Supporting Information

Contribution from The Department of Chemistry and Biochemistry,

University of Notre Dame, Notre Dame, Indiana 46556,

Key Laboratory of Organic Synthesis of Jiangsu Province,

College of Chemistry, Chemical Engineering and Materials Science,

Soochow University, Suzhou 215123, P.R. China,

Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439

and Department of Physics and Center for Interdisciplinary Research on Complex Systems,

Northeastern University, Boston, Massachusetts 02115,

Probing Heme Vibrational Anisotropy: An Imidazole Orientation Effect?

Qian Peng,[1] Ming Li,[†] Chuanjiang Hu,[2,†] Jeffrey W. Pavlik,[†] Allen G. Oliver,[†] E. Ercan Alp,[3] Michael Y. Hu,[§] Jiyong Zhao,[§] J. Timothy Sage,[4,*] and W. Robert Scheidt[†,1]

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[1]The University of Notre Dame
[2]Soochow University
[3]Advanced Photon Source, Argonne National Laboratory
[4]Northeastern University
[1]To whom correspondence should be addressed. E-mail WRS, scheidt.1@nd.edu; JTS, jtsage@neu.edu

Table S1. Predicted frequencies and e^2_{Fe} values for [Fe(OEP)(2MeHIm)] with x and y along the Fe-Im directions.

frequency	e^2x Impara	e^2y Imperp	e^2z	e^2xyz
24.7	0.000	0.010	0.000	0.011
31.6	0.000	0.000	0.011	0.011
34.1	0.000	0.000	0.092	0.093
109.2	0.000	0.000	0.021	0.021
111.2	0.000	0.000	0.035	0.035
116.5	0.002	0.012	0.000	0.014
123.9	0.008	0.000	0.032	0.040
151.7	0.000	0.026	0.000	0.026
152.4	0.028	0.003	0.000	0.031
157.8	0.008	0.005	0.001	0.014
176.3	0.004	0.000	0.111	0.115
194.7	0.006	0.000	0.095	0.102
205.6	0.003	0.003	0.021	0.027
207.3	0.022	0.206	0.001	0.228
212.4	0.108	0.070	0.009	0.186
218.0	0.025	0.041	0.218	0.284
221.7	0.026	0.097	0.105	0.229
228.6	0.164	0.015	0.016	0.195
242.6	0.037	0.137	0.001	0.175
251.9	0.041	0.045	0.001	0.086
255.6	0.006	0.007	0.025	0.037
258.0	0.199	0.072	0.005	0.276
270.7	0.000	0.000	0.050	0.050
278.7	0.128	0.008	0.001	0.137
281.1	0.009	0.093	0.000	0.102
305.4	0.012	0.000	0.000	0.013
307.7	0.001	0.010	0.000	0.011
328.5	0.000	0.000	0.029	0.030
331.8	0.008	0.011	0.000	0.019
334.4	0.014	0.006	0.000	0.019

a. All predicted frequencies are expressed in cm^{-1}

Table S2. Predicted frequencies and e^2_{Fe} values for [Fe(OEP)(2MeHIm)] with x and y along the Fe-N_p directions.

frequency	e^2_x	e^2_y	e^2_z	e^2_{xyz}
24.7	0.002	0.008	0.000	0.011
31.6	0.000	0.000	0.011	0.011
34.1	0.000	0.000	0.092	0.093
109.2	0.000	0.000	0.021	0.021
111.2	0.000	0.000	0.035	0.035
116.5	0.000	0.014	0.000	0.014
123.9	0.008	0.001	0.032	0.040
151.7	0.006	0.020	0.000	0.026
152.4	0.018	0.013	0.000	0.031
157.8	0.012	0.001	0.001	0.014
176.3	0.003	0.001	0.111	0.115
194.7	0.005	0.002	0.095	0.102
205.6	0.001	0.005	0.021	0.027
207.3	0.002	0.226	0.001	0.228
212.4	0.164	0.013	0.009	0.186
218.0	0.005	0.062	0.218	0.284
221.7	0.001	0.123	0.105	0.229
228.6	0.177	0.002	0.016	0.195
242.6	0.001	0.173	0.001	0.175
251.9	0.011	0.075	0.001	0.086
255.6	0.010	0.002	0.025	0.037
258.0	0.266	0.005	0.005	0.276
270.7	0.000	0.000	0.050	0.050
278.7	0.132	0.003	0.001	0.137
281.1	0.001	0.100	0.000	0.102
305.4	0.012	0.001	0.000	0.013
307.7	0.005	0.006	0.000	0.011
328.5	0.000	0.000	0.029	0.030
331.8	0.002	0.017	0.000	0.019
334.4	0.019	0.001	0.000	0.019

a. All predicted frequencies are expressed in cm^{-1}

Table S3. Predicted frequencies and e^2_{Fe} values for [Fe(OEP)] with x and y along the Fe-Np directions.[a]

frequency	e^2_x	e^2_y	e^2_z	e^2_{xyz}
42.9	0.000	0.000	0.154	0.154
59.4	0.000	0.007	0.000	0.007
62.3	0.007	0.000	0.000	0.007
73.8	0.000	0.005	0.000	0.005
74.0	0.000	0.000	0.016	0.016
74.1	0.006	0.000	0.000	0.006
91.5	0.005	0.000	0.000	0.005
91.6	0.000	0.006	0.000	0.006
111.4	0.000	0.000	0.004	0.004
144.6	0.000	0.000	0.328	0.328
163.0	0.030	0.000	0.000	0.030
163.4	0.000	0.029	0.000	0.029
203.2	0.000	0.000	0.031	0.031
231.6	0.037	0.000	0.000	0.037
234.6	0.000	0.030	0.000	0.030
234.9	0.000	0.000	0.205	0.205
239.2	0.057	0.000	0.000	0.057
239.6	0.000	0.062	0.000	0.062
266.3	0.000	0.000	0.011	0.011
288.4	0.000	0.000	0.068	0.068
310.7	0.225	0.000	0.000	0.225
311.2	0.000	0.186	0.000	0.186
341.4	0.255	0.000	0.000	0.255
343.7	0.000	0.275	0.000	0.275
346.5	0.000	0.000	0.002	0.002
350.6	0.000	0.000	0.078	0.078
352.3	0.225	0.000	0.000	0.225
352.7	0.000	0.247	0.000	0.247
470.4	0.000	0.001	0.000	0.001
493.0	0.000	0.000	0.003	0.003
511.5	0.024	0.000	0.000	0.024
512.9	0.000	0.024	0.000	0.024

a. All predicted frequencies are expressed in cm^{-1}

Table ??. Cartestian coordinates for the optimized structures of [Fe(OEP)(2MeHIm)] and [Fe(OEP)].

[Fe(OEP)(2-MeHIm)] BP86/TZVP/6-31G*				[Fe(OEP)] BP86/TZVP/6-31G*			
Fe	-0.014775	0.010579	0.230839	Fe	-0.019229	0.017712	-0.263696
N	1.657119	-1.211067	-0.069261	N	1.657224	-1.091260	-0.287673
N	-1.233035	-1.646274	-0.119260	N	-1.125303	-1.654130	-0.270810
N	-1.688727	1.237575	-0.054797	N	-1.695644	1.126810	-0.244004
N	1.203196	1.672089	-0.084531	N	1.086895	1.689597	-0.256129
C	2.973321	-0.807473	-0.199404	C	2.956995	-0.640033	-0.286663
C	1.665144	-2.593075	-0.120187	C	1.750309	-2.463956	-0.294580
C	-0.828043	-2.966938	-0.095029	C	-0.671242	-2.955215	-0.280944
C	-2.615237	-1.655503	-0.153177	C	-2.500292	-1.745235	-0.256018
C	-3.007168	0.835847	-0.164434	C	-2.995332	0.675470	-0.232942
C	-1.697812	2.618901	-0.081451	C	-1.788649	2.499389	-0.224814
C	0.795850	2.992625	-0.053520	C	0.632906	2.990599	-0.236354
C	2.584966	1.683794	-0.141590	C	2.461966	1.780613	-0.259029
C	3.854551	-1.973502	-0.309439	C	3.895474	-1.751520	-0.297544
C	3.038179	-3.088441	-0.253679	C	3.140315	-2.892942	-0.302355
C	-1.987412	-3.847607	-0.113902	C	-1.778249	-3.886780	-0.275993
C	-3.107724	-3.025984	-0.153956	C	-2.924600	-3.128423	-0.260198
C	-3.890023	2.004068	-0.247940	C	-3.933733	1.786850	-0.210591
C	-3.072242	3.117030	-0.192021	C	-3.178574	2.928269	-0.205354
C	1.953674	3.874478	-0.079868	C	1.739986	3.922071	-0.230131
C	3.075043	3.054751	-0.139190	C	2.886349	3.163704	-0.244177
C	0.515199	-3.393856	-0.081469	C	0.667057	-3.329280	-0.286046
H	0.676327	-4.477369	-0.084057	H	0.881842	-4.391963	-0.283022
C	-3.426275	-0.502696	-0.178133	C	-3.367889	-0.660013	-0.232632
H	-4.507134	-0.674192	-0.227794	H	-4.429802	-0.877692	-0.212621
C	-0.547517	3.418596	-0.034328	C	-0.705274	3.364546	-0.215867
H	-0.708532	4.502027	-0.024153	H	-0.919849	4.426976	-0.190643
C	3.394926	0.530319	-0.198624	C	3.329686	0.695270	-0.267449
H	4.474724	0.701358	-0.269618	H	4.391799	0.912698	-0.258412
C	5.347805	-1.918803	-0.502498	C	5.393232	-1.622309	-0.329194
H	5.798925	-2.871184	-0.163498	H	5.844499	-2.539441	0.068738
H	5.782506	-1.131675	0.145315	H	5.712385	-0.815920	0.344211
C	5.771801	-1.654734	-1.966137	C	5.962338	-1.357325	-1.737332
H	6.872308	-1.607740	-2.058222	H	7.054139	-1.262340	-1.705482
H	5.353238	-0.701274	-2.333338	H	5.551713	-0.435271	-2.163069
H	5.404082	-2.455413	-2.631719	H	5.711204	-2.176003	-2.420717
C	3.430784	-4.538604	-0.368190	C	3.607272	-4.321722	-0.340014
H	2.841699	-5.144948	0.348314	H	2.983970	-4.935497	0.323513
H	4.489109	-4.658925	-0.066718	H	4.624268	-4.381615	0.066634
C	3.245220	-5.120411	-1.789228	C	3.598080	-4.938963	-1.752786
H	3.532275	-6.187307	-1.821226	H	3.936890	-5.981342	-1.725665
H	3.865778	-4.574352	-2.521213	H	4.259452	-4.383012	-2.426415
H	2.194499	-5.034974	-2.117310	H	2.592589	-4.918024	-2.187125
C	-1.941721	-5.354053	-0.118871	C	-1.655761	-5.385348	-0.312761
H	-2.893012	-5.751961	0.283882	H	-2.562871	-5.833817	0.110494
H	-1.151118	-5.707377	0.571935	H	-0.832049	-5.708127	0.337119
C	-1.696029	-5.965013	-1.518344	C	-1.432379	-5.953246	-1.728534
H	-1.662263	-7.068704	-1.467961	H	-1.342681	-7.045569	-1.700881
H	-0.740944	-5.610018	-1.943980	H	-0.519670	-5.546750	-2.177667
H	-2.497986	-5.677136	-2.220624	H	-2.267482	-5.696662	-2.389617
C	-4.556674	-3.435453	-0.216216	C	-4.352116	-3.601615	-0.275146
H	-5.166495	-2.754529	0.409451	H	-4.959386	-2.975755	0.391559
H	-4.674546	-4.441036	0.231725	H	-4.402547	-4.615647	0.140046
C	-5.136107	-3.454924	-1.650021	C	-4.987807	-3.605367	-1.679698
H	-6.201405	-3.749787	-1.642675	H	-6.027647	-3.950101	-1.636338
H	-4.586056	-4.169504	-2.287377	H	-4.437341	-4.267699	-2.356863
H	-5.056784	-2.460552	-2.123682	H	-4.978504	-2.602368	-2.120106
C	-5.386120	1.951792	-0.416990	C	-5.431803	1.658035	-0.223580
H	-5.809952	1.155462	0.226664	H	-5.741590	0.839597	0.439587
H	-5.831170	2.899111	-0.056558	H	-5.877339	2.567787	0.197099
C	-5.834525	1.709195	-1.877050	C	-6.020613	1.418408	-1.628156

Table ??. Continued.

H	-6.936485	1.665169	-1.951690
H	-5.423994	0.760361	-2.264886
H	-5.476442	2.518840	-2.537049
C	-3.464976	4.568925	-0.278040
H	-2.869509	5.162023	0.444189
H	-4.520521	4.684479	0.034625
C	-3.291396	5.175291	-1.690305
H	-3.579697	6.242273	-1.701466
H	-3.917391	4.641330	-2.426625
H	-2.243322	5.097011	-2.028739
C	1.906560	5.380933	-0.074172
H	2.861162	5.776705	0.322958
H	1.121858	5.728524	0.626096
C	1.648144	6.001729	-1.466946
H	1.614595	7.104990	-1.408219
H	0.689314	5.649571	-1.886384
H	2.443752	5.719158	-2.178522
C	4.522528	3.467159	-0.216988
H	5.142020	2.779632	0.391854
H	4.645340	4.467537	0.241291
C	5.082404	3.504471	-1.658177
H	6.147345	3.800687	-1.661716
H	4.522901	4.225807	-2.279443
H	4.997855	2.515627	-2.142388
N	-0.178410	0.007703	2.404386
C	0.739925	-0.222130	3.353279
N	0.140322	-0.166805	4.584712
H	0.617427	-0.302982	5.474029
C	-1.211577	0.104492	4.415198
H	-1.894384	0.199882	5.256264
C	-1.388189	0.211483	3.054325
H	-2.293870	0.421779	2.489243
C	2.193088	-0.513842	3.159383
H	2.343442	-1.522700	2.736697
H	2.737185	-0.449828	4.117691
H	2.640205	0.201488	2.450045

E= -3146.918137 Hartree

H	-7.111871	1.322715	-1.582727
H	-5.616101	0.504243	-2.076172
H	-5.778984	2.249317	-2.300111
C	-3.645828	4.357439	-0.210626
H	-3.013186	4.959200	0.455063
H	-4.657003	4.409849	0.211283
C	-3.656411	5.000109	-1.612004
H	-3.994670	6.041786	-1.561293
H	-4.327260	4.456338	-2.286205
H	-2.657129	4.987148	-2.060747
C	1.617182	5.421043	-0.238067
H	2.530186	5.861898	0.180490
H	0.802693	5.731909	0.429017
C	1.374067	6.014430	-1.640068
H	1.284901	7.106062	-1.591408
H	0.455106	5.616006	-2.083652
H	2.199797	5.769954	-2.317316
C	4.313575	3.637266	-0.270642
H	4.930064	2.999579	0.376097
H	4.369958	4.643667	0.161987
C	4.929484	3.666385	-1.683686
H	5.969875	4.010408	-1.648727
H	4.369651	4.340737	-2.341017
H	4.913867	2.671479	-2.141912

E= -2881.237418 Hartree

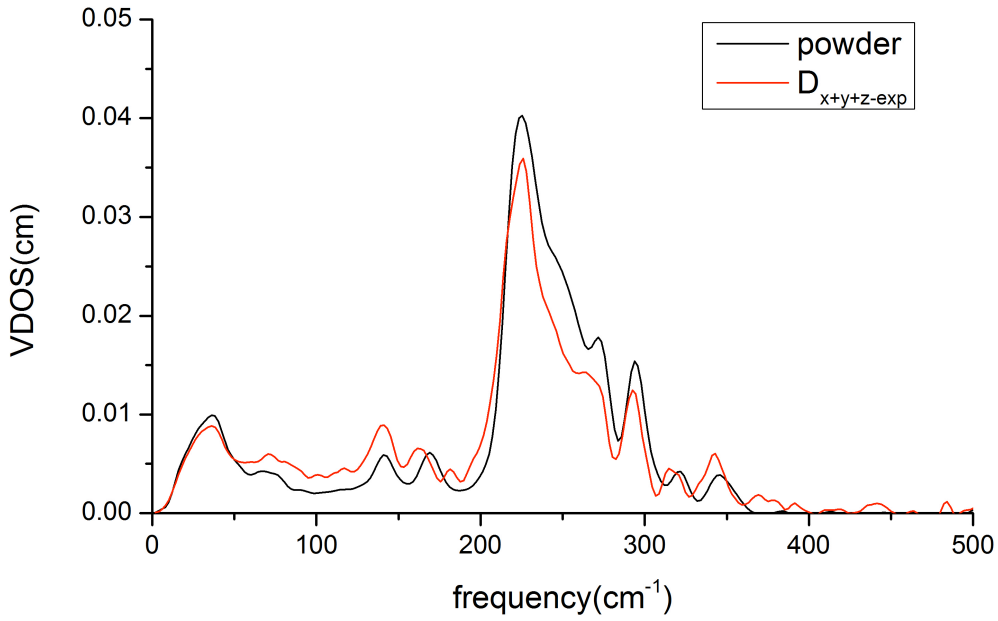

Figure S1. Figure showing a comparison of the experimental powder spectrum with the sum of the measured oriented crystal spectra in the three orthogonal directions.

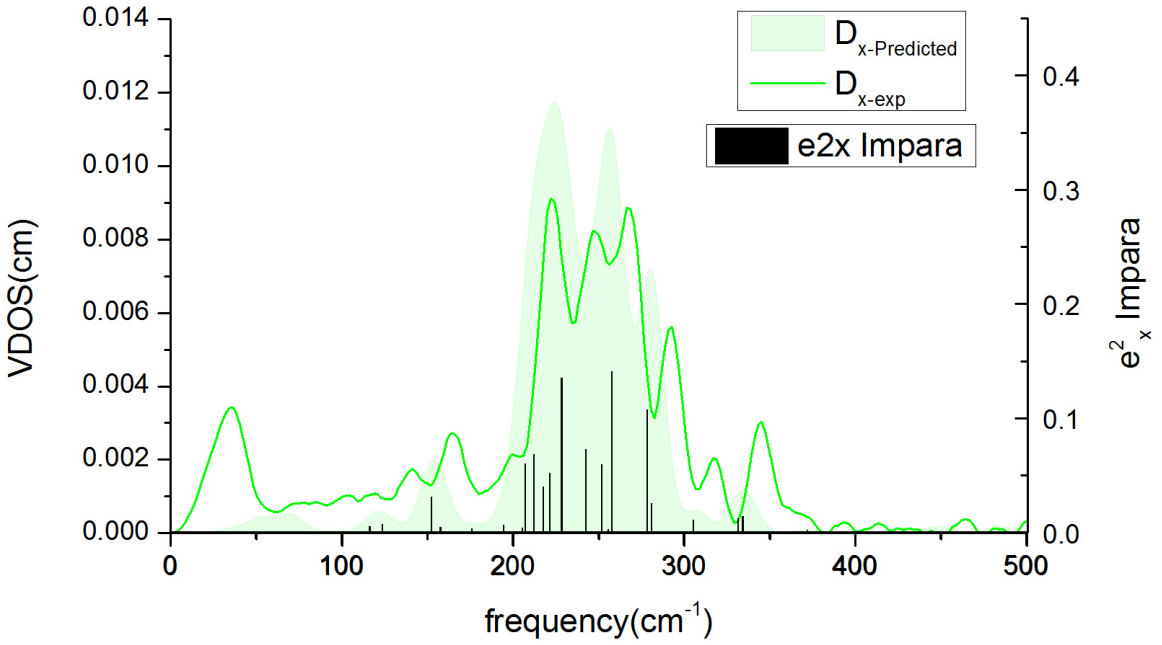

Figure S2. Figure showing a comparison of the in-plane experimental NRVS spectrum taken parallel to the 2-methylimidazole plane vs. the BP86 predicted spectrum. The predicted spectrum has been obtained by convolving the predicted e^2 values with a Gaussian with a FWHH of 15 cm^{-1}.

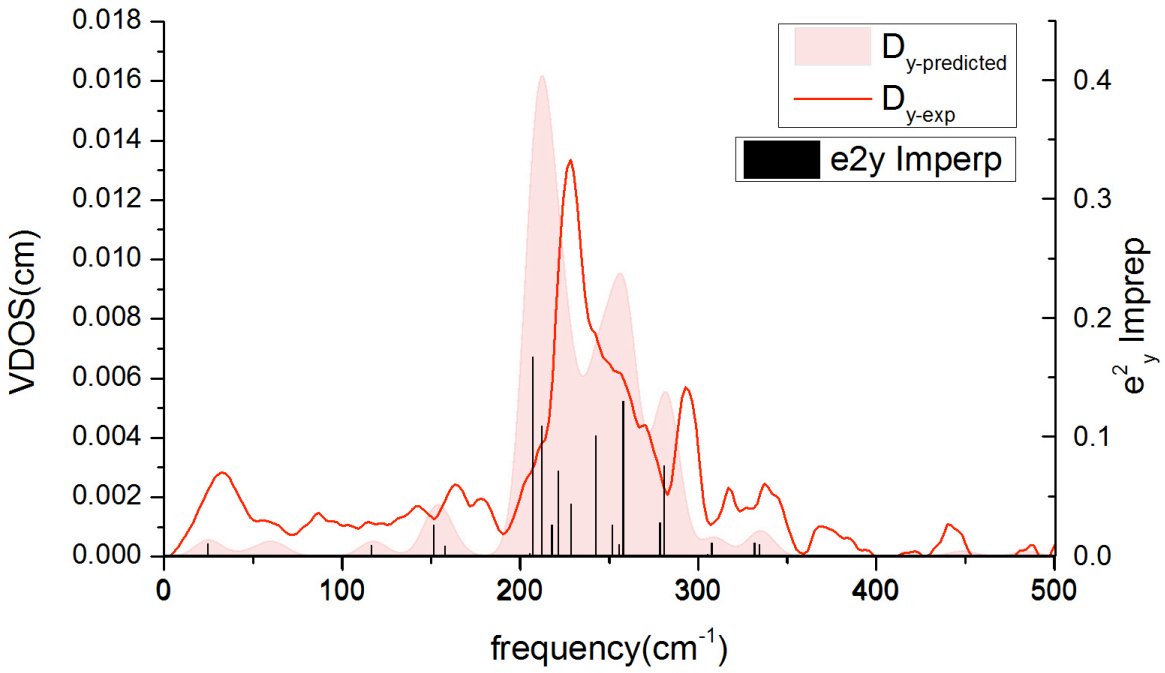

Figure S3. Figure showing a comparison of the in-plane experimental NRVS spectrum taken perpendicular to the 2-methylimidazole plane vs. the BP86 predicted spectrum. The predicted spectrum has been obtained by convolving the predicted e^2 values with a Gaussian with a FWHH of 15 cm^{-1}.

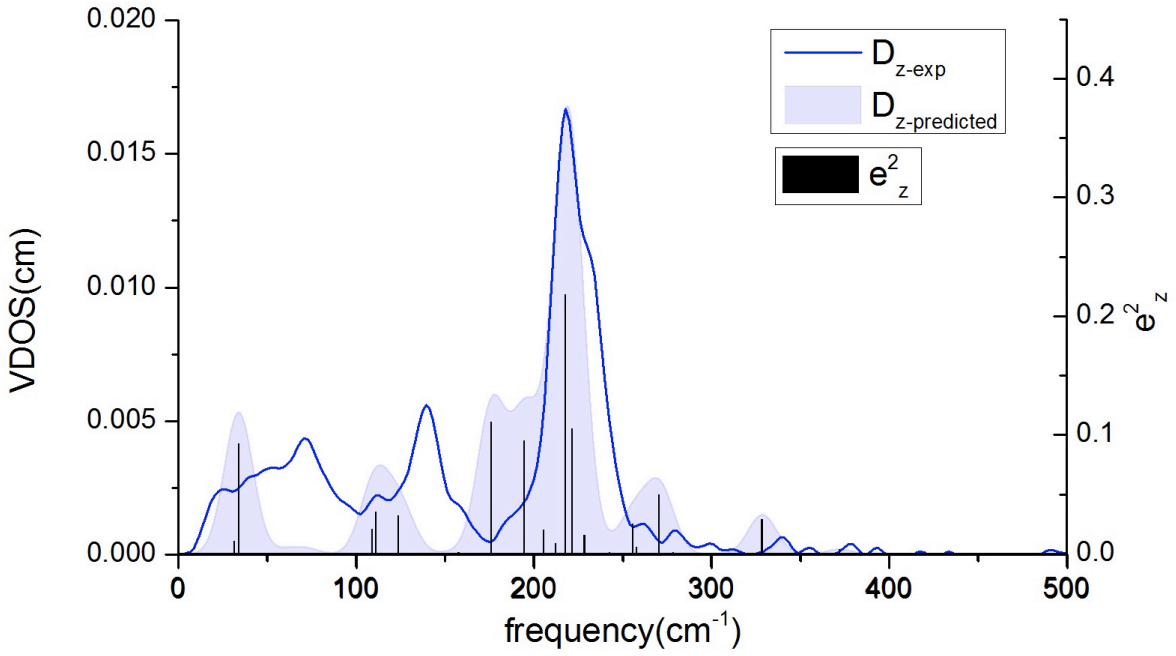

Figure S4. Figure showing a comparison of the out-of-plane experimental NRVS spectrum taken perpendicular to the porphyrin plane vs. the BP86 predicted spectrum. The predicted spectrum has been obtained by convolving the predicted e^2 values with a Gaussian with a FWHH of 15 cm^{-1}.

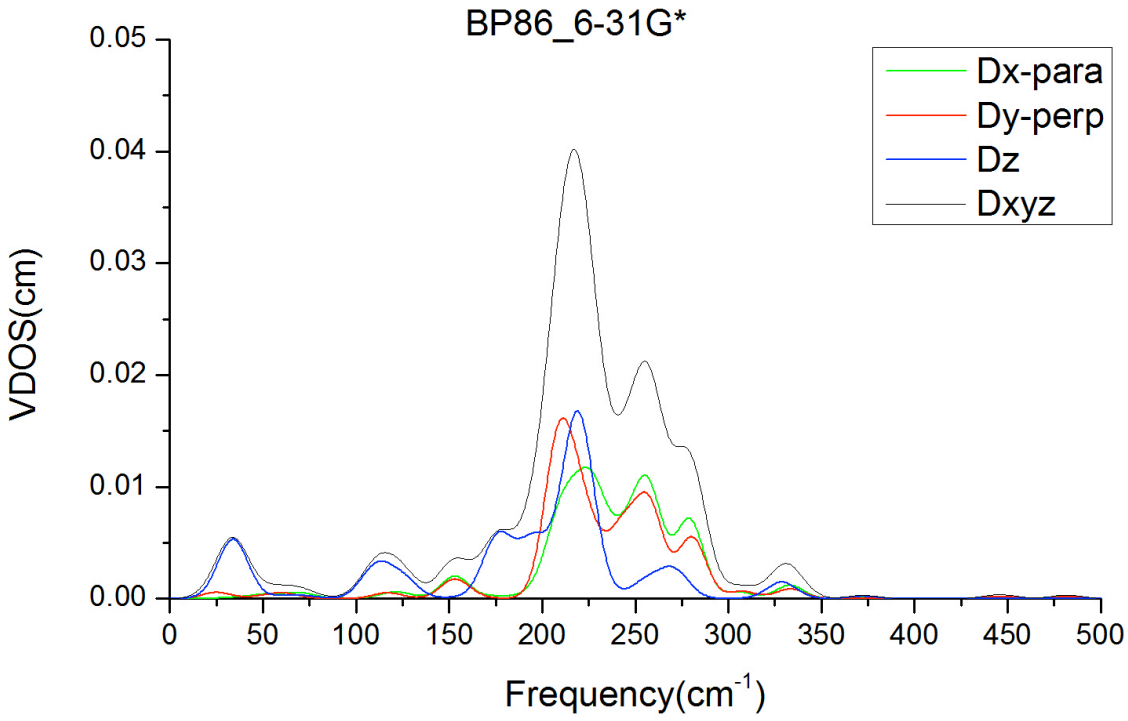

Figure S5. Figure showing predicted NRVS spectra for [Fe(OEP)(2-MeHIm)] based on calculations utilizing the BP86 functional with the basis set TZVP for iron and 6-31G* for all other atoms. The spectra are shown for the coordinate system used to obtain the experimental data and which can be compared with the experimental data of Figure S1. The illustrated spectra has been obtained by convolving the predicted e^2 values with a Gaussian with a FWHH of 15 cm^{-1}.

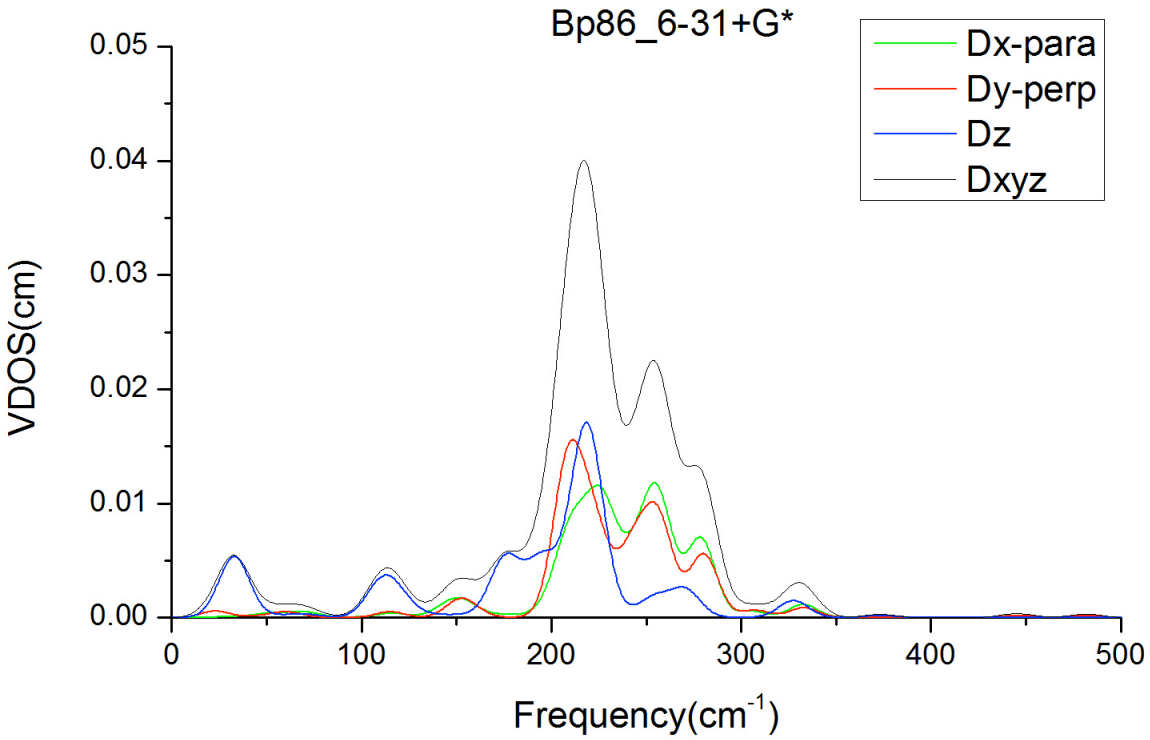

Figure S6. Figure showing predicted NRVS spectra for [Fe(OEP)(2-MeHIm)] based on calculations utilizing the BP86 functional with the basis set TZVP for iron, 6-31+G* for the nitrogen atoms of the molecule and 6-31G* for all other atoms. The spectra are shown for the coordinate system used to obtain the experimental data and which can be compared with the experimental data of Figure S1. The illustrated spectra has been obtained by convolving the predicted e^2 values with a Gaussian with a FWHH of 15 cm^{-1}.

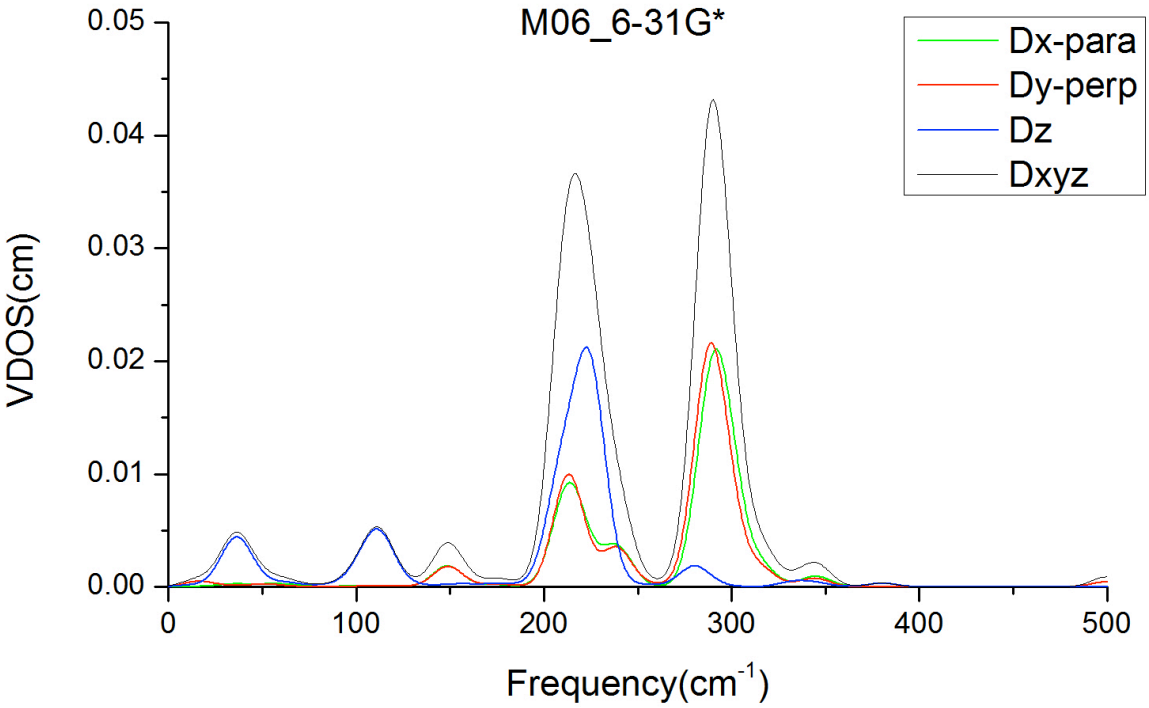

Figure S7. Figure showing predicted NRVS spectra for [Fe(OEP)(2-MeHIm)] based on calculations utilizing the M06 functional with the basis set TZVP for iron and 6-31G* for all other atoms. The spectra are shown for the coordinate system used to obtain the experimental data and which can be compared with the experimental data of Figure S1. The illustrated spectra has been obtained by convolving the predicted e^2 values with a Gaussian with a FWHH of 15 cm^{-1}.

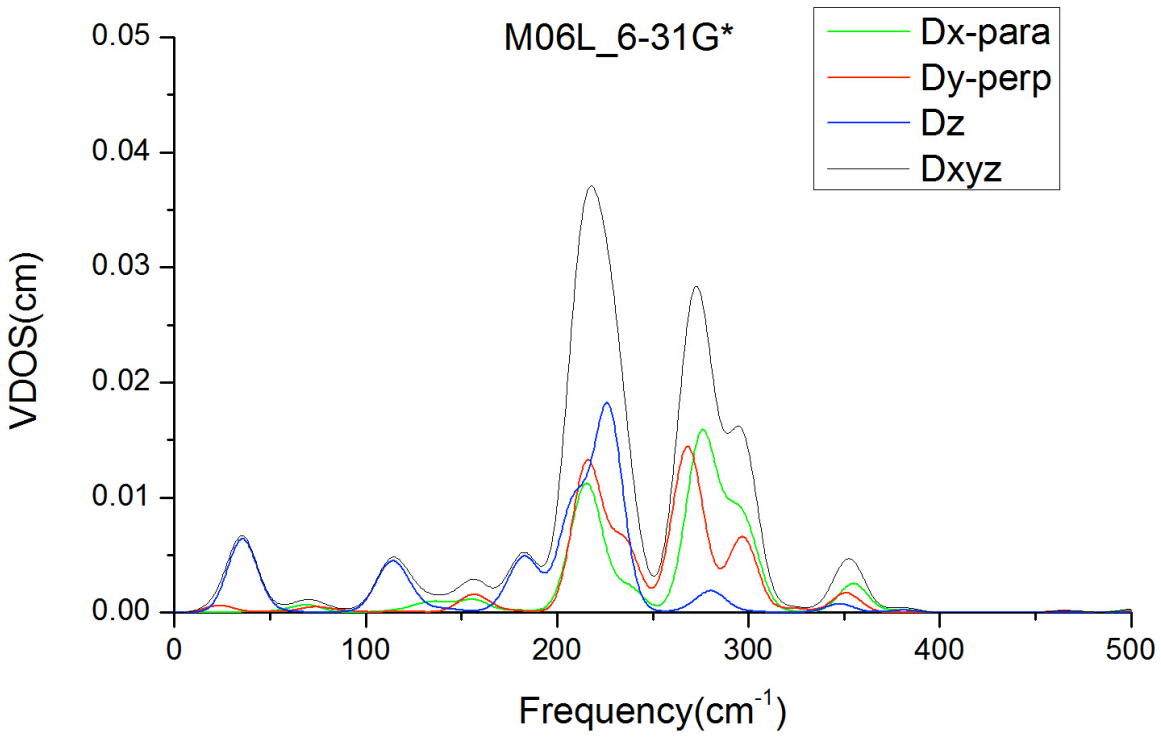

Figure S8. Figure showing predicted NRVS spectra for [Fe(OEP)(2-MeHIm)] based on calculations utilizing the M06L functional with the basis set TZVP for iron and 6-31G* for all other atoms. The spectra are shown for the coordinate system used to obtain the experimental data and which can be compared with the experimental data of Figure S1. The illustrated spectra has been obtained by convolving the predicted e^2 values with a Gaussian with a FWHH of 15 cm^{-1}.

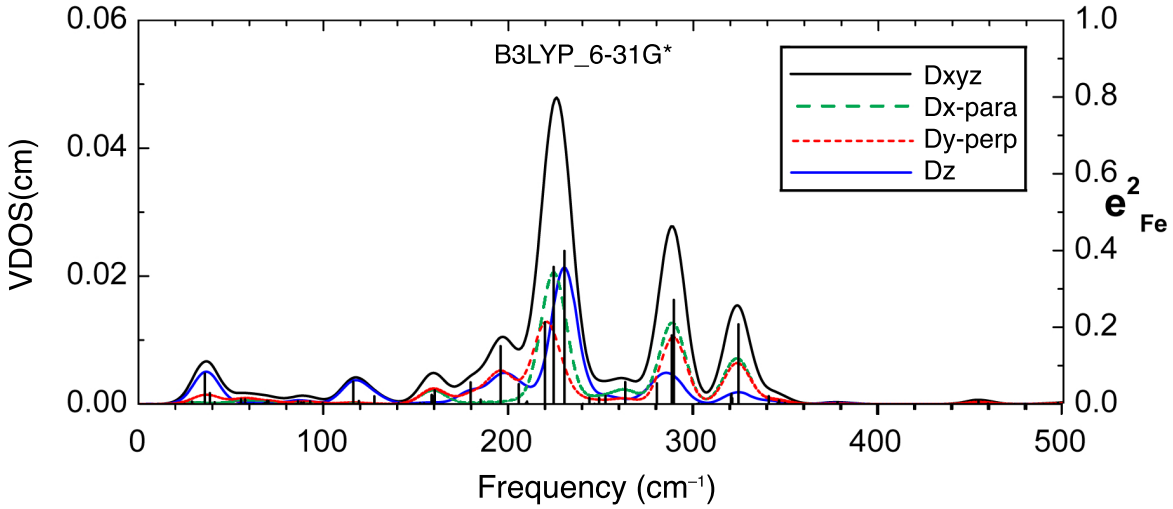

Figure S9. Figure showing predicted NRVS spectra for [Fe(OEP)(2-MeHIm)] based on calculations utilizing the B3LYP functional with the basis set TZVP for iron and 6-31G* for all other atoms. The spectra are shown for the coordinate system used to obtain the experimental data and which can be compared with the experimental data of Figure S1. The illustrated spectra has been obtained by convolving the predicted e^2 values with a Gaussian with a FWHH of 15 cm^{-1}.

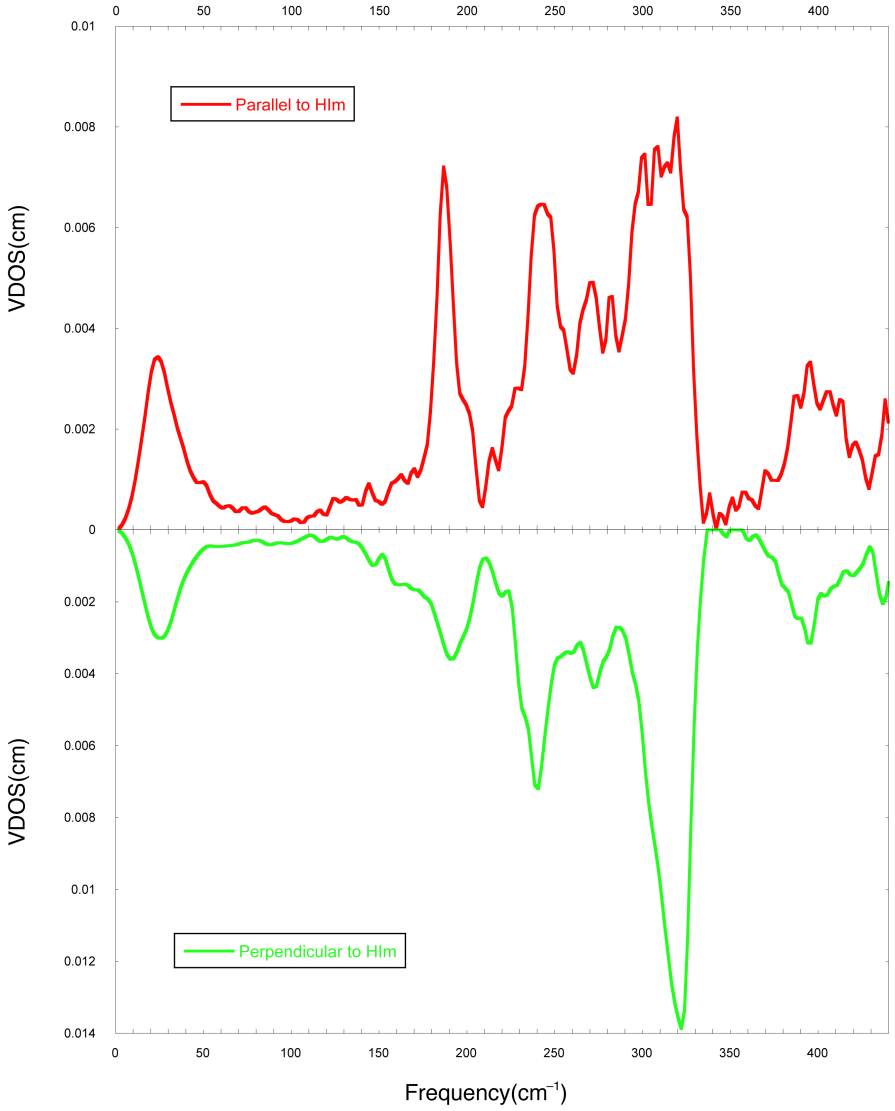

Figure S10. Figure showing the asymmetry in the in-plane vibrational spectrum for Fe(TpivPP)(2-MeHIm)]. Spectra were taken with the exciting X-ray beam parallel and perpendicular to the axial 2-methylimidazole plane.