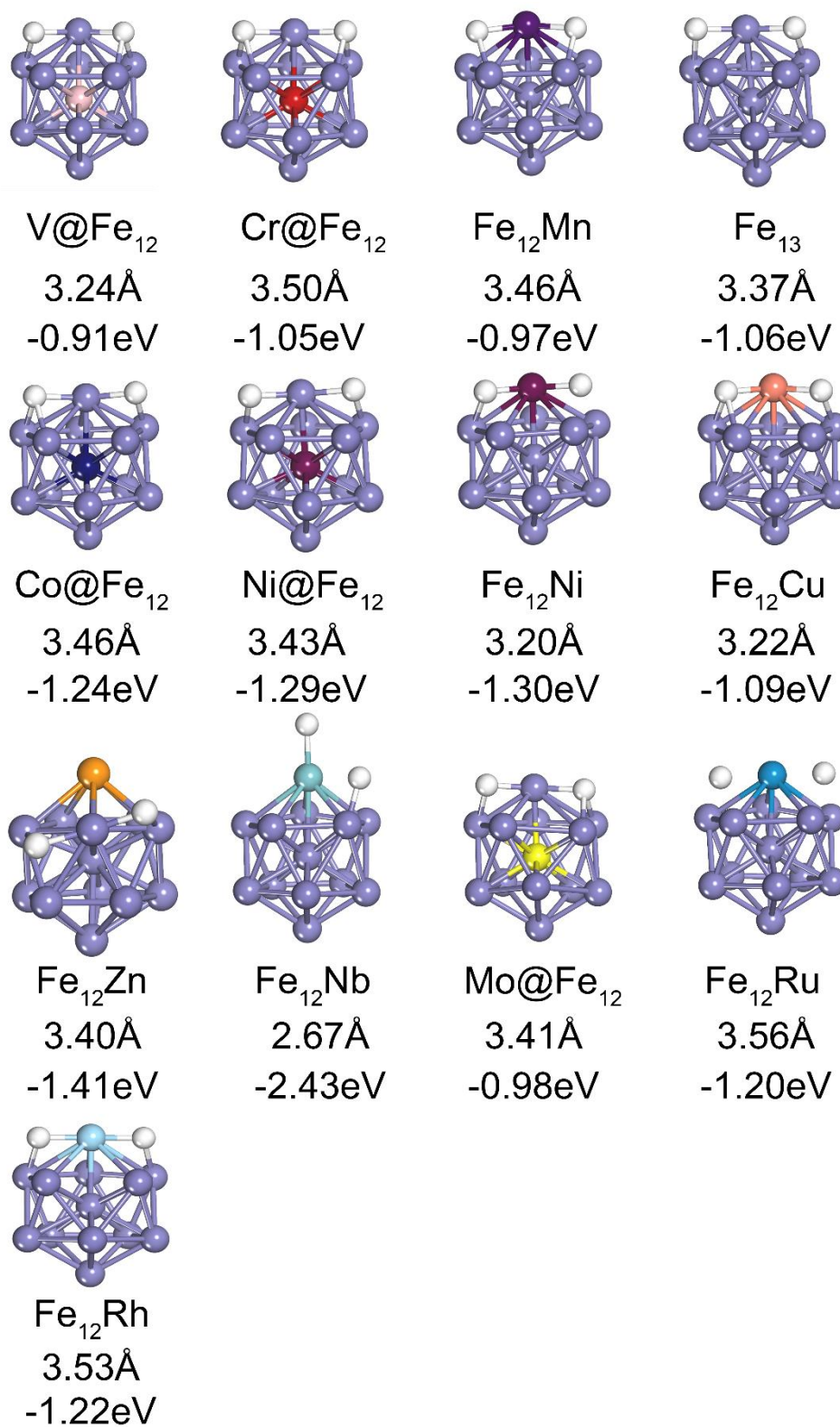


Fig. S9 The optimized geometrical structures and the bond length of the dissociative adsorbed 2H* on Fe₁₃ and 12 doped Fe₁₂X clusters.

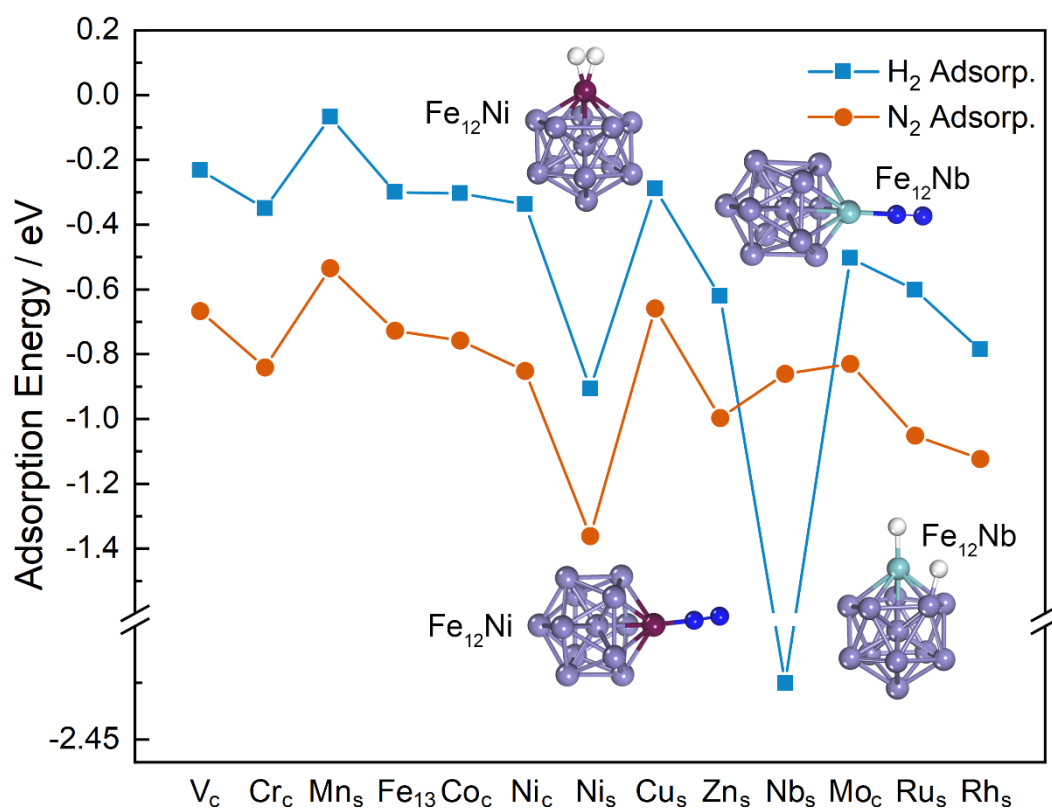


Fig. S10 The adsorption energy of N₂ and H₂ on doped Fe₁₃ clusters. Spontaneous H-H dissociation only occur on the Fe₁₂Nb cluster. The “c” and “s” represent the center- and shell- doped clusters, respectively.

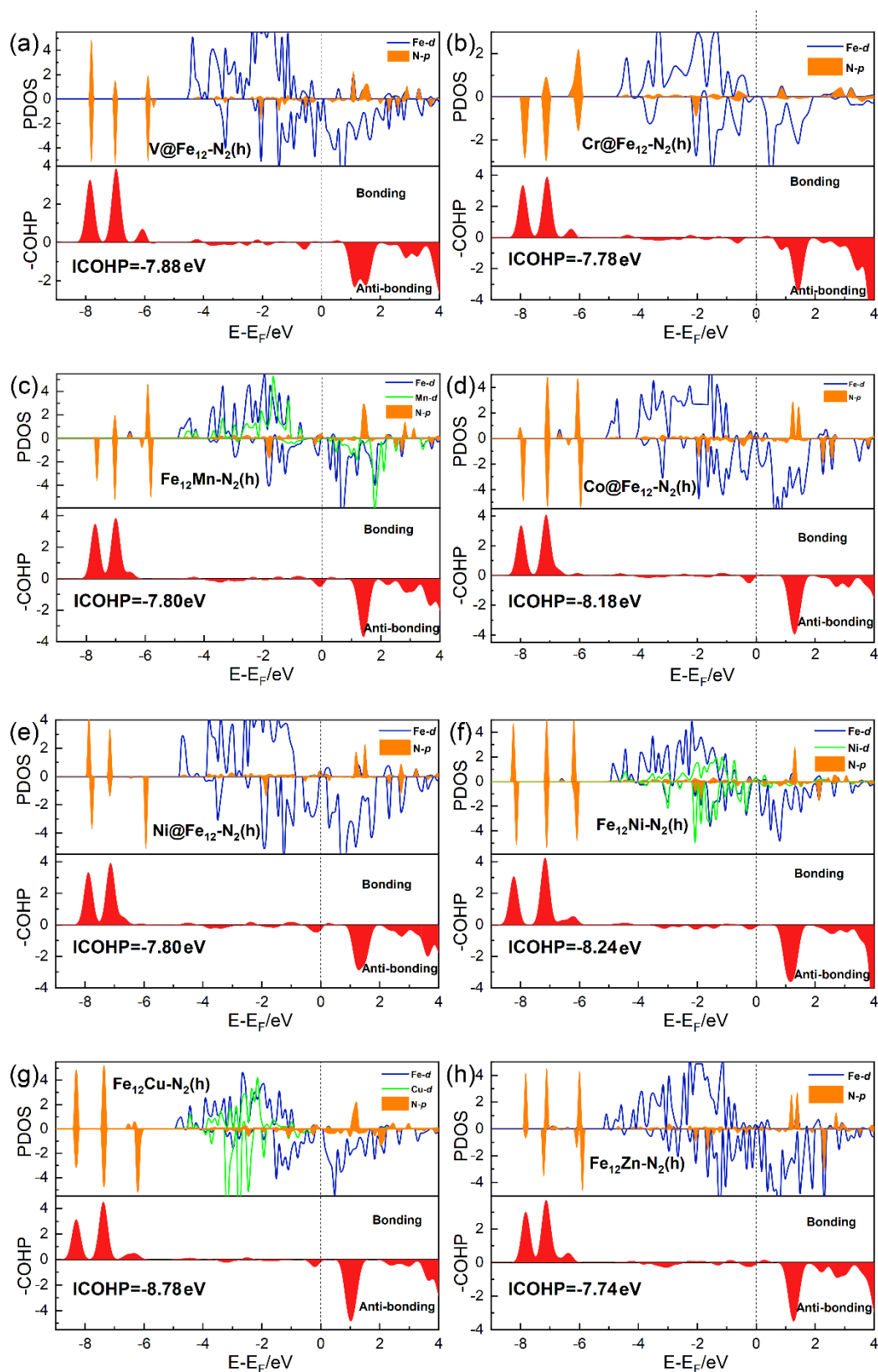


Fig. S11 Calculated crystal orbital Hamilton population (COHP) and partial density of states (PDOS) for N_2 adsorbed on the doped Fe_{13} clusters on hollow site.

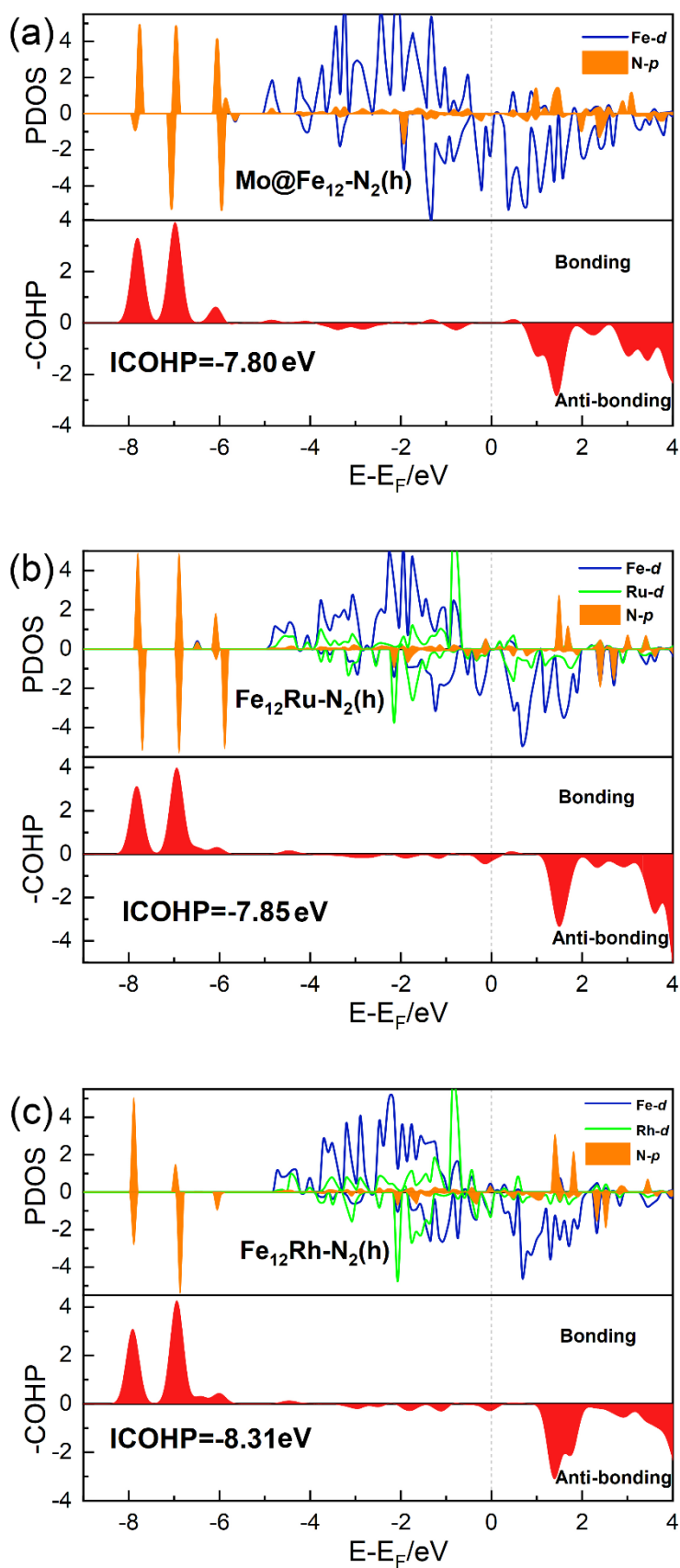


Fig. S12 Calculated crystal orbital Hamilton population (COHP) and partial density of states (PDOS) for N_2 adsorbed on the doped Mo@Fe_{12} (a), Fe_{12}Ru (b), and Fe_{12}Rh (c) clusters on the hollow site.

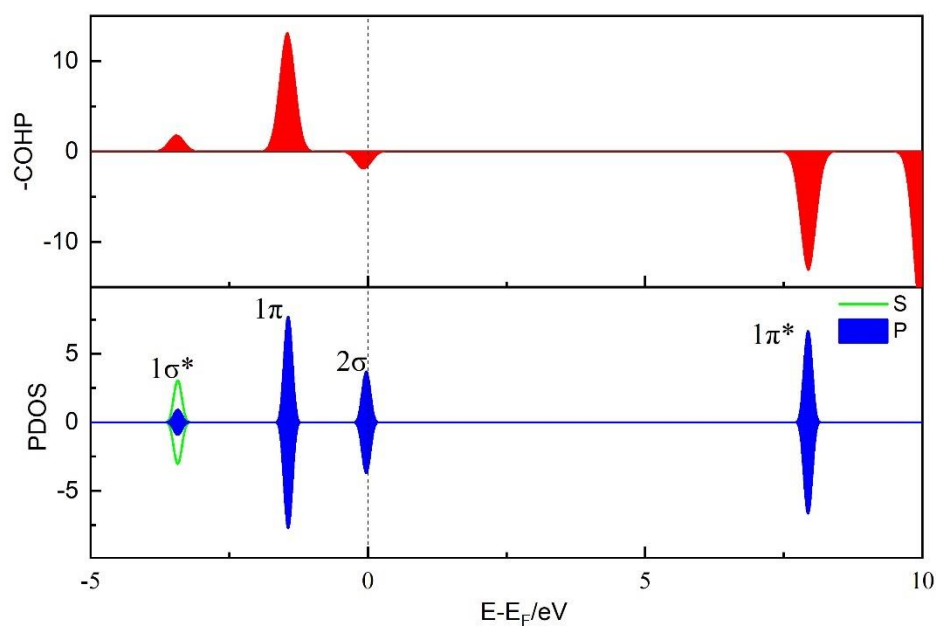


Fig. S13 Calculated crystal orbital Hamilton population (COHP) and partial density of states (PDOS) for N_2 .

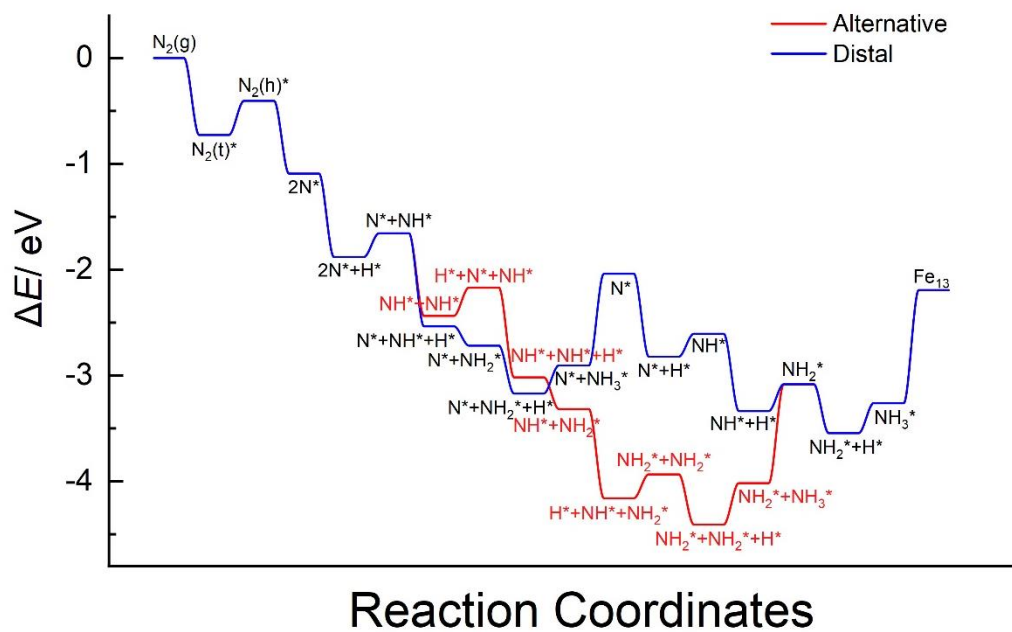


Fig. S14 Free energy changes (in eV) for N_2 activation and reduction to ammonia on Fe_{13} clusters.

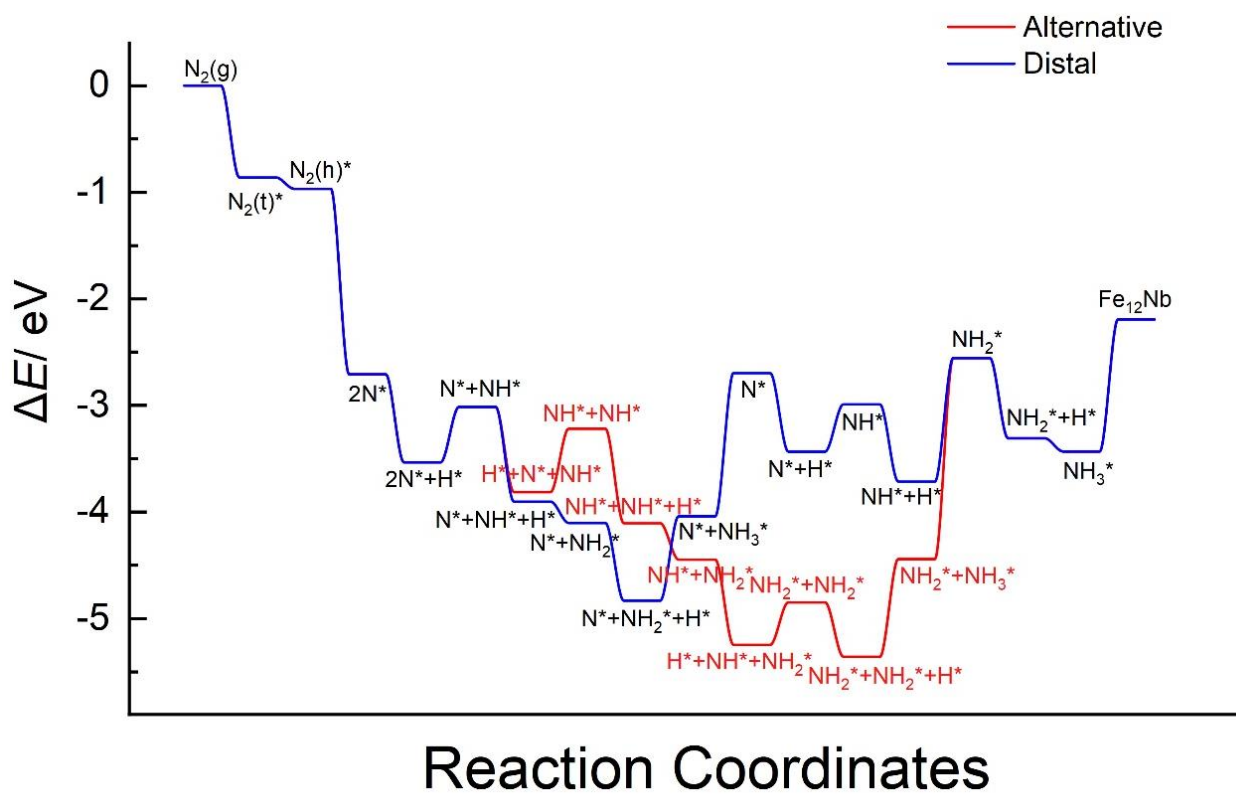


Fig. S15 Free energy changes (in eV) for N_2 activation and reduction to ammonia on $Fe_{12}Nb$ cluster.

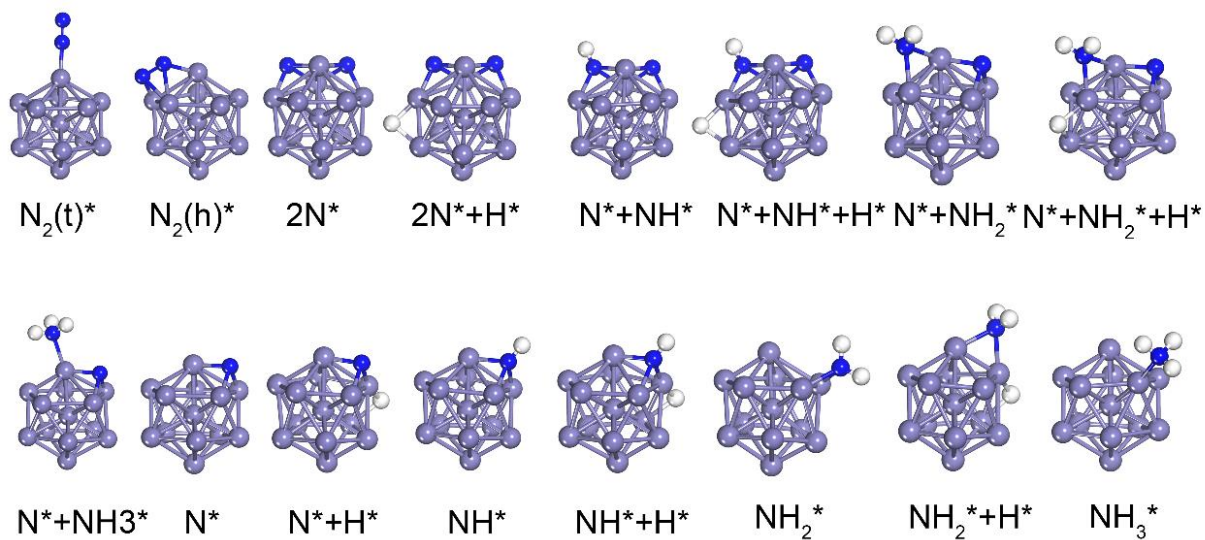


Fig. S16 The optimized structures of the intermediates in the hydrogenation process of N_2 on the Fe_{13} clusters.

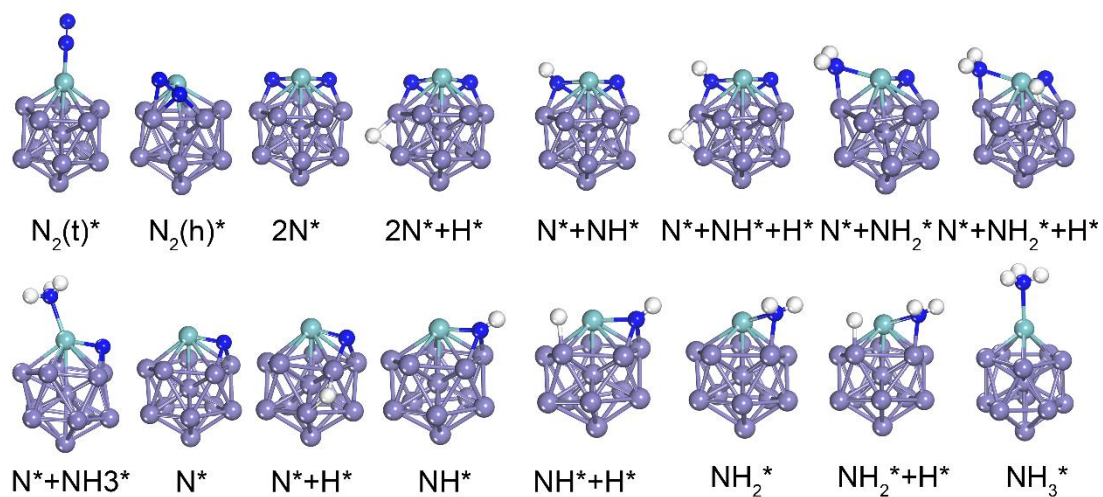


Fig. S17 The optimized structures of the intermediates in the hydrogenation process of N_2 on the $Fe_{12}Nb$ cluster

Table S6 The XYZ coordinates and vibration frequencies of the intermediates in the hydrogenation process of the Fe₁₃ cluster.

coordinates of N ₂ (t)*				vibration frequencies of N ₂ (t)*	
				mode	Frequency/cm ⁻¹
Fe	9.445400238	9.437000155	13.100199699	1	2117.95
Fe	11.446800232	7.907400131	12.430399656	2	323.94
Fe	12.747800350	9.005600214	10.640000105	3	312.73
Fe	11.624000072	11.228200197	10.266200304	4	280.51
Fe	9.584599733	11.497999430	11.715400219	5	46.20
Fe	11.682000160	10.254000425	12.690800428	6	36.20
Fe	11.262199879	9.339600205	8.614199758		
Fe	11.132600307	7.297000289	9.962400198		
Fe	9.117000103	7.547600269	11.464999914		
Fe	7.982000113	9.753400087	11.071799994		
Fe	9.286000133	10.883200169	9.288600087		
Fe	9.042800069	8.513799906	9.103999734		
Fe	10.382200480	9.406599998	10.880399942		
N	12.913000584	11.219600439	13.687599897		
N	13.652600050	11.807800531	14.323999882		

coordinates of N ₂ (h)*				vibration frequencies of N ₂ (h)*	
				mode	frequency/cm ⁻¹
Fe	9.544399977	9.553599954	13.127399683	1	1471.35
Fe	11.368399858	7.904199958	12.404199839	2	368.91
Fe	12.739399672	9.051200151	10.666799545	3	329.13
Fe	11.658600569	11.329799891	10.370800495	4	231.01
Fe	9.528399706	11.564600468	11.771800518	5	158.37
Fe	11.875599623	10.381200314	12.631200552	6	143.99
Fe	11.254999638	9.341999888	8.661599755		
Fe	11.093399525	7.274199724	9.962400198		
Fe	9.090800285	7.537400126	11.483199596		
Fe	8.007799983	9.743999839	11.081199646		
Fe	9.341599941	10.888799429	9.358199835		
Fe	9.006999731	8.409000039	9.161400199		
Fe	10.393600464	9.429000020	10.890200138		
N	10.720200539	11.114799976	13.952800035		
N	9.577800035	11.539200544	13.761399984		

coordinates of 2N*			
Fe	9.428799748	9.711400270	13.284800053
Fe	11.272200346	7.907599807	12.507400513
Fe	12.695399523	9.020799994	10.594400167
Fe	11.594799757	11.386400461	10.271600485
Fe	9.609799981	11.600199938	12.069599628
Fe	11.921800375	10.334399939	12.528200150
Fe	11.219799519	9.408400059	8.708400130
Fe	11.029200554	7.345200181	10.039999485
Fe	9.116200209	7.576000094	11.688200235
Fe	7.999200225	9.735400081	11.023600101
Fe	9.444800019	11.055599451	9.438199997
Fe	9.045400023	8.460000157	9.204800129
Fe	10.343199968	9.491000175	10.989400148
N	10.645999908	11.108599901	13.547199965
N	8.032000065	10.712800026	12.544000149

vibration frequencies of 2N*		
mode	frequency/cm ⁻¹	
1	598.78	
2	560.81	
3	558.30	
4	465.93	
5	321.37	
6	267.43	

coordinates of 2N*+H*			
Fe	9.253799915	9.747999907	13.299800158
Fe	11.165000200	7.983400226	12.676999569
Fe	12.753800154	9.216200113	10.954600573
Fe	11.505000591	11.489599943	10.381400585
Fe	9.443399906	11.625399590	12.075999975
Fe	11.800400019	10.450400114	12.714600563
Fe	11.451599598	9.507600069	8.917999864
Fe	11.245399714	7.444599867	10.261600018
Fe	9.098200202	7.597799897	11.685800552
Fe	7.980999947	9.699400067	10.954799652
Fe	9.425399899	11.032400131	9.441000223
Fe	9.280599952	8.444399834	9.214199781
Fe	10.326600075	9.548199773	11.083199978
N	10.403599739	11.181999445	13.607800007
N	7.858999968	10.686800480	12.457400560
H	13.424199820	10.018199682	12.344800234

vibration frequencies of 2N*+H*		
mode	frequency/cm ⁻¹	
1	1358.24	
2	1023.59	
3	598.82	
4	567.22	
5	547.16	
6	470.63	
7	390.47	
8	315.95	
9	263.99	

coordinates of N*+NH*			
Fe	9.497200251	9.689999819	13.285399675
Fe	11.339000463	7.843800187	12.381600142
Fe	12.790000439	8.993800282	10.564199686
Fe	11.655600071	11.289399862	10.162199736
Fe	9.678999782	11.604399681	12.051999569
Fe	12.107000351	10.288000107	12.482000589
Fe	11.246999502	9.410399795	8.721399903
Fe	11.059999466	7.351400256	10.050400496
Fe	9.027799964	7.714200020	11.731400490
Fe	7.978600264	9.818999767	11.148600578
Fe	9.340400100	11.052600145	9.575200081
Fe	9.062799811	8.506000042	9.285799861
Fe	10.407999754	9.498000145	11.010400057
N	10.800800323	11.111799479	13.568600416
N	8.132600188	10.776799917	12.655199766
H	10.834000111	11.666200161	14.433599710

vibration frequencies of N*+NH*		
mode	frequency/cm ⁻¹	
1	3374.58	
2	691.18	
3	605.38	
4	579.28	
5	520.31	
6	512.52	
7	443.44	
8	315.43	
9	252.67	

coordinates of N*+NH*+H*			
Fe	9.422799945	9.714999795	13.301399946
Fe	11.269999743	7.897800207	12.550400496
Fe	12.829799652	9.136400223	10.846199989
Fe	11.609599590	11.389199495	10.283199549
Fe	9.609400034	11.626199484	12.064199448
Fe	12.061200142	10.361200571	12.682399750
Fe	11.415799856	9.477400184	8.876000047
Fe	11.224000454	7.425199747	10.210000277
Fe	9.035199881	7.716799974	11.698399782
Fe	7.994599938	9.803599715	11.102399826
Fe	9.354799986	11.023399830	9.553200006
Fe	9.234799743	8.489400148	9.289799929
Fe	10.419000387	9.548199773	11.095199585
N	10.658199787	11.179399490	13.643399477
N	8.052600026	10.760600567	12.605600357
H	10.639599562	11.734399796	14.507800341
H	13.614799976	9.866999984	12.221000195

vibration frequencies of N*+NH*+H*		
mode	Frequency/cm ⁻¹	
1	3381.79	
2	1372.58	
3	1065.57	
4	722.08	
5	630.48	
6	582.85	
7	525.49	
8	516.94	
9	457.47	
10	389.73	
11	311.11	
12	255.61	

coordinates of N*+NH ₂ *			
Fe	9.538599849	10.008399487	13.180199862
Fe	11.424000263	8.166400194	12.401399612
Fe	12.648999691	9.320399761	10.501799583
Fe	11.641399860	11.390199661	10.052399635
Fe	9.557399750	11.720399857	11.242400408
Fe	11.629799604	10.654200315	12.507400513
Fe	11.212400198	9.235200286	8.583199978
Fe	10.994000435	7.383800149	10.121799707
Fe	9.154000282	7.740600109	11.907000542
Fe	7.993999720	9.669600129	11.120200157
Fe	9.343799949	10.642399788	8.963199854
Fe	8.903599977	8.318799734	9.329599738
Fe	10.320800543	9.549199939	10.831999779
N	10.985399485	10.681600571	14.398399591
N	8.248400092	11.008199453	12.318199873
H	10.774199963	11.588000059	14.827799797
H	11.413600445	10.093599558	15.116599798

vibration frequencies of N*+NH ₂ *	
mode	frequency/cm ⁻¹
1	3477.06
2	3383.62
3	1506.05
4	656.89
5	634.69
6	585.13
7	552.30
8	474.10
9	434.03
10	397.59
11	268.78
12	117.01

coordinates of N*+NH ₂ *+H*			
Fe	9.582800269	10.061399937	13.101400137
Fe	11.195199490	8.058999777	12.552000284
Fe	12.738399506	9.310399890	10.941400528
Fe	11.556600332	11.495200396	10.104199648
Fe	9.482200146	11.789599657	11.246800423
Fe	11.701400280	10.646400452	12.494599819
Fe	11.374599934	9.412199855	8.869000077
Fe	11.173800230	7.417600155	10.289399624
Fe	9.031199813	7.680799961	11.720999479
Fe	7.926399708	9.689000249	11.101800203
Fe	9.193199873	10.664600134	9.096000195
Fe	9.037799835	8.299199939	9.315999746
Fe	10.312800407	9.583600163	10.906000137
N	10.977400541	10.678800344	14.341399670
N	8.230999708	10.961199999	12.351200581
H	10.788799524	11.595000029	14.760600328
H	11.390600204	10.083999634	15.063199997
H	13.357000351	10.409599543	12.133799791

vibration frequencies of N*+NH ₂ *+H*	
mode	frequency/cm ⁻¹
1	3471.57
2	3383.00
3	1508.11
4	1341.78
5	971.48
6	679.75
7	640.73
8	605.74
9	555.93
10	492.84
11	455.29
12	404.89
13	294.42
14	286.26
15	127.18

coordinates of N*+NH ₃ *				vibration frequencies of N*+NH ₃ *	
				mode	frequency/cm ⁻¹
Fe	10.179599524	10.224000216	13.046000004	1	3497.95
Fe	11.723400354	8.445600271	12.451399565	2	3477.14
Fe	12.709800005	9.124799967	10.257200003	3	3368.66
Fe	11.534399986	11.371400356	9.460999966	4	1612.09
Fe	9.785000086	11.828399897	11.062799692	5	1600.81
Fe	12.197999954	10.920399427	11.699800491	6	1138.32
Fe	10.946400166	9.142000079	8.532599807	7	566.96
Fe	10.934400558	7.334399819	10.255000591	8	546.63
Fe	9.477400184	7.809600234	12.089400291	9	528.13
Fe	8.187199831	9.835199714	11.448199749	10	428.68
Fe	9.035000205	10.584000349	9.061400294	11	404.83
Fe	8.690000176	8.305199742	9.648200274	12	322.26
Fe	10.423599482	9.598199725	10.742199421	13	173.23
N	10.427600145	10.564399958	15.087800026	14	97.19
N	8.748599887	11.240999699	12.452800274	15	71.04
H	9.928399920	11.426199675	12.452800274		
H	10.034400225	9.798200130	15.642800331		
H	11.409800053	10.673400164	15.351799726		

coordinates of N*				vibration frequencies of N*	
				mode	frequency/cm ⁻¹
Fe	8.883951902	9.493344426	12.992488146	1	551.55
Fe	10.975458622	8.023671508	12.699639797	2	422.52
Fe	12.517566681	9.305171967	11.033648252	3	421.05
Fe	11.524119377	11.488271952	10.494816303		
Fe	9.362909198	11.586617231	11.559101343		
Fe	11.170228720	10.408957005	12.884196043		
Fe	11.377856731	9.473564029	8.776189089		
Fe	11.061980724	7.393581271	10.239032507		
Fe	8.912265301	7.533326745	11.539425850		
Fe	7.883105278	9.678127170	10.606583357		
Fe	9.600555897	10.941621065	9.078139067		
Fe	9.162754416	8.346246481	9.032797217		
Fe	10.218933821	9.464575648	10.891965628		
N	7.838714719	10.721124411	12.127978802		

coordinates of N*+H*			
Fe	8.867582679	9.483841062	12.981339693
Fe	10.995278358	8.018876314	12.710368633
Fe	12.516636848	9.283627272	10.994004011
Fe	11.501379013	11.489264965	10.470263958
Fe	9.320968390	11.577817202	11.534439325
Fe	11.143054962	10.404955149	12.860267162
Fe	11.366342306	9.443842173	8.776047826
Fe	11.052668095	7.368297577	10.266435146
Fe	8.958460689	7.501072288	11.577647924
Fe	7.853902578	9.639650583	10.578548908
Fe	9.611541033	10.968468189	9.079589844
Fe	9.128675461	8.394522667	9.076851010
Fe	10.221339464	9.465783834	10.904607773
N	7.830459476	10.686349869	12.108702660
H	7.408710718	8.713829517	9.207885265

vibration frequencies of N*+H*	
mode	frequency/cm ⁻¹
1	1372.12
2	987.47
3	558.24
4	443.17
5	436.83
6	383.99

coordinates of NH*			
Fe	8.959159255	9.500040412	12.963589430
Fe	10.891878605	7.955712080	12.696161270
Fe	12.507256269	9.374983311	11.076374054
Fe	11.522843838	11.536514759	10.484091043
Fe	9.431023598	11.601454020	11.563721895
Fe	11.256850958	10.364642143	12.880176306
Fe	11.284395456	9.491377473	8.797242641
Fe	11.091222763	7.402653694	10.308684111
Fe	8.867951632	7.525375485	11.525696516
Fe	7.895464301	9.702229500	10.584105253
Fe	9.539610744	10.985950232	9.105061293
Fe	9.137341976	8.289664388	9.086499810
Fe	10.224574804	9.477054477	10.879768133
N	7.779198289	10.800206661	12.188042402
H	6.947228312	11.219340563	12.617787123

vibration frequencies of NH*	
mode	frequency/cm ⁻¹
1	3390.54
2	604.77
3	594.50
4	511.54
5	358.14
6	349.04

coordinates of NH*+H*			
Fe	8.893275857	9.493945241	12.983776331
Fe	10.871052742	7.965846062	12.692999840
Fe	12.482513189	9.257346392	11.012219191
Fe	11.493841410	11.489657164	10.445728302
Fe	9.405645728	11.592346430	11.567865610
Fe	11.276965141	10.330659151	12.795858383
Fe	11.246292591	9.543910027	8.799687028
Fe	11.021420956	7.469006181	10.210558176
Fe	8.825486898	7.539463639	11.622281075
Fe	7.700529099	9.766212702	10.673600435
Fe	9.440829754	10.954213142	9.113652110
Fe	8.928439617	8.427580595	9.222398400
Fe	10.136648417	9.478963614	10.907881260
N	7.765713930	10.859959126	12.268095016
N	6.990436912	11.334537268	12.742757797
H	7.235307097	8.817555904	9.349241257

vibration frequencies of NH*+H*	
mode	frequency/cm ⁻¹
1	3396.90
2	1370.45
3	1045.42
4	624.65
5	603.31
6	522.06
7	380.56
8	377.89
9	353.84

coordinates of NH ₂ *			
Fe	9.467595816	8.862472177	13.266227245
Fe	11.444648504	7.790904045	12.527576685
Fe	12.577359676	9.367957711	10.720386505
Fe	11.350013018	11.493519545	10.581122637
Fe	9.298404455	11.250305176	12.038514614
Fe	11.459547281	10.252799988	12.843199968
Fe	11.207256317	9.608536363	8.737902045
Fe	11.143994331	7.373841405	10.164241791
Fe	9.106336236	7.306014895	11.476120949
Fe	7.954739332	9.568678141	11.224377155
Fe	9.361775517	10.968519449	9.402454495
Fe	9.069297910	8.511876464	9.194720387
Fe	10.283286572	9.367067814	11.011519432
N	7.296164036	11.209589243	12.179108858
H	6.747236252	11.910940409	11.677796841
H	6.872744560	11.079779863	13.100131750

vibration frequencies of NH ₂ *	
mode	frequency/cm ⁻¹
1	3489.17
2	3408.94
3	1499.75
4	638.97
5	634.55
6	581.42
7	466.76
8	260.20
9	123.20

coordinates of NH_2^+H^*			
Fe	9.431402683	8.908807635	13.308377266
Fe	11.227995157	7.639645934	12.425271273
Fe	12.516351938	9.269205332	10.728998184
Fe	11.268136501	11.487368345	10.569522381
Fe	9.280327559	11.307063103	12.095012665
Fe	11.351758242	10.257341862	12.835069895
Fe	11.214764118	9.667525887	8.767437935
Fe	11.116334200	7.361742258	10.025950670
Fe	9.028897285	7.312579155	11.473678350
Fe	7.900882363	9.608931541	11.354677677
Fe	9.270977378	10.951790810	9.478949904
Fe	9.183286428	8.423504829	9.159139395
Fe	10.217567682	9.364153147	11.020290852
N	7.298096418	11.335929632	12.195280790
H	6.799780130	12.027295828	11.632009745
H	6.817537546	11.256266832	13.093085289
H	7.449503541	7.939249277	11.614650488

vibration frequencies of NH_2^+H^*	
mode	frequency/ cm^{-1}
1	3495.02
2	3411.80
3	1498.99
4	1225.41
5	1066.22
6	636.52
7	618.05
8	582.04
9	474.53
10	277.74
11	247.48
12	121.21

coordinates of NH_3^*			
Fe	9.294599295	8.616870046	13.055422306
Fe	11.532495022	7.793658972	12.519056797
Fe	12.705136538	9.499657154	10.922899246
Fe	11.033425331	11.444514990	10.510270596
Fe	8.860939741	10.814912319	11.835088730
Fe	11.304346323	10.225878954	12.738770247
Fe	11.423574686	9.740790129	8.877392411
Fe	11.547775269	7.438331246	10.148500204
Fe	9.378836751	6.994059682	11.317435503
Fe	7.863116264	8.835045695	10.878624916
Fe	9.041126370	10.635108948	9.368857145
Fe	9.364994168	8.291198015	9.011152387
Fe	10.279120207	9.205195308	10.938495398
N	7.351849079	12.038996220	12.593710423
H	6.718234420	12.273702621	11.826556921
H	6.818779111	11.512382030	13.288694620
H	7.669650912	12.910298109	13.024473190

vibration frequencies of NH_3^*	
mode	frequency/ cm^{-1}
1	3509.88
2	3505.88
3	3394.55
4	1603.92
5	1594.12
6	1129.23
7	512.24
8	491.49
9	325.52
10	78.38
11	65.39
12	41.78

Table S7 The XYZ coordinates and vibration frequencies of the intermediates in the hydrogenation process of the Fe₁₂Nb cluster.

coordinates of N ₂ (t)*				vibration frequencies of N ₂ (t)*	
Fe	9.106600285	9.018999934	12.984600067	mode	frequency/cm ⁻¹
Fe	10.926799774	7.505000234	12.410999537	1	2094.96
Fe	12.634600401	8.961200118	11.144200563	2	310.45
Fe	11.839200258	11.208000183	10.640200377	3	264.30
Fe	9.848200083	11.302200556	12.036600113	4	254.77
Fe	11.432199478	9.542800188	8.841800094	5	52.63
Fe	10.846400261	7.301800251	9.827600121	6	35.49
Fe	8.790400028	7.381200194	11.173800230		
Fe	8.000800014	9.671000242	10.759400129		
Fe	9.646400213	10.987000465	9.395200014		
Fe	9.068199992	8.602399826	8.936399817		
Fe	10.323799849	9.292799830	10.950200558		
Nb	11.655800343	10.040800571	13.095999956		
N	13.121399879	11.377199888	13.935799599		
N	13.885200024	12.029000521	14.474799633		

coordinates of N ₂ (h)*				vibration frequencies of N ₂ (h)*	
Fe	9.470199943	9.557600021	13.119200468	mode	frequency/cm ⁻¹
Fe	11.382800341	7.902799845	12.344599962	1	1240.45
Fe	12.718600035	9.211999774	10.509400368	2	436.08
Fe	11.607799530	11.394399405	10.448399782	3	412.73
Fe	9.604799747	11.522599459	11.743600368	4	277.31
Fe	11.308399439	9.350200295	8.543000221	5	226.12
Fe	11.010799408	7.324799895	9.822199941	6	194.42
Fe	9.091399908	7.546600103	11.545399427		
Fe	8.085200191	9.691799879	11.046400070		
Fe	9.420999885	10.683599710	9.197999835		
Fe	9.016000032	8.275399804	9.142000079		
Fe	10.404599905	9.415400028	10.832200050		
Nb	11.817799807	10.240999460	12.869000435		
N	12.999999523	8.608599901	13.455200195		
N	13.305200338	8.616600037	12.202199697		

coordinates of 2N*			
Fe	9.272000194	9.301000237	13.028800488
Fe	11.479799747	7.878599763	12.553800344
Fe	12.712399960	8.992800117	10.472199917
Fe	11.668399572	11.314599514	10.342400074
Fe	9.752799869	11.492600441	11.697599888
Fe	11.206200123	9.495999813	8.618400097
Fe	10.962200165	7.258200049	10.017199516
Fe	9.124400020	7.401800156	11.475600004
Fe	7.981399894	9.612399936	10.963399410
Fe	9.334400296	10.859600306	9.341199994
Fe	9.038599730	8.459200263	9.118800163
Fe	10.405199528	9.366800189	10.930399895
Nb	11.967999935	10.235600471	12.928800583
N	10.818599463	9.058399796	13.972400427
N	13.149800301	8.852199912	12.245800495

vibration frequencies of 2N*	
mode	frequency/cm ⁻¹
1	626.33
2	583.05
3	531.38
4	466.46
5	317.36
6	309.17

coordinates of 2N*+H*			
Fe	9.295799732	9.289399981	13.033000231
Fe	11.479400396	7.886000276	12.566200495
Fe	12.717200518	8.963999748	10.453000069
Fe	11.549600363	11.347199678	10.379600525
Fe	9.677799940	11.453000307	11.797800064
Fe	11.283600330	9.355000257	8.657600284
Fe	10.911400318	7.189999819	10.058200359
Fe	9.072999954	7.425400019	11.490399837
Fe	8.018199801	9.716799855	10.911200047
Fe	9.445199966	10.841200352	9.286000133
Fe	9.062799811	8.441799879	9.110800028
Fe	10.406800508	9.338600039	10.949200392
Nb	11.995600462	10.246399641	12.919199467
N	10.842800140	9.085599780	13.976000547
N	13.143399954	8.837400079	12.237800360
H	12.989000082	8.994399905	8.759400249

vibration frequencies of 2N*+H*	
mode	frequency/cm ⁻¹
1	1359.56
2	1011.72
3	627.19
4	587.42
5	526.50
6	469.86
7	392.27
8	333.97
9	311.85

coordinates of N*+NH*			
Fe	9.259799719	9.297000170	13.033599854
Fe	11.455999613	7.888799906	12.561000586
Fe	12.731000185	9.126799703	10.426199436
Fe	11.569399834	11.388599873	10.288000107
Fe	9.754800200	11.472799778	11.764400005
Fe	11.216200590	9.496200085	8.594400287
Fe	10.950399637	7.271800041	10.026600361
Fe	9.122599959	7.387999892	11.534399986
Fe	8.021000028	9.588000178	10.923199654
Fe	9.362999797	10.853799582	9.304800034
Fe	9.082000256	8.400200009	9.092800021
Fe	10.423599482	9.367600083	10.927000046
Nb	11.905000210	10.255800486	12.993400097
N	10.795799494	9.165199995	14.052799940
N	13.235800266	8.850600123	12.254199982
H	14.124799967	8.456599712	12.575999498

vibration frequencies of N*+NH*	
mode	frequency/cm ⁻¹
1	3428.28
2	675.40
3	561.11
4	536.73
5	520.21
6	470.48
7	431.88
8	281.94
9	241.20

coordinates of N*+NH*+H*			
Fe	9.257400036	9.243599772	13.027600050
Fe	11.482199430	7.908200026	12.538399696
Fe	12.803200483	9.248200059	10.473400354
Fe	11.497600079	11.483600140	10.439000130
Fe	9.656999707	11.440199614	11.879800558
Fe	11.329400539	9.564800262	8.703399897
Fe	10.983999968	7.326400280	9.997599721
Fe	9.135800004	7.393400073	11.466000080
Fe	8.035200238	9.613000154	10.866600275
Fe	9.418600202	10.914000273	9.322800040
Fe	9.138799906	8.467400074	9.045199752
Fe	10.424400568	9.390400052	10.963000059
Nb	11.878600121	10.268399715	13.046200275
N	10.776000023	9.128999710	14.062999487
N	13.244600296	8.901600242	12.301800251
H	14.151599407	8.532599807	12.602800131
H	13.071199656	9.434999824	8.810799718

vibration frequencies of N*+NH*+H*	
mode	frequency/cm ⁻¹
1	3422.58
2	1375.75
3	1044.09
4	674.82
5	588.96
6	566.46
7	530.65
8	481.32
9	444.76
10	387.75
11	287.79
12	242.71

coordinates of N*+NH ₂ *			
Fe	9.119600058	9.276199937	12.960799932
Fe	10.856599808	7.430800200	12.465200424
Fe	12.620799541	8.732200265	10.912400484
Fe	11.573599577	11.303199530	10.325599909
Fe	9.800999761	11.460800171	11.825599670
Fe	11.367000341	9.358999729	8.896399736
Fe	10.757199526	7.092000246	10.099600554
Fe	8.667600155	7.451000214	11.329599619
Fe	7.967000008	9.827799797	10.837999582
Fe	9.403799772	10.990400314	9.333599806
Fe	8.990600109	8.519200087	9.056599736
Fe	10.298800468	9.283400178	10.913000107
Nb	11.853799820	9.988999963	12.833600044
N	10.743399858	8.799200058	13.825399876
N	13.904999495	9.408599734	12.335200310
H	14.383399487	8.679199815	12.869000435
H	14.613800049	10.073599815	12.014600039

vibration frequencies of N*+NH ₂ *	
mode	frequency/cm ⁻¹
1	3480.78
2	3393.30
3	1498.61
4	661.76
5	646.00
6	629.91
7	553.12
8	472.35
9	445.35
10	363.74
11	258.95
12	124.40

coordinates of N*+NH ₂ *+H*			
Fe	9.135199785	9.214000106	13.003000021
Fe	10.874999762	7.387400270	12.457200289
Fe	12.632800341	8.719999790	10.867400169
Fe	11.689200401	11.231000423	10.236799717
Fe	9.954599738	11.446000338	11.853200197
Fe	11.397000551	9.320999980	8.876600266
Fe	10.722600222	7.111399770	10.089999437
Fe	8.660200238	7.440199852	11.355199814
Fe	7.997400165	9.810799956	10.929800272
Fe	9.462000132	11.049200296	9.419199824
Fe	9.024000168	8.630399704	9.058600068
Fe	10.305999517	9.277999997	10.932799578
Nb	11.825200319	9.987800121	12.848999500
N	10.788600445	8.714200258	13.831599951
N	13.875999451	9.375200272	12.319200039
H	14.349000454	8.651800156	12.865600586
H	14.587399960	10.045000315	12.017799616
H	11.292200089	11.928199530	12.825000286

vibration frequencies of N*+NH ₂ *+H*	
mode	frequency/cm ⁻¹
1	3486.47
2	3408.02
3	1499.97
4	1258.32
5	977.18
6	655.07
7	637.02
8	620.79
9	549.70
10	467.10
11	445.16
12	374.08
13	291.38
14	269.95
15	129.22

coordinates of N*+NH ₃ *				vibration frequencies of N*+NH ₃ *	
				mode	frequency/cm ⁻¹
Fe	9.344599843	9.108200073	12.970399857		
Fe	10.657999516	7.160000205	12.022999525	1	3488.03
Fe	12.4444000244	8.120200038	10.606000423	2	3474.52
Fe	12.082999945	10.693800449	10.350799561	3	3347.27
Fe	10.424599648	11.182600260	11.983599663	4	1605.34
Fe	11.221400499	9.132199883	8.750600219	5	1592.50
Fe	10.007599592	7.105600238	9.643399715	6	1156.26
Fe	8.252599835	7.688599825	11.215000153	7	627.04
Fe	8.024799824	10.056200027	11.118999720	8	531.27
Fe	9.645000100	10.986800194	9.548199773	9	492.03
Fe	8.621399999	8.902000189	8.968600035	10	447.19
Fe	10.233999491	9.136999846	10.812000036	11	346.03
Nb	12.118599415	9.384800196	12.746599913	12	306.74
N	10.901999474	8.199399710	13.613799810	13	108.46
N	14.094599485	9.989399910	13.857400417	14	90.43
H	14.011600018	10.093400478	14.872800112	15	77.51
H	14.423999786	10.880800486	13.475400209		
H	14.819600582	9.289199710	13.668400049		

coordinates of N*				vibration frequencies of N*	
				mode	frequency/cm ⁻¹
Fe	9.123573303	9.255424142	12.940183878		
Fe	10.994704962	7.497907281	12.433040142	1	647.45
Fe	12.598683834	8.788430095	11.039832830	2	444.08
Fe	11.752158403	11.112947464	10.382813215	3	350.28
Fe	9.869294763	11.462435722	11.827684641		
Fe	11.223485470	9.280700088	8.801620007		
Fe	10.699266195	7.169074416	9.970920682		
Fe	8.750247955	7.421844006	11.334332228		
Fe	7.942582369	9.826657772	10.787469149		
Fe	9.449664354	10.976359844	9.341092110		
Fe	8.866564035	8.542551994	9.017424583		
Fe	10.267300606	9.300315380	10.910230875		
Nb	11.747410297	10.107227564	12.978867292		
N	10.735862255	8.772324324	13.849889040		

coordinates of N*+H*			
Fe	9.061356783	9.325945377	12.960546017
Fe	10.928395987	7.519773841	12.434356213
Fe	12.580851316	8.794631958	11.003925800
Fe	11.770005226	11.096553802	10.348204374
Fe	9.906556010	11.505206823	11.821926832
Fe	11.198618412	9.249027967	8.727405667
Fe	10.742529631	7.127140760	10.002620220
Fe	8.722850084	7.444027066	11.269490719
Fe	7.969108820	9.878202677	10.923817158
Fe	9.500408769	10.994323492	9.337816834
Fe	8.872749805	8.555616736	9.050551653
Fe	10.292743444	9.306116700	10.895819664
Nb	11.728216410	10.131393671	13.014423847
N	10.680223703	8.811022639	13.835422993
H	7.444785833	9.726216197	12.609071732

vibration frequencies of N*+H*	
mode	frequency/cm ⁻¹
1	1356.19
2	1006.41
3	667.30
4	453.05
5	377.64
6	376.12

coordinates of NH*			
Fe	9.245861769	9.242060781	12.932239771
Fe	11.068385839	7.608649135	12.533183098
Fe	12.604818344	8.935765028	10.875577927
Fe	11.761579514	11.191977262	10.272827148
Fe	9.924893975	11.497417688	11.747570038
Fe	11.107872725	9.282854199	8.709074855
Fe	10.728569031	7.119160891	10.127049685
Fe	8.780659437	7.433433533	11.380248070
Fe	7.987869382	9.886517525	10.791500807
Fe	9.482458234	11.021749973	9.266176820
Fe	8.848847151	8.496105075	9.078570008
Fe	10.284793377	9.314289689	10.854771137
Nb	11.701678038	10.054486990	12.879936695
N	10.783138275	8.762173653	14.154298306
H	10.712575912	8.405358791	15.110974312

vibration frequencies of NH*	
mode	frequency/cm ⁻¹
1	3417.62
2	627.77
3	601.36
4	561.14
5	319.70
6	243.09

coordinates of NH ⁺ +H [*]			
Fe	9.238486290	9.149045944	12.985500097
Fe	11.035743952	7.503500581	12.517753839
Fe	12.575353384	8.854646087	11.002073288
Fe	11.809459925	11.082930565	10.172861814
Fe	9.969788194	11.546943188	11.713385582
Fe	11.072579622	9.213812351	8.702954054
Fe	10.831747055	7.152751684	10.123442411
Fe	8.797490001	7.456246614	11.322388649
Fe	8.051391244	10.043859482	10.849748850
Fe	9.531773925	11.041611433	9.234969616
Fe	8.815076947	8.547835350	9.156530499
Fe	10.292702913	9.358739853	10.902602673
Nb	11.540249586	10.168048143	12.941319942
N	10.802911520	8.676397800	14.126137495
H	10.857796669	8.290659189	15.072653294
H	11.086251736	12.122972012	12.885679007

vibration frequencies of NH ⁺ +H [*]	
mode	frequency/cm ⁻¹
1	3422.24
2	1330.79
3	954.17
4	609.89
5	587.06
6	553.11
7	362.42
8	335.36
9	273.22

coordinates of NH ₂ [*]			
Fe	9.551665187	9.003503323	13.071614504
Fe	11.124153137	7.368865013	12.015364170
Fe	12.613296509	8.932862878	10.768542290
Fe	11.811347008	11.200211048	10.352402925
Fe	9.993079901	11.453042030	11.860209703
Fe	11.148903370	9.375971556	8.686563373
Fe	10.648587942	7.203805447	9.637064934
Fe	8.772684932	7.362595797	11.308708191
Fe	8.046067357	9.712932706	11.014623642
Fe	9.493125677	10.971814394	9.446669221
Fe	8.757144213	8.515036106	9.086564779
Fe	10.304964781	9.254595637	10.863461494
Nb	11.662863493	10.040501356	12.890108824
N	10.671701431	9.384911656	14.734247923
H	10.283796787	10.054339170	15.403892994
H	10.964021683	8.556212783	15.256962776

vibration frequencies of NH ₂ [*]	
mode	frequency/cm ⁻¹
1	3482.01
2	3390.85
3	1494.48
4	657.54
5	638.81
6	543.10
7	469.72
8	248.47
9	113.90

coordinates of NH ₂ *+H*			
Fe	9.578164816	8.836210966	13.086920977
Fe	11.330283880	7.389655113	12.065423727
Fe	12.682286501	8.906319141	10.831816196
Fe	11.821331978	11.074632406	10.238819122
Fe	10.020973682	11.392295361	11.828036308
Fe	11.018441916	9.384017587	8.636022806
Fe	10.691593885	7.247210741	9.796764255
Fe	8.803550601	7.424831986	11.284629107
Fe	8.059363961	9.866502285	11.061837673
Fe	9.438200593	11.009110212	9.341509938
Fe	8.679898381	8.642922044	9.147880673
Fe	10.311571360	9.296345711	10.885620117
Nb	11.613838673	10.051723719	12.933734655
N	10.638265610	9.289044738	14.752627611
H	10.200583935	9.931604862	15.417033434
H	10.998055935	8.491309881	15.280154943
H	10.915596485	11.954263449	13.151770830

vibration frequencies of NH ₂ *+H*	
mode	frequency/cm ⁻¹
1	3490.06
2	3400.75
3	1498.76
4	1389.36
5	873.71
6	658.52
7	645.84
8	564.61
9	473.46
10	380.28
11	257.20
12	121.12

coordinates of NH ₃ *			
Fe	9.358091950	9.339267015	13.032523394
Fe	11.040483713	7.735847831	12.489039898
Fe	12.6017111750	9.020767808	10.931316614
Fe	11.755794287	11.195081472	10.202869177
Fe	9.921783805	11.517606974	11.672681570
Fe	11.111449003	9.258187413	8.642084002
Fe	10.660030842	7.177462578	10.015711784
Fe	8.761427999	7.522280812	11.470807791
Fe	7.983268499	9.779170156	10.815607309
Fe	9.478109479	10.893348455	9.193776846
Fe	8.814994097	8.418127894	9.074957967
Fe	10.290806293	9.330106378	10.837945938
Nb	11.791733503	10.294380188	12.777251005
N	13.206602335	11.154515743	14.440684319
H	12.913050652	12.080441713	14.764541388
H	14.158877134	11.237419844	14.071905613
H	13.244184256	10.535788536	15.256494284

vibration frequencies of NH ₃ *	
mode	frequency/cm ⁻¹
1	3487.57
2	3482.17
3	3357.21
4	1601.34
5	1595.37
6	1148.56
7	491.38
8	479.44
9	300.39
10	89.90
11	78.74
12	48.89

coordinates of N ₂ (t)*			
Fe	9.445400238	9.437000155	13.100199699
Fe	11.446800232	7.907400131	12.430399656
Fe	12.747800350	9.005600214	10.640000105
Fe	11.624000072	11.228200197	10.266200304
Fe	9.584599733	11.497999430	11.715400219
Fe	11.682000160	10.254000425	12.690800428
Fe	11.262199879	9.339600205	8.614199758
Fe	11.132600307	7.297000289	9.962400198
Fe	9.117000103	7.547600269	11.464999914
Fe	7.982000113	9.753400087	11.071799994
Fe	9.286000133	10.883200169	9.288600087
Fe	9.042800069	8.513799906	9.103999734
Fe	10.382200480	9.406599998	10.880399942
N	12.913000584	11.219600439	13.687599897
N	13.652600050	11.807800531	14.323999882

vibration frequencies of N ₂ (t)*	
mode	frequency/cm ⁻¹
1	2117.95
2	323.94
3	312.73
4	280.51
5	46.20
6	36.20
