

**The photochemical route to octahedral iron(V).
Primary processes and quantum yields from ultrafast mid-infrared spectroscopy**

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Experimental

The experiments were performed with a laser system based on a 1 kHz Ti:sapphire oscillator/regenerative amplifier producing 150 fs pulses at 800 nm with pulse energies of 0.7 mJ. The excitation wavelength of 267 nm was produced by third harmonic generation of a small portion of the 800 nm regenerative amplifier (RGA) output. Pump pulses at 300 and 450 nm were produced by fourth harmonic generation of the signal and idler output from an optical parametric amplifier (OPA) pumped by 50% of the RGA energy. Pump pulse energies entering the sample were 1-2 μ J. Tunable mid-infrared (MIR) probe pulses were generated by difference frequency mixing of signal and idler pulses from a second OPA pumped by the other half of the RGA output power. The MIR pulses were split into a probe and a reference beam. The latter was superimposed on the pump beam and both were focused into the sample cell. The relative plane of polarization was set to 54.7°. Behind the sample reference and probe beam were directed to a polychromator and their spectra were imaged on a liquid nitrogen cooled HgCdTe detector of 2 x 32 pixels. To avoid spectral and temporal distortion of the MIR pulses by CO₂ and water absorptions in air, the whole pump-probe setup was purged with dry nitrogen.

The experiments were performed with 1 mM solutions of [(cyclam-ac)Fe^{III}(N₃)⁺]PF₆ in acetonitrile-*d*₃ in a stainless steel flow cell with CaF₂ windows of 1 mm thickness. The optical path length inside the cell was 0.6 mm. The solvent acetonitrile-*d*₃ (99.5% deuteration) was purchased from Deutero.

Table S1: Reaction energies (ΔE) and unscaled harmonic stretching frequencies of the various metal complexes from DFT-calculations

2S + 1	$\Delta E / \text{cm}^{-1}$	$\nu_1 (\text{N}_3) / \text{cm}^{-1}$	$\nu_2 (\text{CO}) / \text{cm}^{-1}$	$\nu_3 (\text{NP}) / \text{cm}^{-1}$
1: $^{2S+1}[\text{Fe}^{\text{III}}\text{N}_3\text{Cyclam-ac}]^+ - ^2\mathbf{1}$				
2	0	2134 (2376)	1686 (1355)	
4	2686	2145 (2748)	1660 (1534)	
6	2430	2165 (2749)	1661 (1626)	
2: $^{2S+1}[\text{Fe}^{\text{II}}(\text{Cyclam-ac})]^+ + ^2\text{N}_3 - ^2\mathbf{1}$				
1	18095		1642 (1187)	
3	14740		1631 (1236)	
5	12963		1668 (942)	
3: $^{2S+1}[\text{Fe}^{\text{II}}(\text{MeCN})(\text{Cyclam-ac})]^+ + ^2\text{N}_3 - \text{MeCN} - ^2\mathbf{1}$				
1	11148		1720 (1162)	
3	16895		1976 (479)	
5	12261		1971 (448)	
4: $^{2S+1}[\text{Fe}^{\text{III}}(\text{Cyclam-ac})]^{2+} + \text{N}_3^- - ^2\mathbf{1}$				
2	16090		1740 (876)	
4	12918		1716 (1104)	
6	14980		1743 (941)	
5: $^{2S+1}[\text{Fe}^{\text{III}}(\text{MeCN})(\text{Cyclam-ac})]^{2+} + \text{N}_3^- - \text{MeCN} - ^2\mathbf{1}$				
2	7278		1715 (1088)	
4	9774		1691 (1216)	
6	11386		1713 (1102)	
6: $^{2S+1}[\text{Fe}^{\text{V}}\text{N}(\text{Cyclam-ac})]^+ + \text{N}_2 - ^2\mathbf{1}$				
2	4802		1656 (1392)	
4	9680		1659 (1338)	
6	14360		1674 (1290)	
7: $^{2S+1}[\text{Fe}^{\text{III}}\text{NPM}_3(\text{Cyclam-ac})]^+ + \text{N}_2 - \text{PM}_3 - ^2\mathbf{1}$				
2	-11556		1653.82 (1448)	1148.51 (1860)
4	-10519		1978.14 (514)	1352.41 (229)
6	-13871		1626.1 (1507)	1145.64 (1656)
N₃ radical				
2		1710.04 (522)		

Calculated geometries and IR spectrum (unscaled) at COSMO(Acetonitrile)-B3LYP/TZVP(Fe, N, O, P, C^{Carboxylate})& SVP(C, H)

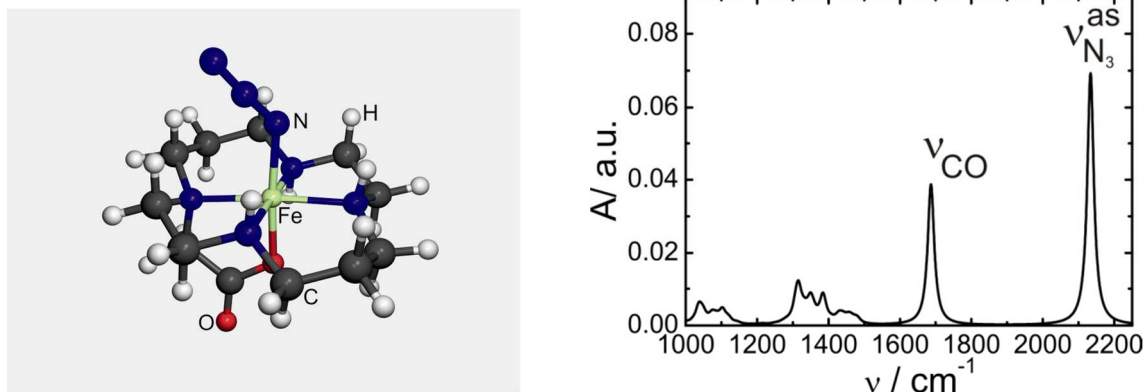


Figure S1. (Left) DFT-optimized geometry of [Fe^{III}N₃Cyclam-ac]⁺ (*S* = 1/2), (Right) Calculated IR spectrum.

Table S2. Optimized cartesian coordinates (in Å) of [Fe^{III}N₃Cyclam-ac]⁺ (*S* = 1/2)

Fe	4.955256	-0.034741	-0.005691	C	4.628417	-1.656549	2.336969
N	4.162396	1.384176	-1.285701	H	4.891863	-2.557954	2.913020
C	5.251804	1.680946	-2.268732	H	4.496717	-0.823989	3.043056
H	5.018642	2.598125	-2.833589	C	3.369218	-1.874756	1.523441
H	5.295793	0.854140	-2.990611	H	2.502141	-2.067321	2.174181
C	6.571102	1.812911	-1.534814	H	3.486660	-2.729275	0.842222
H	7.400389	1.941025	-2.246917	N	3.146907	-0.661153	0.694613
H	6.575552	2.686562	-0.868361	C	2.075553	-0.839090	-0.319924
N	6.770179	0.596827	-0.701654	H	2.386802	-1.656512	-0.984314
C	7.849192	0.765627	0.311534	H	1.153378	-1.156112	0.194397
H	7.566237	1.604956	0.962064	C	1.797345	0.432815	-1.113418
H	8.776310	1.045932	-0.214459	H	0.942341	0.226775	-1.776138
C	8.080905	-0.496262	1.134892	H	1.448904	1.227518	-0.432941
H	8.993612	-0.339014	1.730253	C	2.928507	0.931714	-2.011277
H	8.295172	-1.350429	0.469193	H	2.565769	1.774259	-2.623992
C	6.955692	-0.850643	2.101298	H	3.232071	0.135581	-2.705106
H	7.283582	-1.661596	2.772835	H	4.183211	3.515298	-0.989612
H	6.694106	0.016613	2.724233	H	5.952511	-2.124591	0.854425
C	3.877577	2.602063	-0.460061	H	7.076868	-0.153653	-1.325618
H	2.796329	2.690301	-0.286911	H	2.856037	0.087389	1.330153
C	4.523492	2.548330	0.915957	N	4.956934	-1.571693	-1.218004
O	4.932106	1.370362	1.288774	N	5.214100	-1.677418	-2.383972
O	4.586844	3.546901	1.620874	N	5.444097	-1.851447	-3.495715
N	5.722210	-1.289906	1.401398				

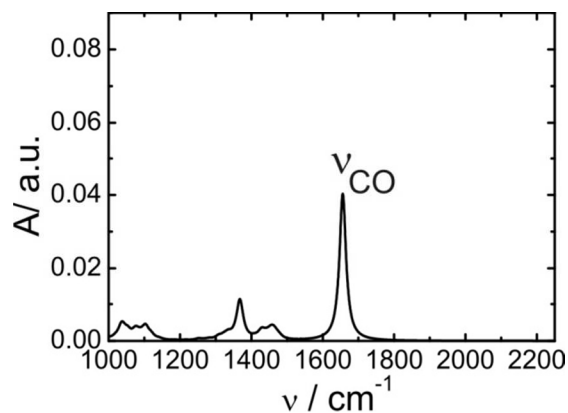
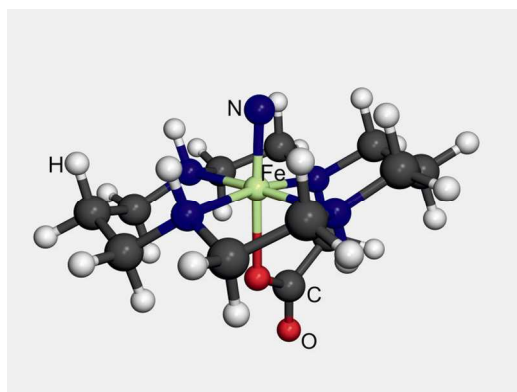


Figure S2. (Left) DFT-optimized geometry of $[\text{Fe}^{\text{V}}\text{NCyclam-ac}]^+$ ($S = 1/2$), (Right) Calculated IR spectrum.

Table S3. Optimized cartesian coordinates (in Å) of $[\text{Fe}^{\text{V}}\text{NCyclam-ac}]^+$ ($S = 1/2$)

Fe	5.007600	-0.114861	-0.009097	N	5.774204	-1.292014	1.474986
N	4.198719	1.315976	-1.277534	C	4.660586	-1.616773	2.406602
C	5.303115	1.591279	-2.250025	H	4.915832	-2.488569	3.029732
H	5.064892	2.480908	-2.855908	H	4.515417	-0.751312	3.068673
H	5.373910	0.726859	-2.924498	C	3.414245	-1.874241	1.586194
C	6.607135	1.775266	-1.500307	H	2.540847	-2.049750	2.233542
H	7.440301	1.918895	-2.205460	H	3.545418	-2.754013	0.939083
H	6.575916	2.658597	-0.847582	N	3.194928	-0.694577	0.710200
N	6.836812	0.577743	-0.649170	C	2.128682	-0.909945	-0.299945
C	7.887399	0.792197	0.379899	H	2.449371	-1.744324	-0.941618
H	7.572761	1.637859	1.007203	H	1.205869	-1.221797	0.216663
H	8.821649	1.080169	-0.129817	C	1.845310	0.336554	-1.130744
C	8.122788	-0.446546	1.236458	H	1.005743	0.100741	-1.803224
H	9.018678	-0.262379	1.849399	H	1.472668	1.141250	-0.475283
H	8.364833	-1.313807	0.597203	C	2.987622	0.830414	-2.017159
C	6.980295	-0.790586	2.185333	H	2.624653	1.651675	-2.658541
H	7.307022	-1.565415	2.898975	H	3.323149	0.017414	-2.677345
H	6.680061	0.095350	2.761605	H	4.189474	3.448582	-1.041767
C	3.885572	2.549383	-0.487133	H	6.040576	-2.162023	1.008440
H	2.799765	2.628226	-0.341286	H	7.172913	-0.165340	-1.265501
C	4.505118	2.557819	0.910303	H	2.914289	0.083783	1.313798
O	4.939167	1.424143	1.329629	N	5.009442	-1.321606	-1.133150
O	4.510881	3.607465	1.557131				

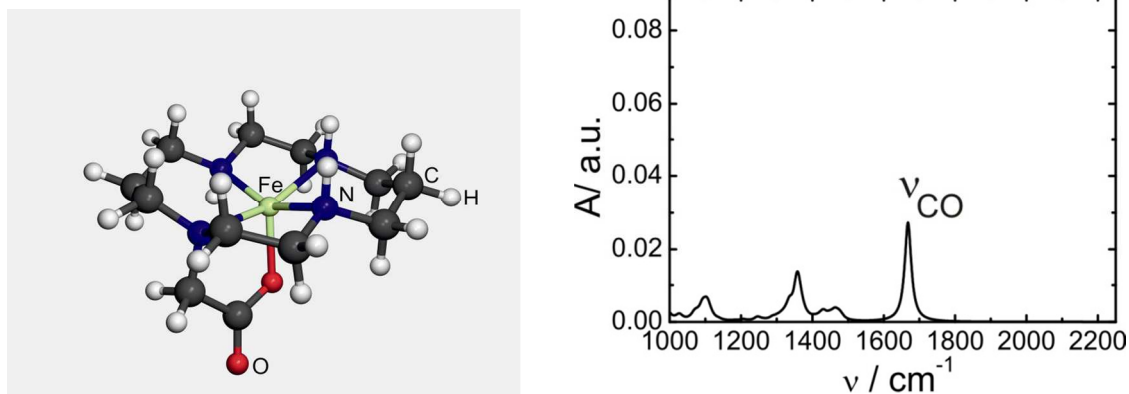


Figure S3. (Left) DFT-optimized geometry of $[\text{Fe}^{\text{II}}\text{Cyclam-ac}]^+$ ($S = 2$), (Right) Calculated IR spectrum.

Table S4. Optimized cartesian coordinates (in Å) of $[\text{Fe}^{\text{II}}\text{Cyclam-ac}]^+$ ($S = 2$)

Fe	4.905017	0.337544	0.408439	N	5.756205	-1.352695	1.492808
N	4.117199	1.548477	-1.283817	C	4.671401	-1.870262	2.353007
C	5.287418	1.654249	-2.206248	H	4.944011	-2.825503	2.834200
H	5.169498	2.513731	-2.890206	H	4.484512	-1.134063	3.150996
H	5.300836	0.743264	-2.822456	C	3.426843	-2.055134	1.488403
C	6.622862	1.761114	-1.469047	H	2.582956	-2.425442	2.093379
H	7.434760	1.853410	-2.210417	H	3.628584	-2.804286	0.707533
H	6.662763	2.659927	-0.835506	N	3.089673	-0.777513	0.805151
N	6.809274	0.576177	-0.599362	C	2.153288	-0.933850	-0.338878
C	7.946708	0.664498	0.349396	H	2.606100	-1.651584	-1.041365
H	7.760027	1.525929	1.010384	H	1.208308	-1.379801	0.016580
H	8.884044	0.869303	-0.198504	C	1.849666	0.384898	-1.056429
C	8.122996	-0.613310	1.177350	H	0.969358	0.205918	-1.694227
H	9.057598	-0.503187	1.750081	H	1.524367	1.142951	-0.322682
H	8.285521	-1.471287	0.500009	C	2.944251	0.936149	-1.978626
C	7.013844	-0.963530	2.176611	H	2.501196	1.677243	-2.669357
H	7.362163	-1.787713	2.824620	H	3.329532	0.114027	-2.600200
H	6.794633	-0.104970	2.833159	H	4.004363	3.690520	-1.376666
C	3.772691	2.862769	-0.686166	H	5.991283	-2.089771	0.821950
H	2.688629	2.904266	-0.501719	H	6.967682	-0.231654	-1.207000
C	4.425673	3.139275	0.675413	H	2.627588	-0.176588	1.494220
O	4.896550	2.116809	1.311667				
O	4.429666	4.290993	1.109417				

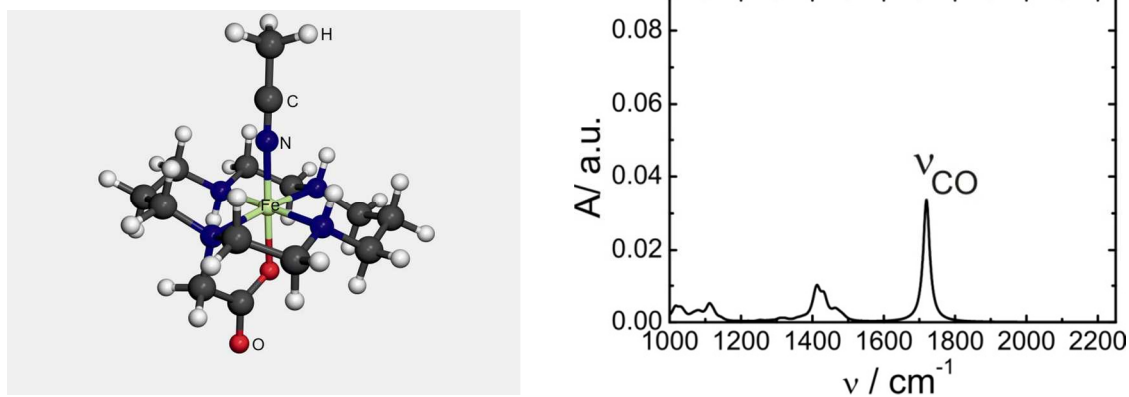


Figure S4. (Left) DFT-optimized geometry of $[\text{Fe}^{\text{II}}(\text{MeCN})\text{Cyclam-ac}]^+$ ($S = 0$), (Right) Calculated IR spectrum.

Table S5. Optimized cartesian coordinates (in Å) of $[\text{Fe}^{\text{II}}(\text{MeCN})\text{Cyclam-ac}]^+$ ($S = 0$)

Fe	4.845335	-0.053616	-0.046336	C	1.663754	0.530909	-1.064386
N	4.044727	1.425948	-1.269910	H	0.788275	0.359986	-1.711390
C	5.128263	1.695594	-2.260150	H	1.354507	1.325616	-0.364751
H	4.922141	2.621996	-2.825568	C	2.793423	1.016000	-1.976619
H	5.140223	0.863227	-2.978362	H	2.427722	1.866045	-2.581435
C	6.472419	1.786978	-1.553910	H	3.066588	0.215238	-2.678772
H	7.279047	1.942496	-2.289479	N	4.829652	-1.457916	-1.385064
H	6.496325	2.642255	-0.863337	H	4.156947	3.546482	-0.929239
N	6.685331	0.550173	-0.762337	C	4.873690	-2.303786	-2.166547
C	7.781930	0.674133	0.227102	C	4.916751	-3.363748	-3.151827
H	7.527938	1.504389	0.901794	H	5.955076	-3.535612	-3.471727
H	8.719665	0.941144	-0.291884	H	4.515267	-4.292904	-2.720228
C	7.987543	-0.608637	1.030601	H	4.312477	-3.084784	-4.028412
H	8.917606	-0.492803	1.609958	H	6.963811	-0.180386	-1.420862
H	8.161446	-1.458753	0.346536	H	5.834648	-2.230001	0.827437
C	6.869946	-0.949199	2.015038	H	2.770012	0.123562	1.344559
H	7.206484	-1.754360	2.692356				
H	6.631524	-0.071563	2.633324				
C	3.808421	2.633777	-0.422205				
H	2.730524	2.771098	-0.259895				
C	4.440288	2.544937	0.966424				
O	4.891636	1.398402	1.311462				
O	4.449683	3.557267	1.681920				
N	5.621059	-1.367580	1.334470				
C	4.527015	-1.684163	2.286301				
H	4.750024	-2.591989	2.872887				
H	4.440575	-0.841179	2.988027				
C	3.234046	-1.848167	1.504581				
H	2.386452	-2.038968	2.184323				
H	3.308370	-2.703439	0.815103				
N	3.019491	-0.625235	0.693016				
C	1.916361	-0.758435	-0.285579				
H	2.175855	-1.577583	-0.971810				
H	0.987512	-1.053092	0.234702				

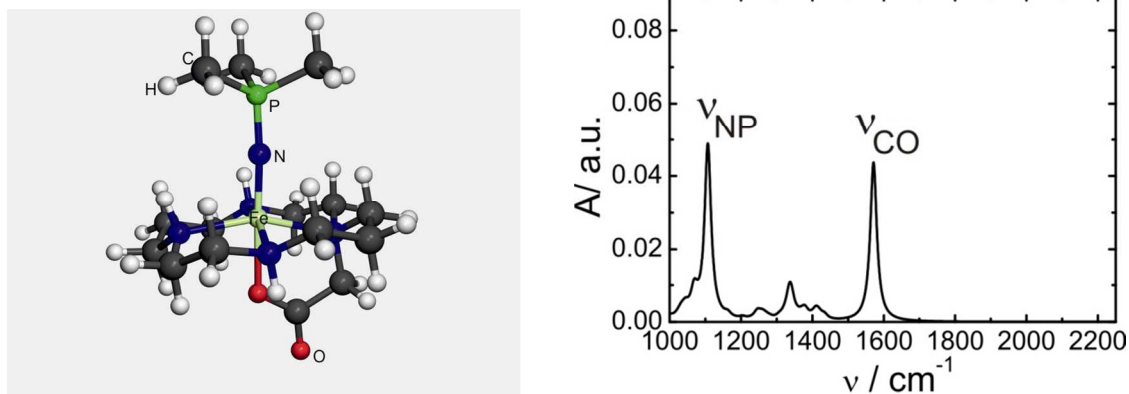


Figure S5. DFT-optimized geometry of $[\text{Fe}^{\text{III}}\text{NPMe}_3\text{Cyclam-ac}]^+$ ($S = 5/2$)

Table S6. Optimized cartesian coordinates (in Å) of $[\text{Fe}^{\text{III}}\text{NPMe}_3\text{Cyclam-ac}]^+$ ($S = 5/2$)

Fe	5.169677	-0.282662	-0.078684	H	3.700759	-2.815509	1.058055
N	4.275350	1.313287	-1.344318	N	3.213689	-0.802383	0.719089
C	5.443385	1.615337	-2.221196	C	2.230471	-1.059863	-0.354411
H	5.230357	2.488593	-2.864142	H	2.617343	-1.893321	-0.958815
H	5.601405	0.746376	-2.875951	H	1.266139	-1.380474	0.078998
C	6.712192	1.883910	-1.402117	C	1.981381	0.175312	-1.232757
H	7.536465	2.138595	-2.088986	H	1.174490	-0.090628	-1.934573
H	6.572436	2.749970	-0.740367	H	1.556552	0.979706	-0.608453
N	7.054350	0.713749	-0.556123	C	3.131885	0.718810	-2.100092
C	7.951669	0.990368	0.590357	H	2.716838	1.478870	-2.788490
H	7.510231	1.817920	1.163979	H	3.545775	-0.092893	-2.714409
H	8.934830	1.330192	0.219810	H	4.202446	3.433806	-1.068620
C	8.153441	-0.229453	1.502059	H	6.217565	-2.169979	1.348468
H	9.014505	-0.002361	2.150519	H	7.502555	0.013244	-1.148710
H	8.462844	-1.103511	0.900335	H	2.902178	0.000092	1.269881
C	6.992307	-0.615954	2.430201	N	5.382955	-1.659667	-1.272125
H	7.373217	-1.282981	3.224508	P	5.688593	-2.878473	-2.259106
H	6.584907	0.282121	2.914467	C	7.379084	-2.844494	-2.963733
C	3.877266	2.509760	-0.564784	C	4.571637	-2.950019	-3.707574
H	2.781915	2.571579	-0.502546	C	5.538742	-4.518261	-1.458399
C	4.393428	2.512127	0.879803	H	7.515166	-1.912389	-3.532461
O	4.922998	1.433208	1.299746	H	7.538840	-3.703952	-3.632796
O	4.231329	3.547115	1.547226	H	8.113235	-2.878626	-2.144684
N	5.874062	-1.282308	1.719288	H	6.243532	-4.573718	-0.615568
C	4.673022	-1.560859	2.546781	H	5.762248	-5.323918	-2.174471
H	4.861456	-2.374535	3.267625	H	4.513447	-4.642801	-1.080275
H	4.448939	-0.649429	3.120696	H	4.672485	-2.021560	-4.288899
C	3.479835	-1.917842	1.655602	H	3.532203	-3.046842	-3.360314
H	2.599784	-2.140183	2.283329	H	4.822572	-3.810274	-4.347056

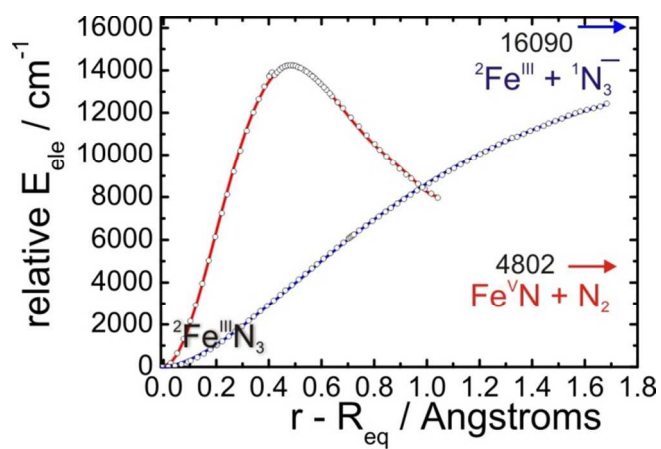


Figure S6. Electronic energies as a function of the relative displacements resulting in N_2 (red solid curve) and N_3 dissociation (blue solid curve). The open circles show the electronic energies as obtained from the corresponding relaxed scans DFT-calculations.