Supporting Information

Peter Sebald[#], Rainer Oswald, and Peter Botschwina*

Institut für Physikalische Chemie, Universität Göttingen,
Tammannstraße 6, D-37077 Göttingen, Germany
[#] permanent address: Madenburgstraße 14, D-76865 Insheim, Germany

Hermann Stoll

Institut für Theoretische Chemie, Universität Stuttgart,
Pfaffenwaldring 55, D-70569 Stuttgart, Germany

Detlev Figgen

Centre for Theoretical Chemistry and Physics, New Zealand Institute for
Advanced Study, Massey University Albany, Auckland 0745, New Zealand

An accurate potential energy surface and calculated spectroscopic properties for CdH_2 isotopomers

8 tables and 5 figures

TABLE S1: Spin-orbit contributions for CdH_2.[a]

Δr^b (Å)	ΔE_{SO} (E_h)	θ (°)	ΔE_{SO} (E_h)
0	-0.0145325225	5	-0.0145324684
-0.4	-0.0145810506	10	-0.0145323126
-0.3	-0.0145669200	20	-0.0145317543
-0.2	-0.0145540709	30	-0.0145309385
-0.1	-0.0145426823	40	-0.0145298895
0.1	-0.0145232677	50	-0.0145286046
0.2	-0.0145147127	60	-0.0145270561
0.3	-0.0145067294	70	-0.0145251246
0.4	-0.0144991995	80	-0.0145225422
0.5	-0.0144920014	90	-0.0145189485
0.6	-0.0144850250		
0.7	-0.0144781841		
0.8	-0.0144714215		
0.9	-0.0144647057		
1.0	-0.0144580244		

[a] SO contributions are calculated around r_e (PP-CCSD(T)) = 1.666792 Å.

[b] Single Cd-H bond stretching coordinate.

TABLE S2: Variation of the PP-CCSD(T) total energy with single Me-H stretch.

Δr (Å)[a]	CdH_2 (+ 168 E_h)	HgH_2 (+ 154 E_h)
-0.45	-0.82518258	-0.42190440
-0.4	-0.85116593	-0.45629838
-0.35	-0.87141753	-0.48279150
-0.3	-0.88696598	-0.50290910
-0.25	-0.89865361	-0.51787614
-0.2	-0.90717204	-0.52867627
-0.15	-0.91309013	-0.53610803
-0.1	-0.91687678	-0.54081960
-0.05	-0.91891933	-0.54333881
-0.025	-0.91938903	-0.54391415
0	-0.91953840	-0.54409640
0.025	-0.91939908	-0.54392729
0.05	-0.91899986	-0.54344454
0.1	-0.91752455	-0.54167167
0.2	-0.91246815	-0.53566768
0.3	-0.90550351	-0.52751835
0.4	-0.89742388	-0.51819909
0.5	-0.88878641	-0.50837651
0.6	-0.87998330	-0.49850708
0.7	-0.87129079	-0.48889033
0.8	-0.86290353	-0.47977836
0.9	-0.85495860	-0.47127699
1.0	-0.84755197	-0.46349607
1.1	-0.84075114	-0.45649890
1.2	-0.83460241	-0.45032474
1.3	-0.82913684	-0.44499491
1.4	-0.82437369	-0.44051646

[a] Reference bond lengths are r_e (PP-CCSD(T)) = 1.666792 Å for CdH_2 and r_e (exp.) = 1.63324 Å for HgH_2.

TABLE S3: Variation of the PP-CCSD(T) total energy with angle θ.[a]

θ	CdH_2 [b] (+ 168 E_h)	HgH_2 [c] (+ 154 E_h)
0	-0.91953840	-0.54409640
1	-0.91952709	-0.54407827
5	-0.91925595	-0.54364383
10	-0.91841227	-0.54229496
15	-0.91701868	-0.54007614
20	-0.91509377	-0.53703008
25	-0.91266211	-0.53321380
30	-0.90975222	-0.52869569
35	-0.90639448	-0.52355202
40	-0.90261885	-0.51786302
45	-0.89845269	-0.51170867
50	-0.89391873	-0.50516440
55	-0.88903328	-0.49829689
60	-0.88380448	-0.49116019
65	-0.87823046	-0.48379209
70	-0.87229755	-0.47621105
75	-0.86597839	-0.46841335
80	-0.85923008	-0.46037039
85	-0.85199218	-0.45202603
90	-0.84418472	-0.44329398

[a] The angle θ measures the deviation from linearity.

[b] Bond lengths fixed at r_e (PP-CCSD(T)) = 1.666792 Å.

[c] Bond lengths fixed at r_e (exp.) = 1.63324 Å.

TABLE S4: Variation of the electric dipole moment (in ea_0) with left Me-H distance ($\theta = 0°$).

Δr (Å)	CdH_2 [a]	HgH_2 [b]
-0.5	-0.306765	-0.351536
-0.4	-0.264436	-0.296216
-0.3	-0.210729	-0.231759
-0.2	-0.147589	-0.160040
-0.1	-0.076765	-0.082364
-0.05	-0.039014	-0.041683
0.05	0.040049	0.042493
0.1	0.080898	0.085590
0.2	0.164028	0.172672
0.3	0.247390	0.259248
0.4	0.328880	0.343083
0.5	0.406290	0.421756
0.6	0.477322	0.492730
0.7	0.539615	0.553432
0.8	0.590797	0.601363
0.9	0.628559	0.634235
1.0	0.650768	0.650147
1.25	0.627674	0.609382
1.5	0.488161	0.465314
1.75	0.266834	0.281660
2.0	0.056848	0.177008

[a] r_e (PP-CCSD(T)) = 1.666792 Å.

[b] r_e (exp.) = 1.63324 Å.

TABLE S5: Variation of the electric dipole moment (in ea_0) with angle θ.

θ (°)	CdH_2 [a]	HgH_2 [b]
0	0.000000	0.000000
1	-0.014782	-0.006899
5	-0.073946	-0.034588
10	-0.148128	-0.069733
15	-0.222751	-0.105961
20	-0.297975	-0.143737
25	-0.373895	-0.183443
30	-0.450530	-0.225351
35	-0.527810	-0.269603
40	-0.605574	-0.316193
45	-0.683568	-0.364954
50	-0.761450	-0.415563
55	-0.838798	-0.467539
60	-0.915116	-0.520260
65	-0.989851	-0.572990
70	-1.062398	-0.624896
75	-1.132121	-0.675078
80	-1.198351	-0.722577
85	-1.260384	-0.766369
90	-1.317442	-0.805301

[a] r_e (PP-CCSD(T)) = 1.666792 Å.

[b] r_e (exp.) = 1.63324 Å.

TABLE S6: Rovibrational term energies of interacting levels (in cm^{-1}) for $^{114}CdH_2$. [a]

J	$(0,4^0,0)e$	$(0,4^2,0)e$	$(04^4,0)e$	$(0,1^1,1)e$
0	2366.900			
1	2372.763			2367.410
2	2384.522	2379.905		2378.976
3	2402.230	2397.369		2396.323
4	2425.955	2420.550	2407.280	2419.449
5	2455.743	2449.409	2436.501	2448.349
6	2491.612	2483.940	2471.518	2483.020
7	2533.554	2524.168	2512.301	2523.455
8	2581.553	2570.135	2558.811	2569.642
9	2635.594	2621.900	2611.001	2621.559
10	2695.662	2679.516	2668.814	2679.200
11	2761.743	2742.962	2732.187	2742.626
12	2833.823	2812.237	2801.068	2811.870
13	2911.890	2887.432	2875.427	2886.846
14	2995.929	2968.579	2955.257	2967.502
15	3085.926	3055.630	3040.568	3053.844
16	3181.866	3148.537	3131.375	3145.873
17	3283.733	3247.263	3227.689	3243.580
18	3391.511	3351.775	3329.517	3346.953
19	3505.183	3462.044	3436.860	3455.979
20	3624.731	3578.045	3549.715	3570.645
21	3750.137	3699.756	3668.074	3690.935
22	3881.381	3827.153	3791.929	3816.834
23	4018.444	3960.216	3921.266	3948.325
24	4161.305	4098.925	4056.074	4085.392
25	4309.942	4243.256	4196.336	4228.016
26	4464.334	4393.191	4342.037	4376.178
27	4624.456	4548.706	4493.160	4529.860
28	4790.287	4709.779	4649.685	4689.039
29	4961.801	4876.389	4811.593	4853.698
30	5138.972	5048.510	4978.866	5023.813

[a] From variational calculations with PEF PP-CCSD(T)+corr.

TABLE S7: Rovibrational term energies of interacting levels (in cm^{-1}) for $^{114}CdD_2$.[a]

J	$(0,4^0,0)e$	$(0,4^2,0)e$	$(04^4,0)e$	$(0,1^1,1)e$
0	1717.596			
1	1720.548			1709.680
2	1726.460	1724.362		1715.528
3	1735.347	1733.183		1724.300
4	1747.230	1744.914	1738.781	1735.995
5	1762.127	1759.537	1753.515	1750.612
6	1780.049	1777.046	1771.182	1768.150
7	1800.999	1797.441	1791.777	1788.609
8	1824.975	1820.729	1815.289	1811.986
9	1851.971	1846.922	1841.706	1838.281
10	1881.984	1876.033	1871.016	1867.491
11	1915.008	1908.079	1903.200	1899.615
12	1951.041	1943.074	1938.239	1934.651
13	1990.077	1981.033	1976.117	1972.596
14	2032.114	2021.967	2016.820	2013.448
15	2077.147	2065.877	2060.339	2057.204
16	2125.174	2112.760	2106.675	2103.861
17	2176.189	2162.606	2155.830	2153.417
18	2230.188	2215.405	2207.810	2205.867
19	2287.169	2271.146	2262.619	2261.208
20	2347.125	2329.819	2320.262	2319.434
21	2410.053	2391.417	2380.766	2380.517
22	2475.947	2455.931	2444.009	2444.573
23	2544.803	2523.353	2510.152	2511.436
24	2616.616	2593.679	2579.119	2581.177
25	2691.380	2666.900	2650.910	2653.787
26	2769.091	2743.012	2725.524	2729.260
27	2849.741	2822.008	2802.958	2807.591
28	2933.326	2903.882	2883.206	2888.775
29	3019.840	2988.628	2966.266	2972.806
30	3109.276	3076.241	3052.131	3059.679
31	3201.627	3166.713	3140.797	3149.389
32	3296.889	3260.039	3232.259	3241.929
33	3395.052	3356.212	3326.511	3337.294
34	3496.111	3455.225	3423.547	3435.477
35	3600.059	3557.073	3523.361	3536.472

[a] From variational calculations with PEF PP-CCSD(T)+corr.

TABLE S8: Rovibrational term energies of interacting levels (in cm^{-1}) for $^{114}CdH_2$ in the region of the first Darling-Dennison resonance system.[a]

J	$(2,0^0,0)e$	$(0,6^0,0)e$	$(0,6^2,0)e$	$(0,6^4,0)e$	$(0,6^6,0)e$	$(0,3^1,1)e$	$(0,3^3,1)e$	$(0,0,2)e$
0	3491.056	3505.228						3542.483
1	3496.808	3511.081				3525.376		3548.237
2	3508.310	3522.848	3517.914			3536.816		3559.746
3	3525.562	3540.631	3535.240			3553.985	3545.500	3577.006
4	3548.561	3564.535	3558.181	3544.447		3576.893	3568.674	3600.017
5	3577.303	3594.612	3586.714	3573.550		3605.557	3597.600	3628.774
6	3611.785	3630.861	3620.877	3608.396	3584.697	3640.004	3632.246	3663.276
7	3652.002	3673.267	3660.745	3648.931	3625.434	3680.265	3672.567	3703.517
8	3697.947	3721.808	3706.415	3695.080	3671.913	3726.375	3718.521	3749.492
9	3749.615	3776.469	3757.999	3746.752	3724.103	3778.366	3770.063	3801.196
10	3806.998	3837.246	3815.603	3803.859	3781.969	3836.241	3827.164	3858.622
11	3870.088	3904.102	3879.290	3866.359	3845.471	3900.018	3889.814	3921.763
12	3938.877	3977.040	3949.063	3934.270	3914.560	3969.663	3958.013	3990.612
13	4013.353	4056.044	4024.888	4007.659	3989.180	4045.156	4031.765	4065.159
14	4093.508	4141.097	4106.717	4086.608	4069.265	4126.473	4111.075	4145.394
15	4179.329	4232.185	4194.507	4171.209	4154.735	4213.590	4195.947	4231.310
16	4270.805	4329.290	4288.232	4261.549	4245.503	4306.486	4286.367	4322.893
17	4367.923	4432.396	4387.842	4357.698	4341.495	4405.140	4382.349	4420.134
18	4470.668	4541.484	4493.320	4459.689	4442.666	4509.535	4483.873	4523.019
19	4579.028	4656.537	4604.640	4567.511	4549.010	4619.651	4590.933	4631.536
20	4692.986	4777.534	4721.775	4681.119	4660.553	4735.471	4703.518	4745.671
21	4812.526	4904.454	4844.702	4800.457	4777.330	4856.975	4821.613	4865.410
22	4937.633	5037.278	4973.395	4925.467	4899.372	4984.147	4945.207	4990.738
23	5068.287	5175.983	5107.830	5056.101	5026.700	5116.966	5074.284	5121.640
24	5204.472	5320.545	5247.982	5192.318	5159.327	5255.414	5208.828	5258.099
25	5346.165	5470.942	5393.823	5334.082	5297.255	5399.454	5348.825	5400.119
26	5493.334	5627.150	5545.319	5481.363	5440.481	5549.163	5494.272	5547.591
27	5646.059	5789.143	5702.402	5634.134	5588.998	5704.445	5645.048	5700.616
28	5804.152	5956.895	5865.785	5792.366	5742.794	5864.594	5801.303	5859.119
29	5967.690	6130.380	6033.873	5956.033	5901.856	6031.154	5962.918	6023.084
30	6136.637	6309.570	6207.766	6125.107	6066.168	6202.972	6129.890	6192.489

[a] From variational calculations with PEF PP-CCSD(T)+corr.

Figures of Supporting Information

Figures 1-5 show predicted gas-phase IR absorption spectra of the three fundamental vibrations of $^{114}CdH_2$, $^{114}CdD_2$, and $^{114}CdHD$ at a temperature of 293 K. The spectra for the three stretching vibrational bands (Figs. 1 and 2) are normalized with respect to the strongest line in the R branch of $^{114}CdH_2$. Each spectrum of a bending vibration (Figs. 3-5) is normalized independently with respect to the most intense line of its Q branch.