

Supplementary Information:

Time-Resolved IR Spectroscopy of a Trinuclear Palladium Complex in Solution

by

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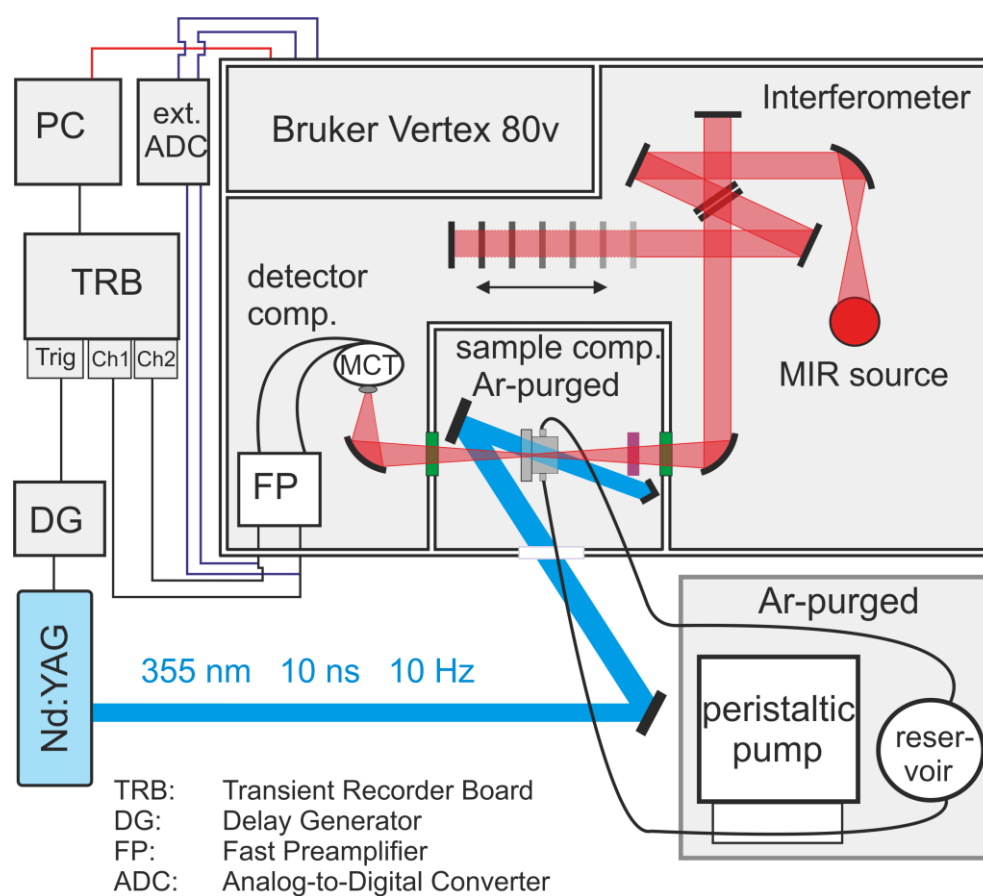


Fig. SI_1: Schematic view of the time-resolved step-scan FTIR setup including the Bruker VERTEX 80v spectrometer, for more details cf. section 2 of the paper.

As mentioned in the experimental section of the paper DC and AC spectra were used to calculate ΔA (change in absorbance). The advantage of this method over the pure DC detection is that the AC channel only measures the changes that occur due to the excitation, while the DC channel detects the complete IR signal. Thus, the AC channel provides a greater amplification than the DC channel leading to a better signal-to-noise ratio and small signals that would be lost in the "bit noise" of the DC channel can only be detected with the AC channel.

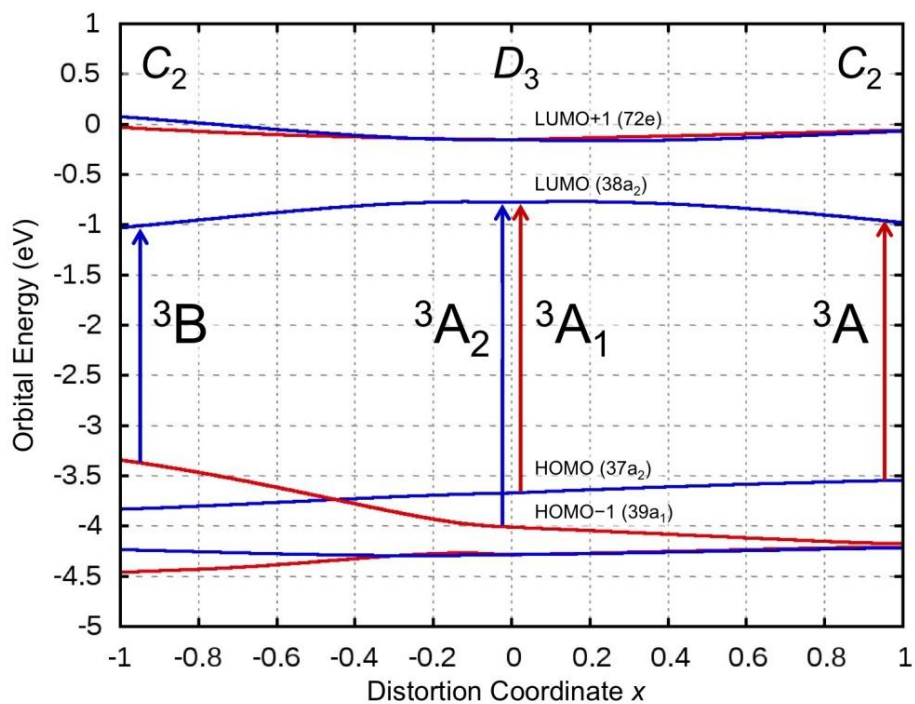


Fig. SI_2: Correlation diagram showing the energies of the frontier orbitals as a function of the distortion coordinate x (B3LYP/TZVP level). The orbitals exhibit either a (red) or b (blue) symmetry.

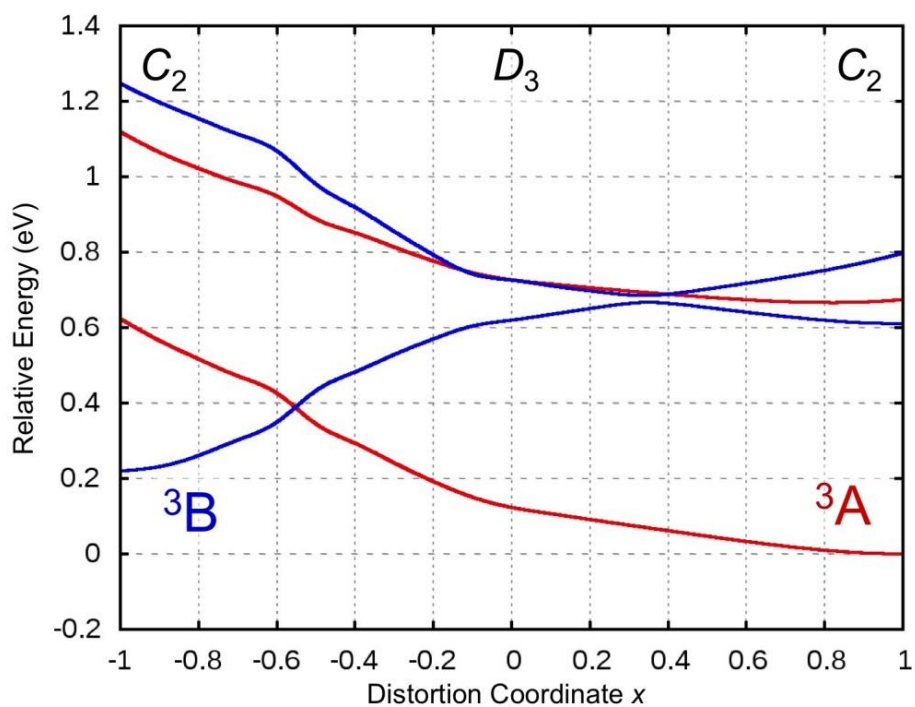


Fig. SI_3: Energies of low-lying 3A (red) and 3B (blue) excited states as a function of the distortion coordinate x (B3LYP/TZVP level; energies are given relative to the lowest triplet state in its optimized C_2 -symmetric geometry).

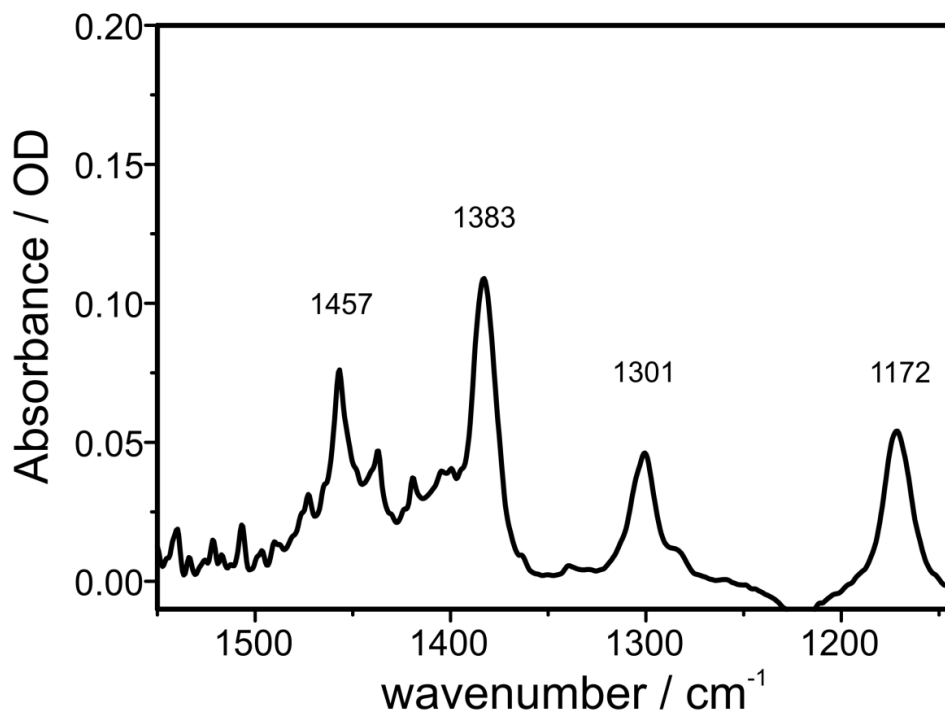


Fig. SI_4: Steady state FTIR spectrum of **1** in DMSO-d₆ in the relevant region of the time-resolved measurements; solvent contributions are subtracted (a negative absorbance occurs at 1220 cm⁻¹ due to a strong DMSO-d₆ absorption). Note that below 1100 cm⁻¹ IR transitions are hidden by the solvent, and between 1500 cm⁻¹ and the region of the CH stretching vibrations no vibrational transitions are observed.

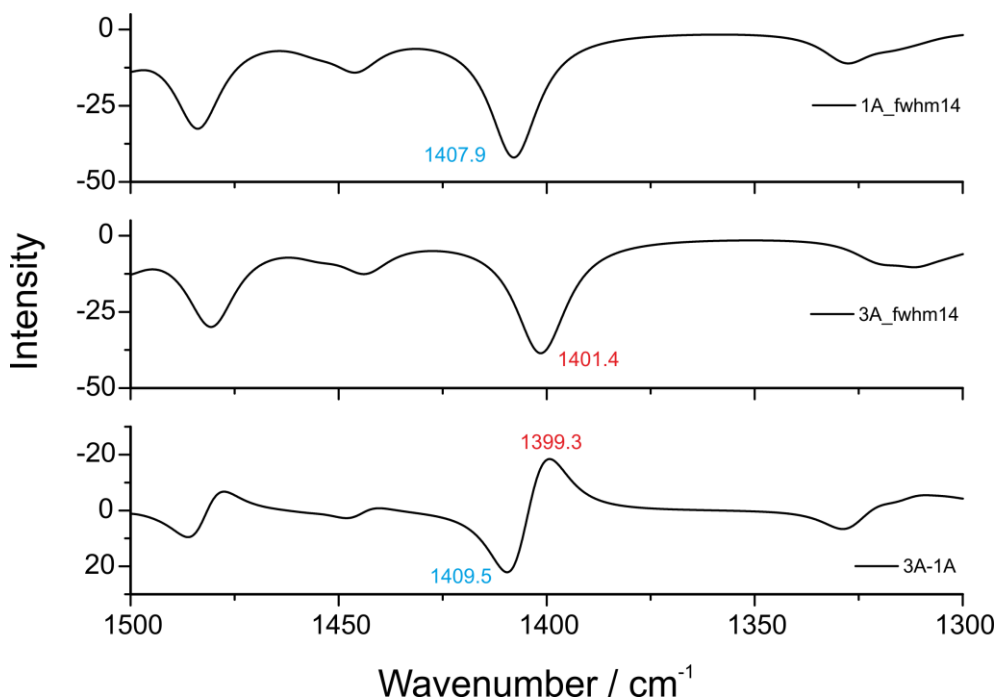


Fig. SI_5: This graph illustrates how the apparent peaks observed in the IR difference spectrum (bottom) of the electronic ground state (¹A, top) and the excited state (³A, middle) spectrum are shifted with respect to the peaks observed in the corresponding “pure” spectra. The apparent peak positions of the difference spectra are mentioned in the manuscript. For comparison between experiment and theory always this shift of the spectra has to be taken into account.

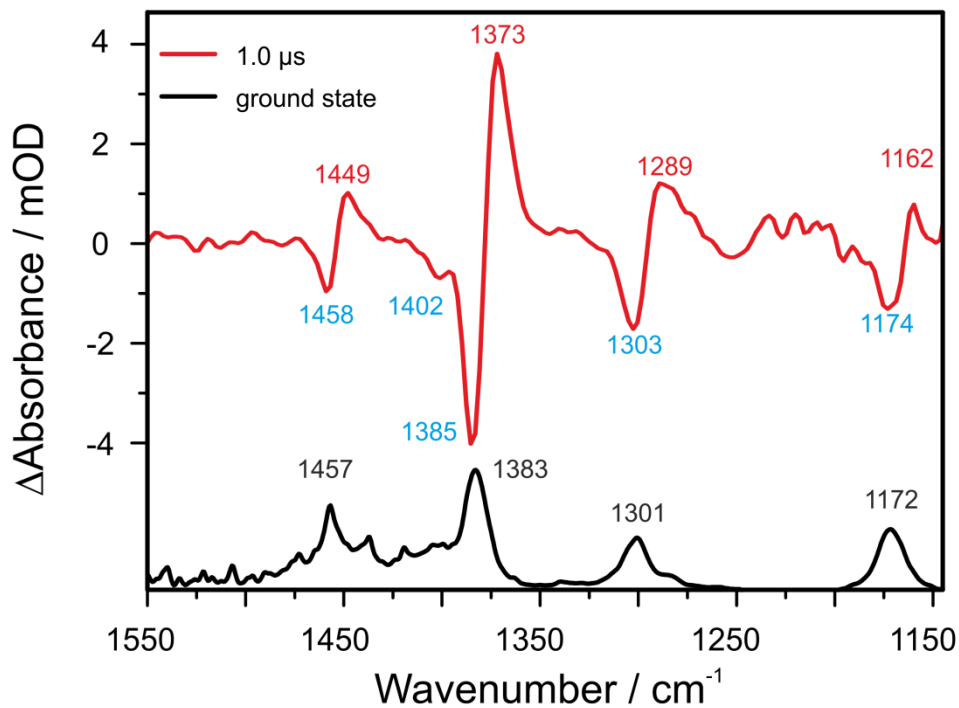


Fig. SI_6: Ground state FTIR spectrum (bottom) and TR-FTIR spectrum 1.0 μs after UV excitation at 355 nm (top).

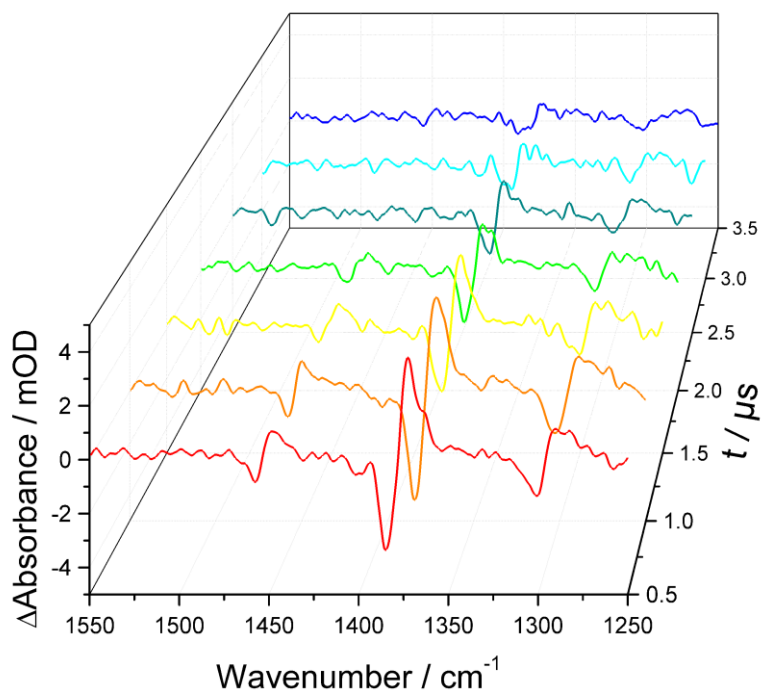


Fig. SI_7: Transient IR spectra in the region from 500 ns to 3.5 μs in steps of 500 ns. The spectra show the decay of the long-lived ^3A state.

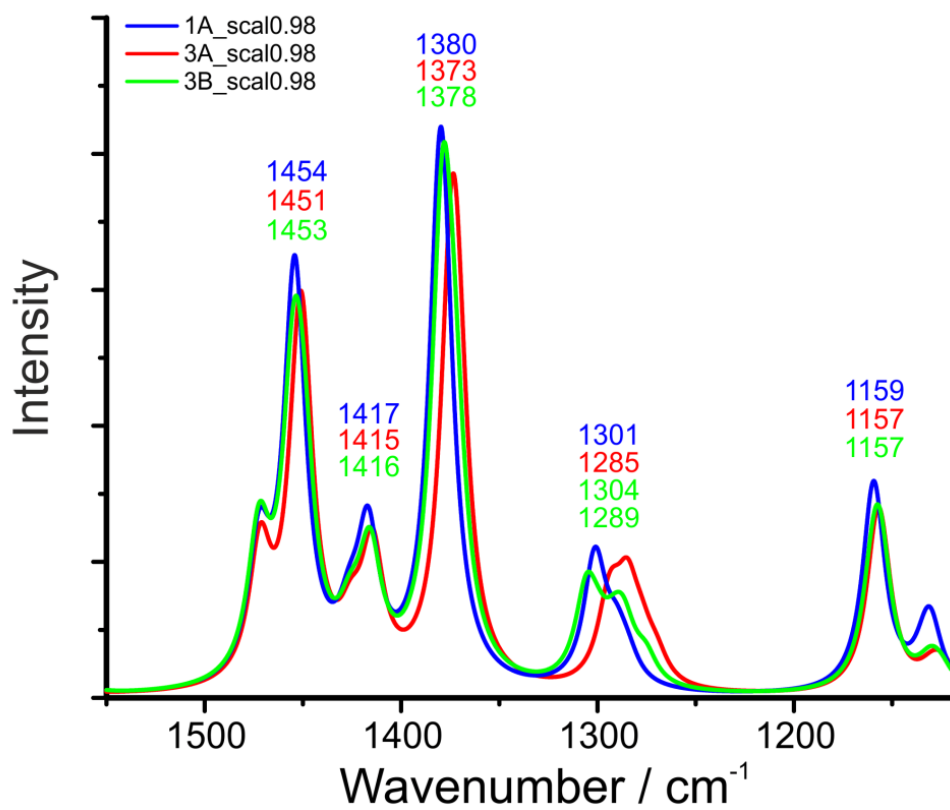
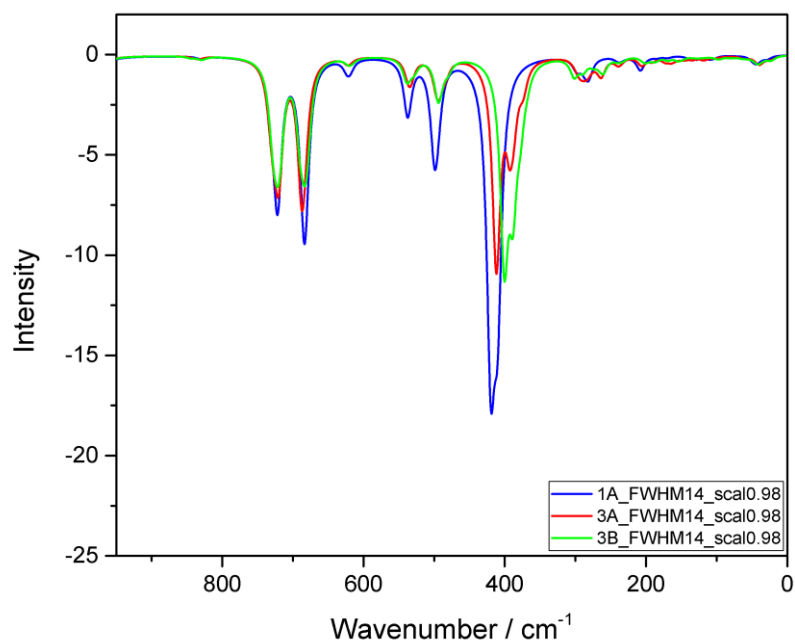


Fig. SI_8: Calculated spectra for the 1A (blue), 3A (red) and 3B (green) states (Lorentzian functions with a FWHM of 14 cm^{-1} are used).



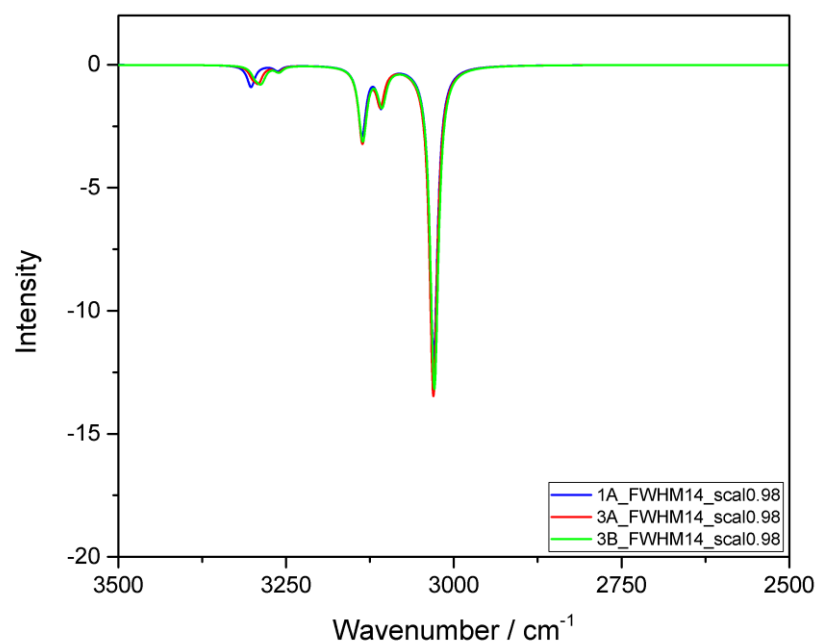
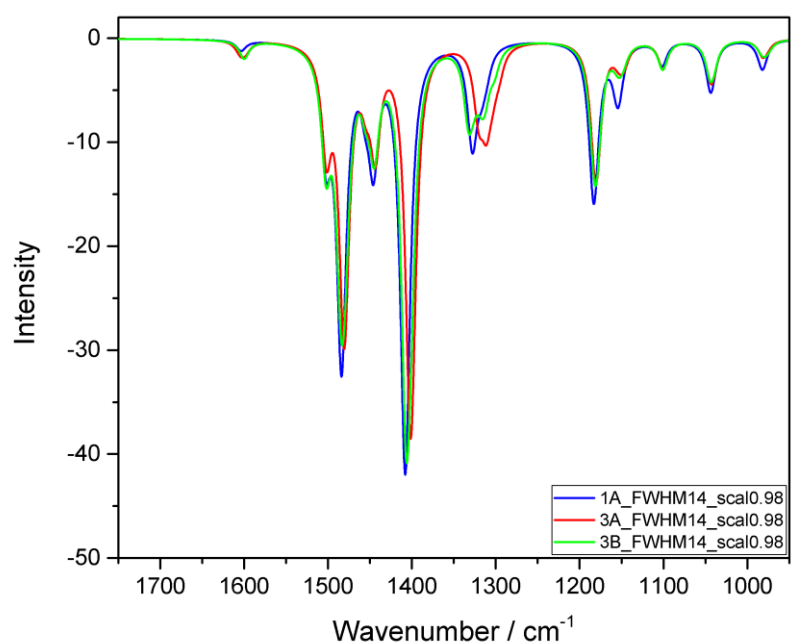


Fig. SI_9: Calculated IR spectra for the 1A , 3A , and 3B states in the complete IR region up to 3500 cm^{-1} . No transitions are observed in the region from 1700 to 2500 cm^{-1} . It is obvious that the red and green curves (3A and 3B states) show differences only in the measured region from 1100 to 1600 cm^{-1} and in the region around 400 cm^{-1} which is not accessible with our IR set-ups.

Table SI_1: Cartesian coordinates (in Å) of the 1A_1 ground state of $[Pd_3\{Si(mt^{Mc})_3\}_2]$. The B3LYP/TZVP energy is -4938.263624 Hartree.

H	-5.5177782	0.6889601	-4.3269591
H	-5.4102038	1.0737491	-2.5704154
H	-5.5177782	-0.6889601	4.3269591
H	-4.7836185	2.2376234	-3.7717760
C	-4.9030875	1.1635666	-3.5460714
H	-4.7836185	-2.2376234	3.7717760
C	-4.9030875	-1.1635666	3.5460714
H	-5.4102038	-1.0737491	2.5704154
H	-3.8079458	0.9333994	5.1210978
N	-3.6131742	0.5032239	-3.5024360
H	-3.8079458	-0.9333994	-5.1210978
N	-3.6131742	-0.5032239	3.5024360
C	-3.1778529	0.5215421	4.3354879
C	-3.1778529	-0.5215421	-4.3354879
S	-2.7110267	2.0146202	-1.4170612
C	-2.6260674	0.7920709	-2.6005028
C	-2.6260674	-0.7920709	2.6005028
C	-1.9199457	0.8485875	3.9328329
S	-2.7110267	-2.0146202	1.4170612
C	-1.9199457	-0.8485875	-3.9328329
H	-1.2486690	1.6082782	4.3191649
H	0.4539706	5.2615468	3.7717760
N	-1.5752732	-0.0368514	-2.8590270
N	-1.5752732	0.0368514	2.8590270
S	-0.3891990	3.3551281	1.4170612
H	-0.7684752	1.8855182	-4.3191649
H	-1.2486690	-1.6082782	-4.3191649
Pd	-0.8123350	1.4070056	0.0000000
C	1.4438655	4.8279816	3.5460714
H	2.1622321	5.1230162	4.3269591
H	1.7752079	5.2222485	2.5704154
C	0.2250745	2.0870155	-3.9328329
Pd	-0.8123350	-1.4070056	0.0000000
C	0.6270802	2.6702765	2.6005028
H	-0.7684752	-1.8855182	4.3191649
N	1.3707824	3.3807126	3.5024360
H	1.0956253	3.7644775	-5.1210978
Si	0.0000000	0.0000000	-1.8098837
Si	0.0000000	0.0000000	1.8098837
S	-0.3891990	-3.3551281	-1.4170612
C	1.1372578	3.0128724	-4.3354879
N	0.7557223	1.3826523	-2.8590270
N	0.8195509	1.3458009	2.8590270
C	2.0405951	2.4913303	4.3354879
C	0.2250745	-2.0870155	3.9328329
N	0.8195509	-1.3458009	-2.8590270
C	0.6270802	-2.6702765	-2.6005028
C	1.6948712	1.2384280	3.9328329
H	2.7123205	2.8310781	5.1210978
N	0.7557223	-1.3826523	2.8590270
C	1.9989872	1.8782057	-2.6005028
N	2.2423918	2.8774887	-3.5024360
Pd	1.6246701	0.0000000	0.0000000
H	2.0171443	0.2772400	4.3191649
H	1.7752079	-5.2222485	-2.5704154

C	1.6948712	-1.2384280	-3.9328329
N	1.3707824	-3.3807126	-3.5024360
H	0.4539706	-5.2615468	-3.7717760
H	2.0171443	-0.2772400	-4.3191649
C	1.1372578	-3.0128724	4.3354879
H	1.0956253	-3.7644775	5.1210978
C	1.4438655	-4.8279816	-3.5460714
H	3.3555461	4.4340560	-4.3269591
C	2.0405951	-2.4913303	-4.3354879
C	3.4592220	3.6644151	-3.5460714
C	1.9989872	-1.8782057	2.6005028
S	3.1002257	1.3405078	-1.4170612
H	2.7123205	-2.8310781	-5.1210978
H	3.6349959	4.1484994	-2.5704154
N	2.2423918	-2.8774887	3.5024360
H	2.1622321	-5.1230162	-4.3269591
H	4.3296479	3.0239235	-3.7717760
S	3.1002257	-1.3405078	1.4170612
C	3.4592220	-3.6644151	3.5460714
H	3.3555461	-4.4340560	4.3269591
H	4.3296479	-3.0239235	3.7717760
H	3.6349959	-4.1484994	2.5704154

Table SI_2: Cartesian coordinates (in Å) of the 3A state.
The B3LYP/TZVP energy is -4938.197791 Hartree.

H	0.8748276	-4.1871795	-5.5984547
H	1.2459921	-2.4357379	-5.3953101
H	-0.8748276	4.1871795	-5.5984547
H	2.4143738	-3.6600678	-4.8248996
C	1.3396363	-3.4361616	-4.9405572
H	-2.4143738	3.6600678	-4.8248996
C	-1.3396363	3.4361616	-4.9405572
H	-1.2459921	2.4357379	-5.3953101
H	0.7303072	5.1009991	-3.9431038
N	0.6690034	-3.4657344	-3.6550935
H	-0.7303072	-5.1009991	-3.9431038
N	-0.6690034	3.4657344	-3.6550935
C	0.3415322	4.3379719	-3.2720341
C	-0.3415322	-4.3379719	-3.2720341
S	2.1384931	-1.3996620	-2.6565499
C	0.9358540	-2.6087381	-2.6217803
C	-0.9358540	2.6087381	-2.6217803
C	0.6893185	4.0048788	-1.9992719
S	-2.1384931	1.3996620	-2.6565499
C	-0.6893185	-4.0048788	-1.9992719
H	1.4509870	4.4317117	-1.3549825
H	5.2926646	3.7721119	0.6701934
N	0.1014426	-2.9370974	-1.5914833
N	-0.1014426	2.9370974	-1.5914833
S	3.3353873	1.6342837	-0.4930266
H	1.7579743	-4.5528915	-0.5265018
H	-1.4509870	-4.4317117	-1.3549825
Pd	1.3745789	0.0779309	-0.8381850
C	4.7938913	3.5105848	1.6195270
H	5.0821162	4.2323757	2.3999153

H	5.1229008	2.4986486	1.9108596
C	2.0736286	-4.0240618	0.3676504
Pd	-1.3745789	-0.0779309	-0.8381850
C	2.6489539	2.7553691	0.5927308
H	-1.7579743	4.5528915	-0.5265018
N	3.3529018	3.5449887	1.4634546
H	3.8320845	-5.0993035	1.2242639
Si	-0.0001430	-1.9390473	0.0004931
Si	0.0001430	1.9390473	0.0004931
S	-3.3353873	-1.6342837	-0.4930266
C	3.0940013	-4.2997428	1.2230307
N	1.4309116	-2.8694562	0.8016883
N	1.3233815	3.0498118	0.7529966
C	2.4639145	4.3423272	2.1721433
C	-2.0736286	4.0240618	0.3676504
N	-1.3233815	-3.0498118	0.7529966
C	-2.6489539	-2.7553691	0.5927308
C	1.2138115	4.0332206	1.7295383
H	2.8006672	5.0495468	2.9273365
N	-1.4309116	2.8694562	0.8016883
C	2.0646233	-2.4307275	1.9332635
N	3.0862559	-3.3049186	2.1925416
Pd	0.0000000	0.0000000	1.4872471
H	0.2509468	4.4269755	2.0415379
H	-5.1229008	-2.4986486	1.9108596
C	-1.2138115	-4.0332206	1.7295383
N	-3.3529018	-3.5449887	1.4634546
H	-5.2926646	-3.7721119	0.6701934
H	-0.2509468	-4.4269755	2.0415379
C	-3.0940013	4.2997428	1.2230307
H	-3.8320845	5.0993035	1.2242639
C	-4.7938913	-3.5105848	1.6195270
H	4.7620088	-3.9814347	3.2283178
C	-2.4639145	-4.3423272	2.1721433
C	4.0102868	-3.1799312	3.3028538
C	-2.0646233	2.4307275	1.9332635
S	1.6918532	-1.0913204	2.9224468
H	-2.8006672	-5.0495468	2.9273365
H	4.5107330	-2.1973411	3.2723194
N	-3.0862559	3.3049186	2.1925416
H	-5.0821162	-4.2323757	2.3999153
H	3.4757379	-3.2614805	4.2652531
S	-1.6918532	1.0913204	2.9224468
C	-4.0102868	3.1799312	3.3028538
H	-4.7620088	3.9814347	3.2283178
H	-3.4757379	3.2614805	4.2652531
H	-4.5107330	2.1973411	3.2723194

Table SI_3: Cartesian coordinates (in Å) of the 3B state.
The B3LYP/TZVP energy is -4938.189711 Hartree.

H	0.9962251	-4.0225473	-5.5372223
H	1.4124360	-2.2934011	-5.2486265
H	-0.9962251	4.0225473	-5.5372223
H	2.5028232	-3.5773106	-4.6552960
C	1.4447118	-3.3116778	-4.8255032
H	-2.5028232	3.5773106	-4.6552960

C	-1.4447118	3.3116778	-4.8255032
H	-1.4124360	2.2934011	-5.2486265
H	0.7395342	4.9339027	-4.0097373
N	0.6975424	-3.3609359	-3.5844263
H	-0.7395342	-4.9339027	-4.0097373
N	-0.6975424	3.3609359	-3.5844263
C	0.3625962	4.2111836	-3.2890849
C	-0.3625962	-4.2111836	-3.2890849
S	2.1505536	-1.3617144	-2.4227853
C	0.9286421	-2.5476249	-2.5085016
C	-0.9286421	2.5476249	-2.5085016
C	0.7723236	3.9071530	-2.0269947
S	-2.1505536	1.3617144	-2.4227853
C	-0.7723236	-3.9071530	-2.0269947
H	1.5872068	4.3226097	-1.4426444
H	5.3033516	3.8929305	0.6240733
N	0.0281200	-2.8815269	-1.5415676
N	-0.0281200	2.8815269	-1.5415676
S	3.3575724	1.6358085	-0.3679581
H	1.4263405	-4.7492574	-0.3743776
H	-1.5872068	-4.3226097	-1.4426444
Pd	1.4062096	0.0135065	-0.5308291
C	4.8283695	3.6658617	1.5945227
H	5.1179768	4.4284488	2.3347284
H	5.1846177	2.6747536	1.9236783
C	1.8816132	-4.1786087	0.4302795
Pd	-1.4062096	-0.0135065	-0.5308291
C	2.6809646	2.8137802	0.6544196
H	-1.4263405	4.7492574	-0.3743776
N	3.3848982	3.6643791	1.4671995
H	3.6512007	-5.3182137	1.1805215
Si	-0.0483792	-1.9335142	0.0783896
Si	0.0483792	1.9335142	0.0783896
S	-3.3575724	-1.6358085	-0.3679581
C	2.9747452	-4.4659405	1.1885621
N	1.3747155	-2.9492718	0.8323310
N	1.3533955	3.0913030	0.8196644
C	2.4909816	4.4801654	2.1496915
C	-1.8816132	4.1786087	0.4302795
N	-1.3533955	-3.0913030	0.8196644
C	-2.6809646	-2.8137802	0.6544196
C	1.2407091	4.1225107	1.7461219
H	2.8250788	5.2326471	2.8611796
N	-1.3747155	2.9492718	0.8323310
C	2.1635231	-2.4785483	1.8336830
N	3.1472130	-3.3996690	2.0628621
Pd	0.0000000	0.0000000	1.9580860
H	0.2773821	4.5164646	2.0562196
H	-5.1846177	-2.6747536	1.9236783
C	-1.2407091	-4.1225107	1.7461219
N	-3.3848982	-3.6643791	1.4671995
H	-5.3033516	-3.8929305	0.6240733
H	-0.2773821	-4.5164646	2.0562196
C	-2.9747452	4.4659405	1.1885621
H	-3.6512007	5.3182137	1.1805215
C	-4.8283695	-3.6658617	1.5945227
H	4.8606231	-4.1340547	2.9935198
C	-2.4909816	-4.4801654	2.1496915
C	4.2090482	-3.2475335	3.0395183

C	-2.1635231	2.4785483	1.8336830
S	2.0259751	-1.0003265	2.6835643
H	-2.8250788	-5.2326471	2.8611796
H	4.8017519	-2.3422998	2.8230059
N	-3.1472130	3.3996690	2.0628621
H	-5.1179768	-4.4284488	2.3347284
H	3.7891605	-3.1507458	4.0555210
S	-2.0259751	1.0003265	2.6835643
C	-4.2090482	3.2475335	3.0395183
H	-4.8606231	4.1340547	2.9935198
H	-3.7891605	3.1507458	4.0555210
H	-4.8017519	2.3422998	2.8230059