Crystal Alignment. The monoclinic crystals of [Fe(T*p*FPP)(NO)(1-MeIm)] have one molecule per asymmetric unit, and the unit cell contains two pairs of inversion related molecules. The unit cell dimensions were: a = 14.1135(4), b = 18.7149(6), c = 14.8501(4), α = 90, β = 97.825(1), γ = 90 and the space group was $P2_1/n$. The crystal was mounted on to a goniometer head using the copper wire and glass rod setup described. The best fit to the porphyrin planes, (0 1 0), and to the O_{NO}–N_{NO}–Fe–N_{Im} plane, (−8 1 20) were determined using *Mercury*. After alignment to have (0 1 0) parallel to the laboratory floor the APEX II software was used to determine that a 59° clockwise rotation would put the O_{NO}–N_{NO}–Fe–N_{Im} plane normal to the beam, and therefore 149° clockwise rotation would put this plane perpendicular to the beam. Red tape was used to mark the O_{NO}–N_{NO}–Fe–N_{Im} plane and black tape for its normal plane. Genereral in-plane and out-of-plane measurements for the triclinic form of [Fe(T*p*FPP)(NO)(1-MeIm)] and [Fe(T*p*OCH_3PP)(NO)(1-MeIm)] were carried out as in Silvernail, N. J.; Barabanschikov, A,; Pavlik, J. W.; Noll, B. C.; Zhao, J.; Alp, E. E.; Sturhahn, W.; Sage, J. T.; Scheidt, W. R. *J. Am. Chem. Soc.* **2007**, *129*, 2200.

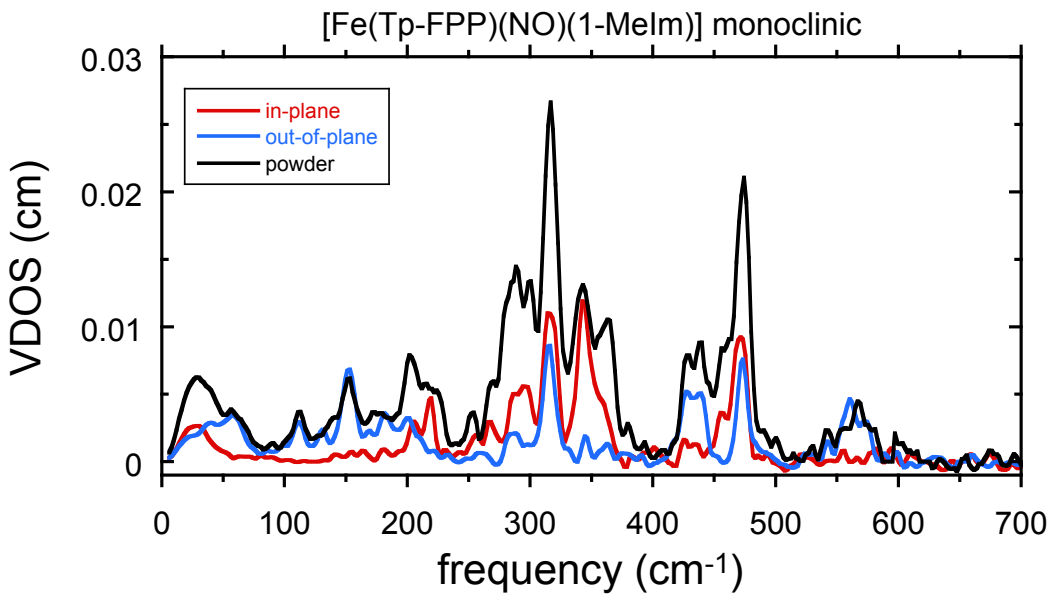

Figure S1. Comparison of the density of states from a powder sample of monoclinic [Fe(T*p*FPP)(1-MeIm)(NO)] and two oriented crystal components: out-of-plane (blue line), general in-plane ("gen-ip," red line), and powder (black).

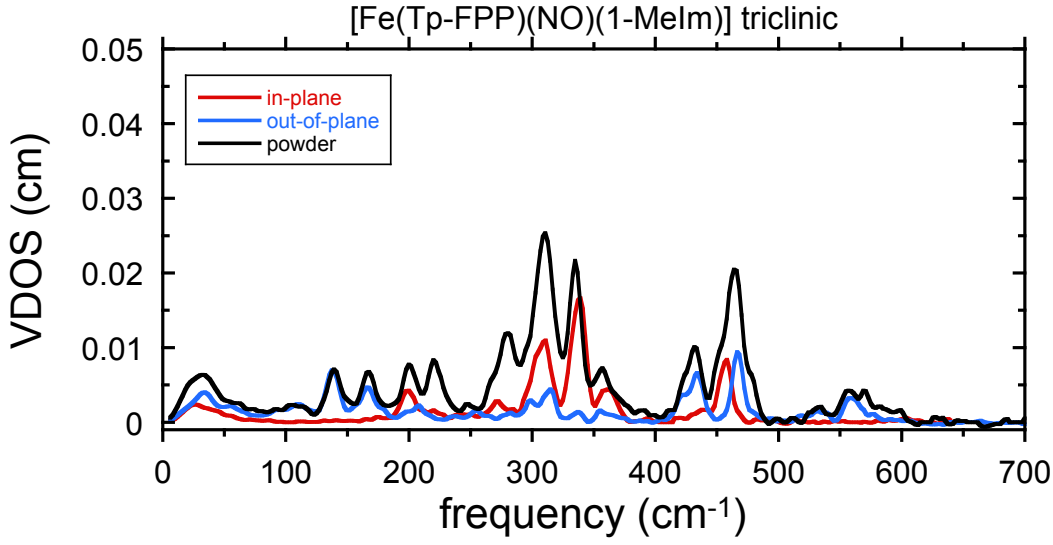

Figure S2. Comparison of the density of states from a powder sample of triclinic [Fe(T*p*FPP)(1-MeIm)(NO)] and two oriented crystal components: out-of-plane (blue line), general in-plane ("gen-ip," red line), and powder (black).

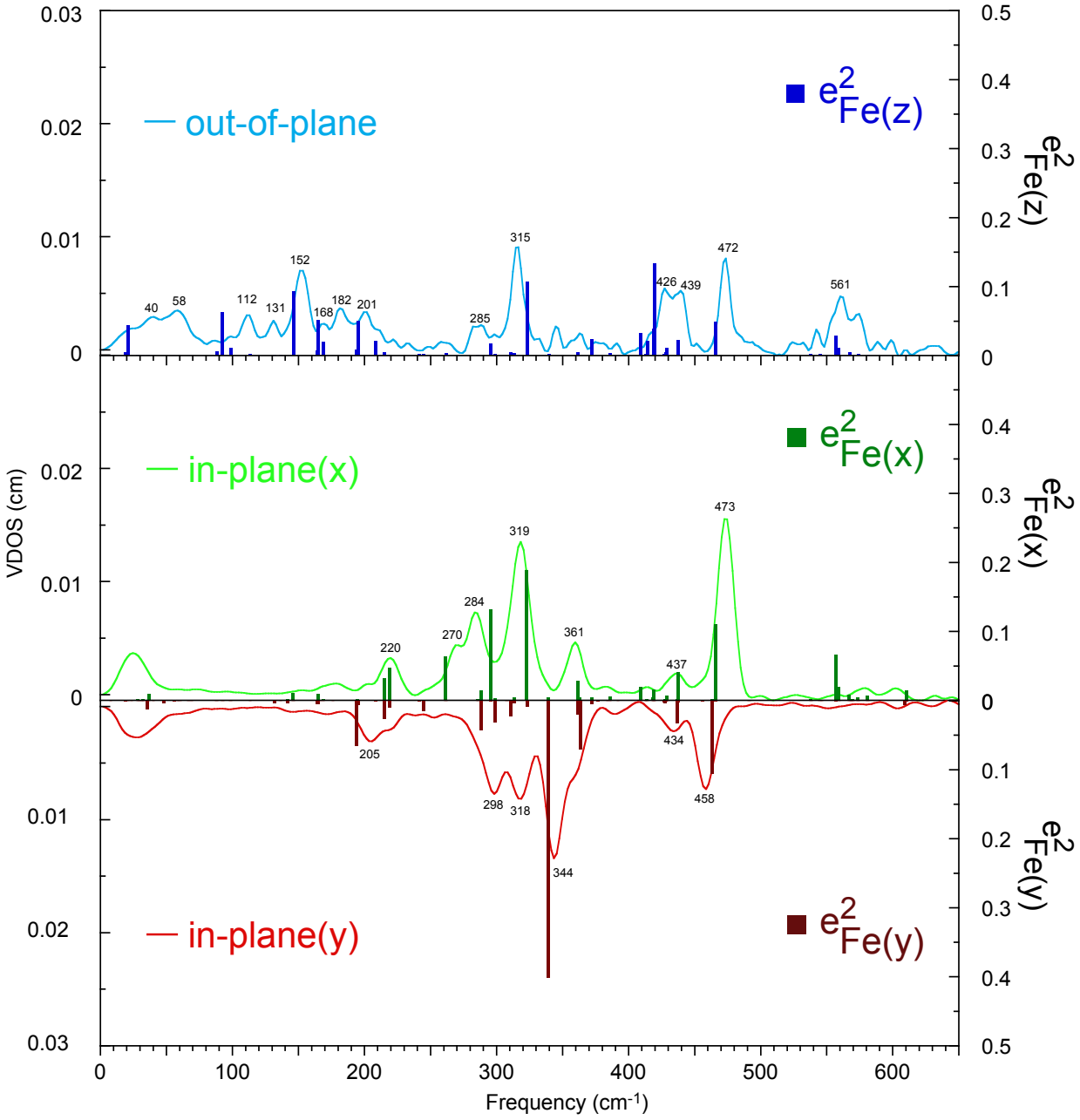

Figure S3. Comparison of the the experimental and predicted vibrational spectra for *mono*-[Fe(T*p*FPP)(1-MeIm)(NO)] based on a B3LYP predcition.

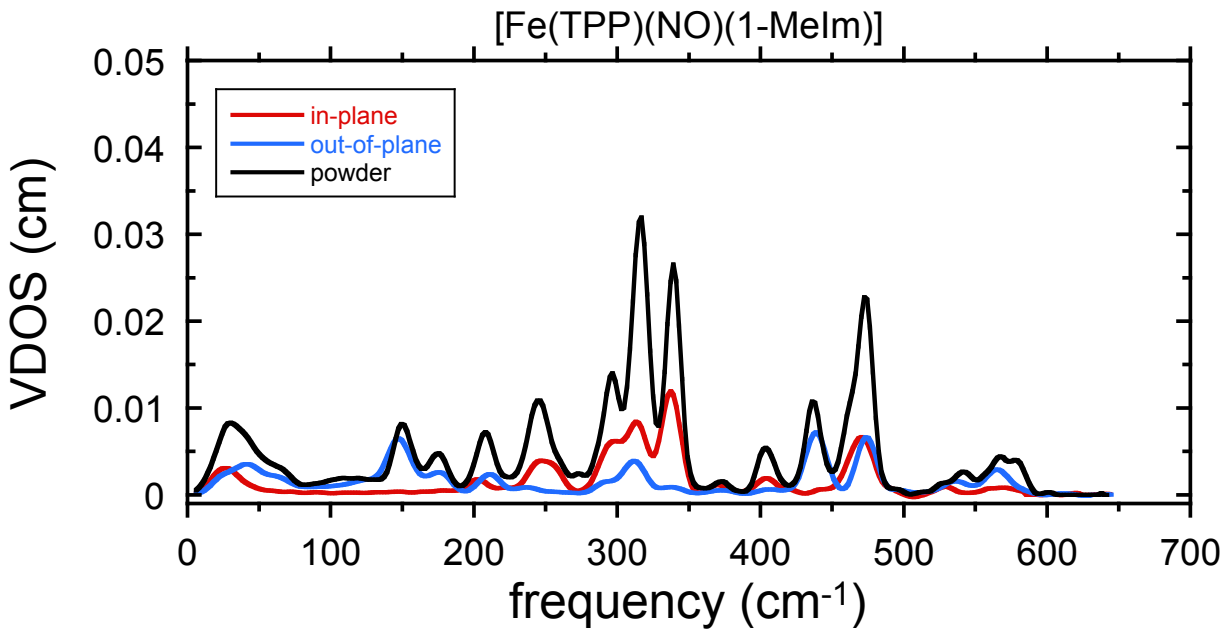

Figure S4. Comparison of the density of states from a powder sample of [Fe(TPP)(1-MeIm)(NO)] with two oriented crystal components: out-of-plane (blue line), and general in-plane ("gen-ip," red line) and powder (black).

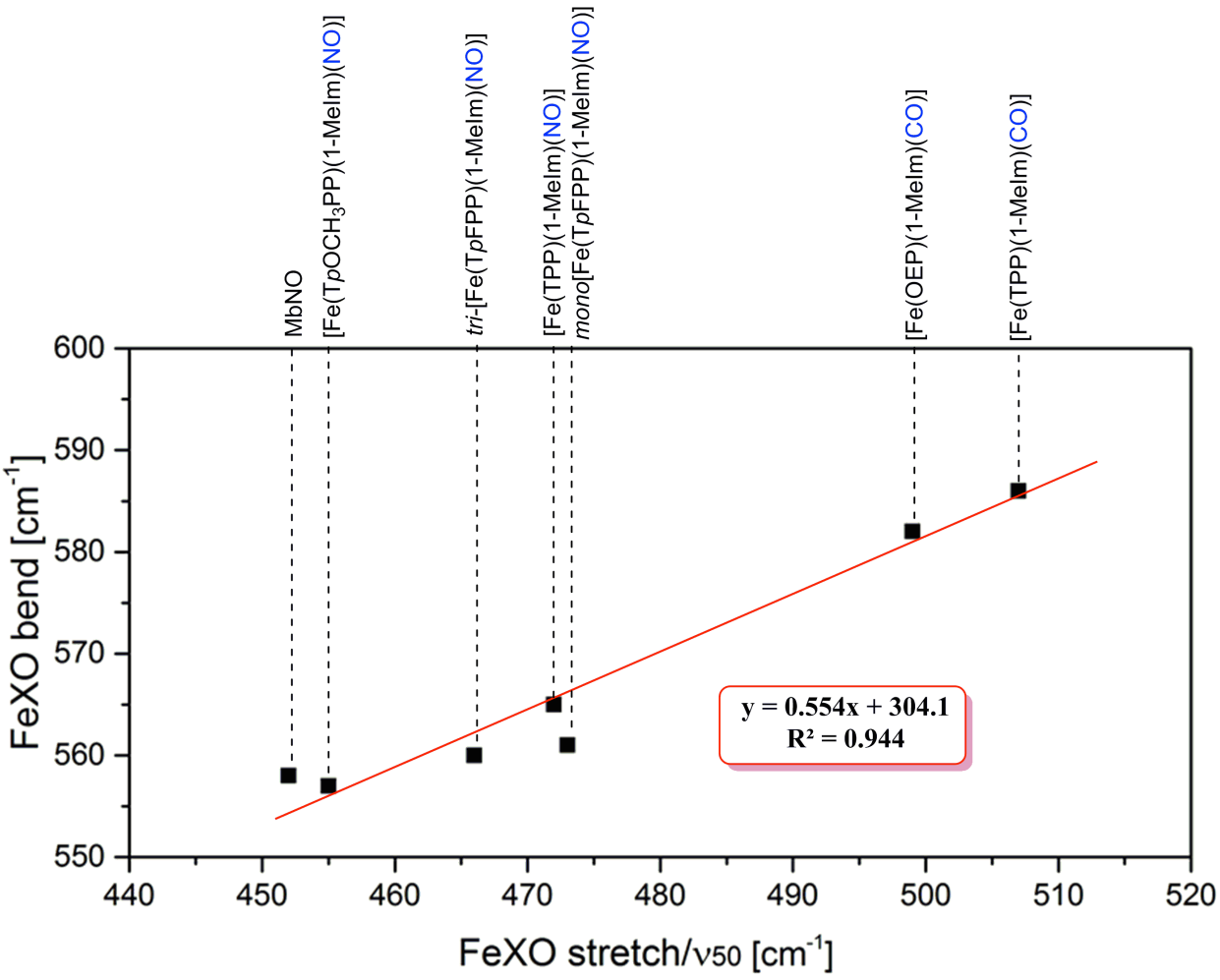

Figure S5. Figure showing the correlation between the NRVS assigned bend and the assigned stretch for all FeXO species with iron in the Fe(II) state.

Table S1. COMPONENT AND TOTAL MODE COMPOSITION FACTORS OF [Fe(T*p*FPP)(1-MeIm)(NO)] FOR MODES WITH e^2_{Fe}>0.005. TOTAL MODE COMPOSITION FACTORS REPRESENT THE IRON FRACTION OF KINETIC ENERGY WITHIN EACH MODE. PREDICTIONS MADE USING M06L/TZVP.

frequency	e2x	e2y	e2z	e2xyz
20.9	0.001540	0.000018	0.030490	0.032040
24.5	0.001810	0.000038	0.021560	0.023410
39.1	0.009140	0.000094	0.000366	0.009600
39.9	0.000009	0.009330	0.000016	0.009360
46.7	0.005670	0.000000	0.000675	0.006350
87.6	0.000001	0.000064	0.044570	0.044630
90.4	0.000026	0.000409	0.010990	0.011430
129.4	0.003490	0.000014	0.199220	0.202730
143.1	0.003540	0.000055	0.029730	0.033330
145.9	0.003250	0.000358	0.024150	0.027760
146.8	0.000456	0.000000	0.007210	0.007660
164.2	0.000366	0.024930	0.001790	0.027090
172.2	0.000538	0.001430	0.003930	0.005900
181.8	0.001970	0.009080	0.000083	0.011130
200.1	0.004240	0.000032	0.023470	0.027750
213.2	0.000859	0.057940	0.002000	0.060800
216.6	0.000028	0.000099	0.021460	0.021590
220.7	0.104880	0.000183	0.001870	0.106940
236.8	0.003230	0.011960	0.007740	0.022930
239.1	0.004430	0.000283	0.002190	0.006900
259.4	0.040590	0.000681	0.002020	0.043300
278.2	0.066460	0.021710	0.003200	0.091380
281.2	0.031680	0.041490	0.042140	0.115300
290.0	0.003850	0.009630	0.007150	0.020630
292.6	0.005380	0.049550	0.001690	0.056620
306.1	0.050870	0.035690	0.028920	0.115480
309.3	0.001100	0.008700	0.001080	0.010880
312.4	0.054360	0.007580	0.017340	0.079280
314.7	0.159770	0.011430	0.047900	0.219100
327.2	0.002020	0.409480	0.002400	0.413910
361.6	0.009160	0.035030	0.000569	0.044750
363.1	0.001730	0.004460	0.003270	0.009460
365.2	0.024030	0.023130	0.006580	0.053740
385.7	0.006470	0.000007	0.003080	0.009550
427.3	0.000159	0.001440	0.013310	0.014910
428.4	0.000196	0.006010	0.005020	0.011220
429.1	0.000124	0.005820	0.002480	0.008420
439.1	0.005460	0.000894	0.052080	0.058440
446.0	0.002100	0.014170	0.006670	0.022930
448.4	0.011470	0.001260	0.015430	0.028160
460.4	0.000381	0.091610	0.000063	0.092050
480.8	0.233920	0.000118	0.102270	0.336310
487.3	0.010130	0.000152	0.004850	0.015130
573.1	0.001210	0.000000	0.012210	0.013430
576.7	0.000571	0.000000	0.009370	0.009940
598.8	0.024660	0.000020	0.082160	0.106840
611.6	0.000636	0.004900	0.000060	0.005590
612.5	0.014430	0.000375	0.003270	0.018070

Table S2 [Fe(T*p*OMePP)(NO)(1-MeIm)] with $e^2_{Fe} \geq 0.005$ (e2x: parallel to Fe-N-O plane, e2y: perpendicular to Fe-N-O plane) by M06L functional

frequency	e2x	e2y	e2z	e2xyz
26.2	0.001930	0.000579	0.027130	0.029640
27.0	0.000008	0.003120	0.004400	0.007530
34.1	0.004400	0.006690	0.000033	0.011130
36.9	0.003890	0.001140	0.000493	0.005520
39.6	0.001950	0.001030	0.018800	0.021780
39.8	0.000351	0.001890	0.006510	0.008750
71.4	0.000639	0.000365	0.004360	0.005370
81.6	0.002310	0.001970	0.000973	0.005250
86.8	0.000045	0.000334	0.027200	0.027580
92.7	0.000006	0.000033	0.007740	0.007780
95.2	0.000028	0.000622	0.030300	0.030950
105.2	0.000509	0.000005	0.007520	0.008030
109.2	0.001810	0.002210	0.002330	0.006350
118.2	0.000136	0.000212	0.012020	0.012370
118.7	0.000081	0.000078	0.006700	0.006860
127.0	0.000318	0.000707	0.156700	0.157720
145.8	0.004760	0.000000	0.044110	0.048870
146.4	0.007100	0.000462	0.035130	0.042700
168.1	0.000317	0.031560	0.000215	0.032090
169.1	0.000341	0.006360	0.000178	0.006880
181.3	0.002360	0.003360	0.002010	0.007740
183.3	0.002230	0.000320	0.007820	0.010370
209.6	0.055360	0.010330	0.000019	0.065710
211.3	0.038380	0.007810	0.001200	0.047380
219.7	0.000160	0.032680	0.006290	0.039130
234.0	0.000364	0.002810	0.002980	0.006150
245.6	0.010970	0.004710	0.000149	0.015830
251.8	0.024620	0.000529	0.000003	0.025160
255.4	0.002700	0.003780	0.002050	0.008530
271.4	0.040310	0.008720	0.022070	0.071100
278.7	0.018770	0.000572	0.056800	0.076150
283.5	0.037710	0.015110	0.004790	0.057610
285.3	0.004460	0.032530	0.000336	0.037320
289.6	0.004780	0.016390	0.000783	0.021950
290.6	0.001880	0.030020	0.000013	0.031920
298.2	0.005420	0.001250	0.003060	0.009730
307.4	0.178180	0.028210	0.013210	0.219600
307.8	0.039670	0.035700	0.014590	0.089970
318.8	0.038930	0.062120	0.038450	0.139500
327.5	0.012220	0.379090	0.019380	0.410690
341.6	0.003870	0.001110	0.000962	0.005940
352.2	0.009590	0.013440	0.004220	0.027250
365.7	0.018140	0.013700	0.002470	0.034310
370.2	0.002030	0.002680	0.003600	0.008310
375.8	0.001020	0.028660	0.000579	0.030250
384.7	0.007750	0.001010	0.004410	0.013170
427.0	0.000091	0.000005	0.016510	0.016610
431.9	0.000136	0.000302	0.009710	0.010150
432.9	0.000882	0.007920	0.002990	0.011790
435.4	0.000810	0.001510	0.004990	0.007310
437.1	0.005890	0.000659	0.023910	0.030460
444.7	0.000194	0.022930	0.000019	0.023140
450.1	0.005230	0.001680	0.018730	0.025650
458.7	0.000000	0.056010	0.000423	0.056430
472.7	0.228260	0.000243	0.085290	0.313800
507.2	0.000220	0.019790	0.001520	0.021530
511.1	0.047830	0.000052	0.005290	0.053170
580.6	0.000205	0.000258	0.021670	0.022130
593.6	0.001790	0.000141	0.013690	0.015620
600.3	0.017030	0.000645	0.084580	0.102250
621.0	0.002890	0.002470	0.000254	0.005610
621.4	0.004200	0.001320	0.000639	0.006160