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Supplementary Information

Further details of Franck-Condon fitting procedure

The results of the pure *ab initio* Franck-Condon simulations were used to inform a fitting procedure in which the simulated spectra were fitted to the experimental spectra for both σ- and π-complexes of 4FT-NH_3. In the case of the σ-complex, this was achieved by shifting the position of the ammonia along both the in-plane bend and 11 mode normal coordinates in the S_1 state. For the π-complex, the ammonia was shifted along the long and short axis bending mode normal coordinates in the S_0 state.

The choice of whether to adjust the geometry of ground or excited state is somewhat arbitrary because the changes in geometry that are reflected in the simulation will in practice be aggregated across both states. For the σ-complex, the S_1 state was chosen because it was felt that the optimised excited state geometries are subject to greater error than the optimised ground state geometries. However, for the π-complex, the ground state was chosen for the fit because deviations to the S_1 state geometry along the short axis bending mode coordinate would have resulted in a much more asymmetric excited state structure than was predicted by the *ab initio* calculations. As the ground state structure was already highly asymmetric, it was felt that it would be the more appropriate choice.

The Franck-Condon simulations resulting from the fitting procedure are compared to experiment and to the pure *ab initio* results in Figures 6 and 7 in the article, whilst changes in key geometrical parameters upon excitation are compared to the *ab initio* values in Table 6.

Cartesian Coordinates in Ångströms for the σ-complex

Counterpoise corrected MP2/cc-pVTZ (Gaussian 03)

S_0

C	0.036503000	0.001416000	0.016463000
C	0.030030000	0.006485000	1.402092000
C	1.197188000	0.009748000	2.147905000
C	2.416021000	0.011095000	1.473313000
C	2.472692000	0.009332000	0.077584000
C	1.269200000	0.002803000	-0.632791000
F	-1.155057000	0.001994000	2.052500000
C	3.792304000	0.045477000	-0.641427000
N	-3.447120000	-0.025818000	-0.371672000
H	1.144599000	0.007164000	3.226931000
H	3.335846000	0.009838000	2.044185000
H	1.291738000	-0.005029000	-1.715231000
H	-0.900054000	-0.007325000	-0.524713000
H	-3.140194000	-0.019320000	0.593097000
H	-4.055284000	0.775724000	-0.477127000
H	-4.041642000	-0.838354000	-0.470582000
H	3.734180000	-0.478406000	-1.593799000
H	4.096305000	1.072354000	-0.847629000
H	4.576675000	-0.417815000	-0.045727000

RICC2/def2-TZVPP (Turbomole 5.9)

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S_0

C	0.5969737	0.7157046	0.0036233
C	-0.5003869	1.5592111	-0.0022961
C	-1.7722909	0.9906164	-0.0093604
C	-1.9471427	-0.3948474	-0.0112612
C	-0.8088057	-1.2053114	-0.0087071
C	0.4747155	-0.6638144	-0.0014604
H	-0.3574299	2.6281848	-0.0047074
H	-2.6384618	1.6369199	-0.0176554
H	-0.9231434	-2.2801489	-0.0165760
H	1.3616688	-1.2805105	-0.0030596
F	1.8384833	1.2660331	0.0076027
N	3.8309544	-1.2898983	-0.0006952
H	3.6050609	-0.3037529	0.0031300
H	4.4141916	-1.4551993	0.8080631
H	4.4145947	-1.4488157	-0.8104397
C	-3.3214585	-0.9987880	0.0152377
H	-3.3445041	-1.9388693	-0.5301038
H	-3.6370259	-1.2013099	1.0375413
H	-4.0511061	-0.3275738	-0.4303322

S_1

C	0.5842970	0.7239361	-0.0006815
C	-0.5256229	1.6048829	-0.0039392
C	-1.8210298	1.0109575	-0.0223158
C	-1.9516180	-0.4160515	-0.0265307
C	-0.7965585	-1.2620403	-0.0353212
C	0.5100265	-0.6894187	-0.0143219
H	-0.3662269	2.6693798	0.0107559
H	-2.7077927	1.6245091	-0.0265186
H	-0.9246157	-2.3326735	-0.0478491
H	1.4183622	-1.2713744	-0.0072281
F	1.8080146	1.2828427	0.0190146
N	3.8813312	-1.2635403	0.0078955
H	3.6686881	-0.2747396	0.0176467
H	4.4636390	-1.4410826	0.8147222
H	4.4606654	-1.4255780	-0.8043202
C	-3.3050588	-1.0244310	0.0472854
H	-3.3202265	-2.0043385	-0.4251083
H	-3.6032870	-1.1586352	1.0905012
H	-4.0487380	-0.3857206	-0.4248727

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Cartesian Coordinates in Ångströms for the π-complex

Counterpoise corrected MP2/cc-pVTZ (Gaussian 03)

S_0

C	1.018273000	-0.125906000	1.220070000
C	1.674905000	-0.008951000	0.005142000
C	1.044670000	-0.296217000	-1.195406000
C	-0.286589000	-0.707577000	-1.168272000
C	-0.988220000	-0.829928000	0.034354000
C	-0.312678000	-0.537671000	1.222234000
F	2.960903000	0.387886000	-0.008823000
C	-2.442167000	-1.204323000	0.045042000
N	-1.903781000	2.382234000	-0.116570000
H	1.591859000	-0.203791000	-2.122399000
H	-0.787596000	-0.935287000	-2.100593000
H	-0.834308000	-0.632330000	2.166160000
H	1.545616000	0.096825000	2.136364000
H	-1.537191000	2.467442000	0.823152000
H	-1.899208000	3.319116000	-0.499609000
H	-1.198742000	1.865843000	-0.629117000
H	-2.687174000	-1.852318000	-0.794557000
H	-2.707301000	-1.722238000	0.964992000
H	-3.056775000	-0.306432000	-0.027986000

RICC2/def2-TZVPP (Turbomole 5.9)

S_0

C	0.0108844	0.0693761	1.5271551
C	-1.1788772	0.3906034	0.8941318
C	-1.1436728	0.7326641	-0.4564495
C	0.0558970	0.7511440	-1.1725711
C	1.2334327	0.4301129	-0.4929579
C	1.2233161	0.0868398	0.8570746
F	-0.0108448	-0.2619985	2.8358346
H	-2.1024162	0.3779812	1.4512534
H	-2.0661470	0.9838431	-0.9605697
H	2.1740180	0.4472573	-1.0253037
H	2.1307997	-0.1574692	1.3864769
N	-0.2049298	-2.4482885	-1.6939979
H	0.7464867	-2.4985356	-1.3545218
H	-0.5972468	-3.3732273	-1.5772277
H	-0.6913913	-1.8431450	-1.0442116
C	0.0705944	1.0392675	-2.6437032
H	-0.7429948	1.7047832	-2.9206069
H	1.0083759	1.5009324	-2.9421942
H	-0.0435161	0.1103521	-3.2005338

S_1

C	-0.0050750	0.1923811	1.4506484
C	-1.2626409	0.2540689	0.8033187
C	-1.2586193	0.5114665	-0.5992153
C	-0.0145043	0.6420991	-1.2960796
C	1.2337878	0.5879481	-0.5955931
C	1.2481517	0.3362606	0.8078274
F	0.0000336	-0.0305426	2.7703322
H	-2.1650684	0.1414785	1.3798445
H	-2.1827748	0.5706380	-1.1516854
H	2.1543248	0.7082007	-1.1441827
H	2.1538474	0.2801533	1.3875513
N	0.0547745	-2.4813417	-1.0689256
H	0.8511230	-2.0724500	-0.5967212
H	0.1224459	-3.4828379	-0.9436253
H	-0.7568499	-2.1749981	-0.5478436
C	-0.0158435	0.7369430	-2.7758305
H	-0.9170105	1.2264754	-3.1392204
H	0.8591890	1.2722141	-3.1384700
H	0.0096527	-0.2732516	-3.1933624