Magnetic anisotropy of a Co^{II} Single Ion Magnet with distorted trigonal prismatic coordination: Theory and Experiment

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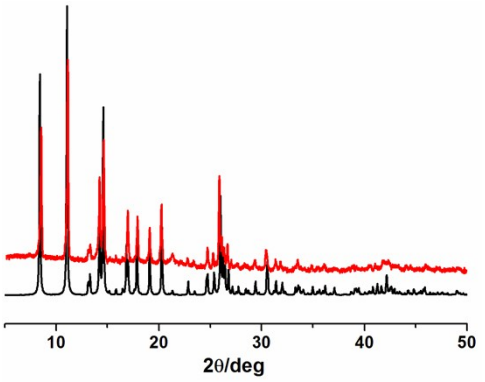

Fig S1 The powder XRD of compound **1**

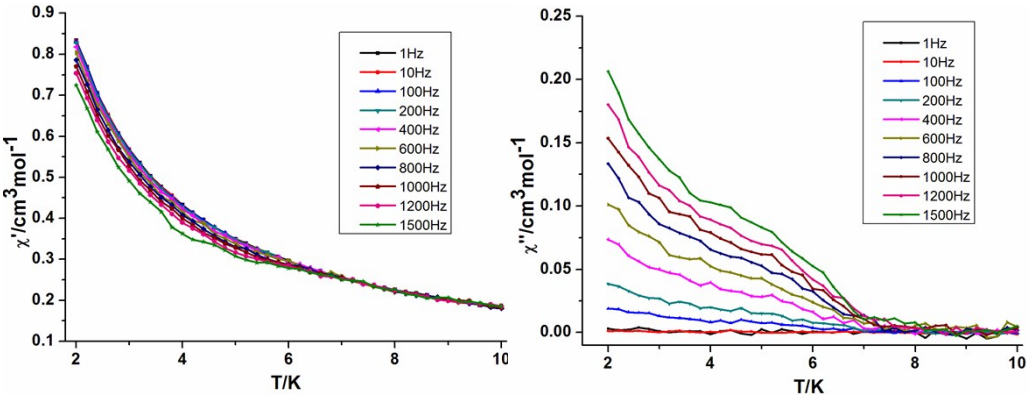

Fig S2 Plots of χ' (left) and χ'' (right) vs frequency under different dc magnetic fields for **1** in zero dc field

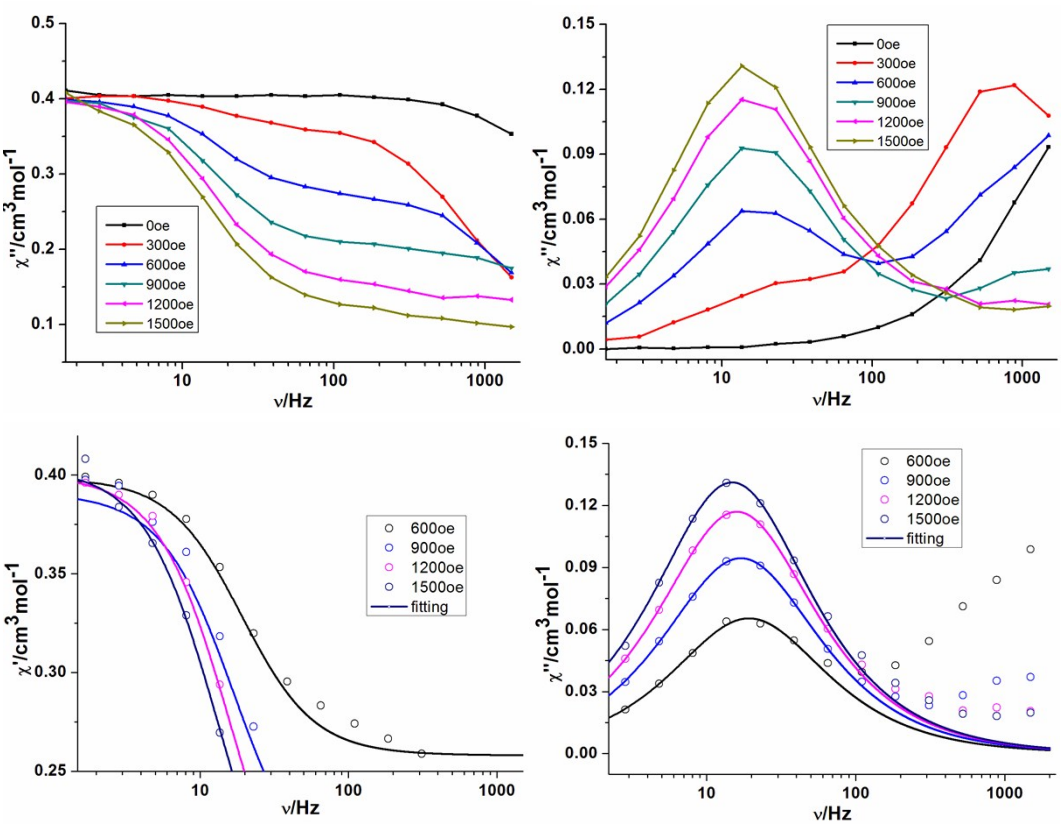

Fig S3 Plots of χ' (upper left) and χ'' (upper right) vs frequency under different dc magnetic fields for **1** at 4.3 K; Fitted Plots of χ' (lower left) and χ'' (lower right) vs frequency in selected dc magnetic fields for **1** at 4.3 K

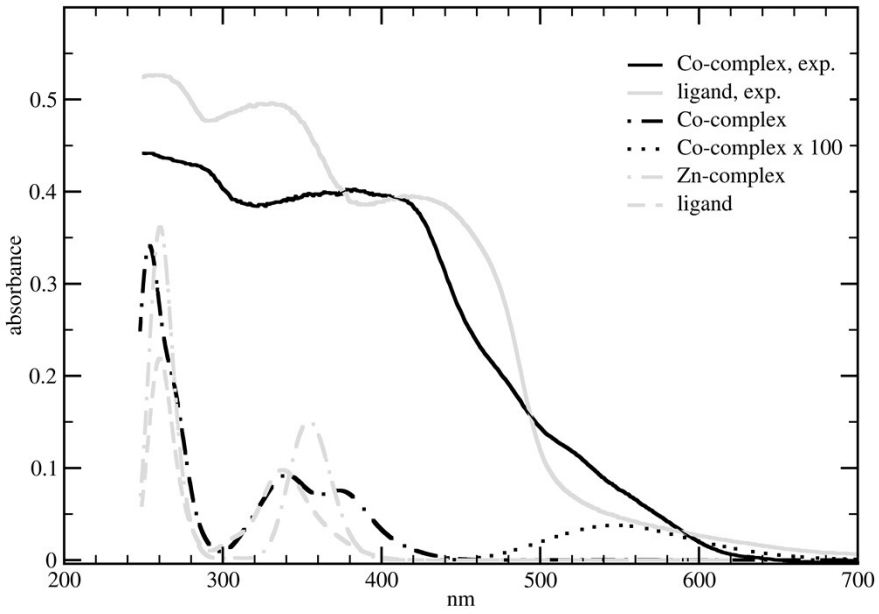

Fig. S4 Experimental UV/VIS spectra of the ligand molecule and the Co complex and the respective calculated spectra obtained with time dependent density functional theory (TDDFT). Additional TDDFT results for a model complex where Co was substituted by Zn. In the TDDFT calculations, as well as for the geometry optimisation of the ligand molecule, the B3-LYP functional, def2-TZVPP bases and an integration grid of size m4was used. The calculations were performed with the program package TURBOMOLE. The spectrum of the complex is dominated by ligand transitions. Influence of the Co ion occurs in the splitting in the range between 300 nm and 400 nm. An additional very weak peak is observed between 500 nm and 600 nm.

Table S1 Field-dependent fit parameter for the generalized Debye-model

$\mu_0 H$ / Oe	χ_T / cm^3mol^{-1}	χ_S / cm^3mol^{-1}	α	$2\pi\times\tau$ / s	$2\pi\times\tau \mid_{\alpha=0}$ / s
600	0.398903	0.257969	0.0475834	0.0521957	0.0521957
900	0.391389	0.186784	0.0507055	0.0590476	0.0590476
1200	0.400840	0.148245	0.0490920	0.0628693	0.0628693
1500	0.390220	0.105824	0.0517360	0.0675013	0.0675013

Table S2 Temperature dependent fit parameter for the generalized Debye-model

T / K	χ_T / cm^3mol^{-1}	χ_S / cm^3mol^{-1}	α	$2\pi\times\tau$ / s	$2\pi\times\tau \mid_{\alpha=0}$ / s
3.8	0.437001	0.15502	0.0735649	0.175133	0.174934
4.0	0.419521	0.152916	0.0579084	0.119207	0.120045
4.2	0.40439	0.146202	0.0511255	0.0763394	0.076054
4.4	0.388501	0.140825	0.0449693	0.0499268	0.0501665
4.6	0.372482	0.133795	0.0371786	0.0299989	0.0300101
4.8	0.358514	0.125242	0.0388919	0.0180132	0.0179468
5.0	0.345661	0.117794	0.0402048	0.0107559	0.0108505
5.2	0.333662	0.109693	0.0492966	0.00649022	0.00652676
5.4	0.322742	0.103908	0.0404562	0.003899	0.00393807
5.6	0.312043	0.0934408	0.057716	0.00237807	0.0023917
5.8	0.302519	0.0952547	0.0256652	0.00145008	0.00145808
6.0	0.292821	0.0927703	0.0170987	0.000947623	0.000958081

Accuracy of the quantum chemical calculations

In order to assess the accuracy of our computational protocol, we performed various test calculations where we tested our active space and the effect of energy corrections to the shifted spin-orbit CI method SOCI*.

1) we included a double d-shell into the CASSCF calculation. However, In all quartet states, the occupation summed over these set of orbitals stayed well below 0.002.

2) we included those two ligand orbitals which had significant d-contributions to the active space but those remained doubly occupied.

3) We performed ACPF calculations on the lowest 7 quartet states and calculated the magnetic data from SOCI calculations were the ACPF energies were used on the diagonal matrix elements. (see Table S3 and Figures S6)

Table S3 Energies in cm^{-1} of the seven lowest quartet states and the corresponding Kramers doublets obtained at three different levels of accuracy.

State	CASSCF	ACPF(2)	ACPF(7)	SOCI	CASSCF	ACPF(2)	ACPF(7)
$^4A_1$	0	0	0	E_1	0	0	0
				E_2	101	82	86
$^4A_1$	1567	1925	1923	E_3	1675	2001	2014
				E_4	1884	2189	2192
$^4A_1$	4667	5052	5675	E_5	4435	4764	5428
				E_6	4773	5102	5752
$^4A_1$	4915	5273	5981	E_7	5188	5516	6209
				E_8	5492	5821	6500
$^4A_1$	6340	6698	7419	E_9	6506	6834	7561
				E_{10}	6641	6969	7682
$^4A_1$	9409	9767	11169	E_{11}	9357	9686	11031
				E_{12}	9668	9998	11365
$^4A_1$	10180	10538	11755	E_{13}	10508	10838	12052
				E_{14}	10699	11028	12277
				D	-50	-41	-43
				g1	8.14	7.86	7.86
				g2	0.08	0.04	0.00
				g3	0.07	0.05	0.00

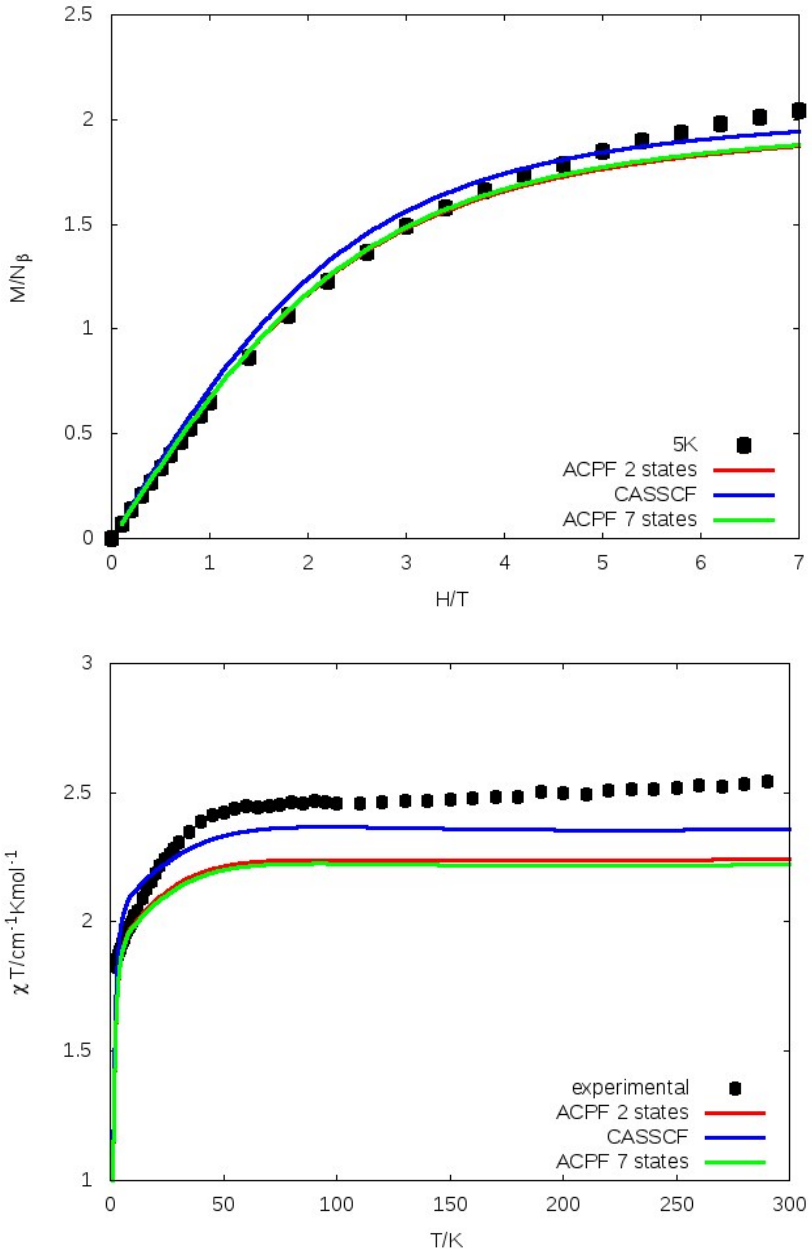

Fig. S5 Comparison of three levels of quantum chemical calculations. Upper panel: Magnetization at 5 K. Lower panel: Magnetic susceptibilities. The ACPF calculations with 2 and 7 states behave identically. Inclusion of dynamic correlation is most important for the first excitation energy.

Details on the Calculations of the model complexes

Model a

Coordinates (Å)

```
   23

CO     0.007907    -0.330364    -0.038796
 O     0.023528    -1.323634     1.709083
 O    -0.014123    -0.954574    -1.940756
 N     0.781437     1.465845     1.103933
 N    -2.109012    -0.743904    -0.021746
 N     2.118327    -0.755834    -0.127207
 N    -0.793752     1.676305    -0.791076
 H    -0.609024    -1.993722     2.015783
 H    -0.689815    -0.765597    -2.610971
 H     1.330533     2.078596     0.505341
 H     1.397513     1.289185     1.899658
 H    -2.633401    -0.308341    -0.777502
 H    -2.578139    -0.433572     0.829444
 H     2.593679    -0.318323    -0.916953
 H     2.326043    -1.751999    -0.211377
 H    -1.407291     1.660123    -1.607807
 H    -0.076178     2.345344    -1.062774
 H     2.647074    -0.453741     0.688393
 H     0.701650    -1.280942     2.401822
 H    -2.329348    -1.737842    -0.099191
 H    -1.351955     2.143489    -0.079976
 H     0.053367     2.051496     1.507492
 H     0.610980    -1.557995    -2.374817
```

Energy levels (cm^{-1})

CASSCF	SOCI	SOCI*
0	0.00	0.00
	108.08	87.14
1423.90446	1556.97	1848.95
	1765.45	2035.00
5090.70693	4893.50	5189.58
	5189.94	5485.93
5527.71214	5766.81	6060.89
	6042.58	6338.57
6223.96052	6423.38	6719.06

	6590.15	6884.26
9201.48795	9279.12	9575.43
	9489.65	9785.93
10878.0557	11187.48	11483.75
	11280.75	11577.06

SOCI* wave functions, projected onto the $^4A_1$ (CASSCF) ground state

state	M_S=–3/2 (GS)		M_S=–1/2 (GS)		M_S=1/2 (GS)		M_S=3/2 (GS)	
	Re	Im	Re	Im	Re	Im	Re	Im
E_1	0.960	–0.000	0.000	–0.005	0.009	–0.001	–0.000	0.000
	0.000	0.000	0.009	0.001	–0.000	–0.005	0.960	0.000
E_2	–0.009	–0.001	–0.000	–0.002	0.988	0.000	–0.000	–0.000
	0.000	–0.000	0.988	0.000	0.000	–0.002	–0.009	0.001

Model b

Coordinates (Å)

```
   23

CO     0.003632    -0.320202    -0.036417
 O    -0.107898    -1.123401     1.884312
 O     0.108932    -0.745271    -2.069617
 N    -1.986137    -0.923812    -0.192217
 N     0.816982     1.493318     1.073572
 N     1.986721    -0.944811     0.006413
 N    -0.837848     1.669158    -0.755957
 H    -0.768661    -1.744473     2.231286
 H    -2.361458    -0.716231    -1.115617
 H    -2.618619    -0.476895     0.471549
 H     1.279813     2.166357     0.466615
 H     1.507567     1.330280     1.808520
 H     2.549242    -0.534949    -0.739232
 H     2.093438    -1.953995    -0.109382
 H    -0.142189     2.334032    -1.088386
 H    -1.339502     2.149534    -0.012045
 H    -0.029662    -0.135102    -2.811003
 H     2.490742    -0.735481     0.865617
 H     0.454208    -1.558003    -2.473895
 H     0.083501     2.009646     1.554677
 H    -2.147658    -1.925477    -0.075257
```

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 H     0.484931    -0.952367     2.632730
 H    -1.520080     1.638148    -1.516265
```

Energy levels (cm^{-1})

CASSCF	SOCI	SOCI*
0	0.00	0.00
	144.25	124.40
1164.78	1353.00	1534.22
	1597.14	1757.16
4858.82	4672.78	4857.61
	5018.70	5202.64
5001.74	5295.27	5480.01
	5592.17	5777.57
6979.51	7153.76	7338.98
	7227.62	7412.04
8322.03	8288.58	8474.09
	8648.40	8833.87
8673.34	9140.79	9326.28
	9386.44	9571.94

SOCI* wave functions, projected onto the $^4A_1$ (CASSCF) ground state

state	M_S=–3/2 (GS)		M_S=–1/2 (GS)		M_S=1/2 (GS)		M_S=3/2 (GS)	
	Re	Im	Re	Im	Re	Im	Re	Im
E_1	–0.000	–0.000	0.032	–0.009	0.000	0.003	0.940	0.000
	0.940	–0.000	–0.000	0.003	0.032	0.009	0.000	–0.000
E_2	–0.000	–0.000	0.983	0.000	–0.000	0.002	–0.032	0.009
	–0.032	0.009	0.000	0.002	0.983	0.000	0.000	–0.001

Model c

Coordinates (Å)

```
   23

CO     0.007261    -0.316557    -0.036820
 O    -0.141579    -1.115787     1.842659
 O     0.149640    -0.745567    -2.029019
 N    -1.945199    -0.924137    -0.151370
 N     0.895010     1.489052     1.155420
 N     1.953270    -0.937226    -0.034990
 N    -0.908619     1.680712    -0.838610
```

H	-0.663669	-1.883174	2.128198
H	-0.307944	-0.297873	-2.757925
H	-2.416763	-0.657175	-1.013364
H	-2.527741	-0.551235	0.598624
H	1.336490	2.158530	0.527952
H	1.607733	1.312647	1.863800
H	2.539322	-0.436473	-0.703516
H	2.078980	-1.925110	-0.263733
H	-1.613447	1.633279	-1.574660
H	-0.201419	2.311625	-1.212661
H	2.424322	-0.832853	0.861659
H	0.689937	-1.428651	-2.458469
H	0.311153	-0.811616	2.644901
H	0.176069	2.014025	1.650537
H	-2.073999	-1.936625	-0.105229
H	-1.368807	2.200188	-0.093384

Energy levels (cm^{-1})

CASSCF	SOCI	SOCI*
0.00	0.00	0.00
	175.38	153.26
923.25	1158.79	1305.01
	1431.29	1554.23
4763.68	4581.71	4732.90
	4939.09	5089.80
4839.42	5226.98	5377.78
	5529.37	5681.08
7479.18	7657.70	7809.19
	7731.34	7882.40
8660.21	8698.61	8850.39
	9036.54	9188.29
9151.79	9635.54	9787.31
	9851.38	10003.16

SOCI* wave functions, projected onto the $^4A_1$ (CASSCF) ground state

state	M_S=–3/2 (GS)		M_S=–1/2 (GS)		M_S=1/2 (GS)		M_S=3/2 (GS)	
	Re	Im	Re	Im	Re	Im	Re	Im
E_1	–0.000	–0.000	–0.044	0.009	–0.000	–0.002	0.920	0.000
	0.920	–0.000	0.000	0.002	–0.044	–0.009	0.000	–0.000
E_2	0.042	–0.009	0.000	0.003	0.978	–0.000	–0.000	0.002
	0.000	0.002	0.978	–0.000	–0.000	0.003	0.042	0.009

Model d

Coordinates (Å)

```
   23

CO     0.051632     0.032373    -0.042304
 O     1.129142     1.590022     0.954705
 O     0.121263    -0.811097    -2.008274
 N    -0.674477     1.781672    -1.039314
 N    -0.193698    -0.777627     1.923665
 N     1.924881    -1.002757    -0.014244
 N    -1.997317    -0.585977    -0.070364
 H     0.969230     2.546612     0.924964
 H    -1.247137     1.552122    -1.850124
 H     0.065989     2.377242    -1.411210
 H    -0.429336    -1.769629     1.947767
 H    -0.933843    -0.315455     2.451761
 H     2.612663    -0.552806    -0.618600
 H     1.824652    -1.945713    -0.387221
 H    -2.467243    -0.480664    -0.969513
 H    -2.563378    -0.037660     0.577045
 H     0.757285    -0.584518    -2.705288
 H     1.857896     1.491620     1.588204
 H    -0.410318    -1.532645    -2.380577
 H     0.623114    -0.698507     2.527660
 H     2.402837    -1.119861     0.877910
 H    -2.170898    -1.555867     0.192482
 H    -1.252940     2.399117    -0.469130
```

Energy levels (cm^{-1})

CASSCF	SOCI	SOCI*
0.00	0.00	0.00
	258.65	232.81
435.00	824.93	909.76
	1176.90	1234.94
5541.22	5541.09	5639.02
	5849.29	5946.58
5845.69	6161.87	6259.69
	6392.93	6490.88
6564.05	6713.52	6811.41
	6900.49	6998.11
6997.14	7439.99	7538.02

	7878.43	7976.49
8202.15	8732.18	8830.33
	8926.51	9024.65

SOCI* wave functions, projected onto the $^4A_1$ (CASSCF) ground state

state	M_S=–3/2 (GS)		M_S=–1/2 (GS)		M_S=1/2 (GS)		M_S=3/2 (GS)	
	Re	Im	Re	Im	Re	Im	Re	Im
E_1	0.825	0.000	–0.000	–0.000	0.003	0.008	–0.000	–0.000
	0.000	–0.000	0.003	–0.008	0.000	–0.000	0.825	–0.000
E_2	0.003	–0.001	0.932	–0.000	0.005	0.003	–0.001	0.005
	–0.001	0.005	–0.005	0.003	0.932	–0.000	–0.003	–0.001

Model e

For symmetry reasons the first two quartet states in the CASSCF calculation are degenerate. Therefore dynamic correlation effects were not considered. The shift of the energy of the third quartet state (from 4189.95cm^{-1} to 4788.33cm^{-1}) was negligible for the magnetic properties of the two lowest Kramers doublets of this complex.

Coordinates (Å)

```
 19

CO     0.000000     0.000000     0.000000
 O     1.662790     0.000000     1.347770
 O    -0.831393     1.440010     1.347770
 O    -0.831393    -1.440010     1.347770
 O     1.662790     0.000000    -1.347770
 O    -0.831393     1.440010    -1.347770
 O    -0.831393    -1.440010    -1.347770
 H     1.538031     0.000000     2.300540
 H     2.615550     0.000000     1.223010
 H    -0.769013     1.331970     2.300540
 H    -1.307780     2.265130     1.223010
 H    -0.769013    -1.331970     2.300540
 H    -1.307780    -2.265130     1.223010
 H     1.538031     0.000000    -2.300540
 H    -0.769013     1.331970    -2.300540
 H    -0.769013    -1.331970    -2.300540
 H     2.615550     0.000000    -1.223010
 H    -1.307780     2.265130    -1.223010
 H    -1.307780    -2.265130    -1.223010
```

Energy levels (cm^{-1})

CASSCF	SOCI
0.00	0.00
	301.89
0.25	667.34
	1093.03
4189.85	4573.80
	4647.86
4190.24	4674.35
	4903.30
5180.41	5037.88
	5530.06
5186.03	6110.23
	6650.14
6564.13	7281.56
	7447.07

SOCI wave functions, projected onto the $^4A_1$ (CASSCF) ground state

state	M_S=–3/2 (GS)		M_S=–1/2 (GS)		M_S=1/2 (GS)		M_S=3/2 (GS)	
	Re	Im	Re	Im	Re	Im	Re	Im
E_1	0.000	0.705	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.705	0.000
E_2	0.000	0.000	0.000	–0.699	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.699	0.000	0.000	0.000

Model f

Dynamic correlation effects were negligible (see model e).

```
   25

CO     0.000001     0.000000     0.000000
 N     1.662791     0.000000     1.347770
 N    -0.831392     1.440010     1.347770
 N    -0.831392    -1.440010     1.347770
 N     1.662791     0.000000    -1.347770
 N    -0.831392     1.440010    -1.347770
 N    -0.831392    -1.440010    -1.347770
 H    -1.019399     1.765650     2.288720
 H    -1.725109     1.358200     0.877293
```

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H    -0.313681     2.173090     0.877293
H     2.038791     0.000000     2.288720
H     2.038791     0.814890     0.877293
H     2.038791    -0.814890     0.877293
H    -1.019399    -1.765650     2.288720
H    -0.313681    -2.173090     0.877293
H    -1.725109    -1.358200     0.877293
H    -1.019399     1.765650    -2.288720
H    -1.725109     1.358200    -0.877293
H    -0.313681     2.173090    -0.877293
H     2.038791     0.000000    -2.288720
H     2.038791     0.814890    -0.877293
H     2.038791    -0.814890    -0.877293
H    -1.019399    -1.765650    -2.288720
H    -0.313681    -2.173090    -0.877293
H    -1.725109    -1.358200    -0.877293
```

Energy levels (cm^{-1})

CASSCF	SOCI
0.00	0.0
	317.50
0.00	682.01
	1088.09
5804.81	5525.90
	6139.66
5813.59	6703.14
	6719.33
6589.75	6831.55
	6942.64
6589.78	7238.02
	7393.28
7153.73	7998.33
	8326.32

SOCI wave functions, projected onto the $^4A_1$ (CASSCF) ground state

state	M_S=–3/2 (GS)		M_S=–1/2 (GS)		M_S=1/2 (GS)		M_S=3/2 (GS)	
	Re	Im	Re	Im	Re	Im	Re	Im
E_1	0.000	–0.705	0.000	0.000	0.000	0.000	0.000	0.000
	0.000	0.000	0.000	0.000	0.000	0.000	0.705	0.000
E_2	0.000	0.000	0.000	0.000	0.703	0.000	0.000	0.000
	0.000	0.000	0.000	–0.703	0.000	0.000	0.000	0.000