Computational Analysis of the Ground and Lowest Excited Electronic States of 4-Cyclopentene-1,3-dione

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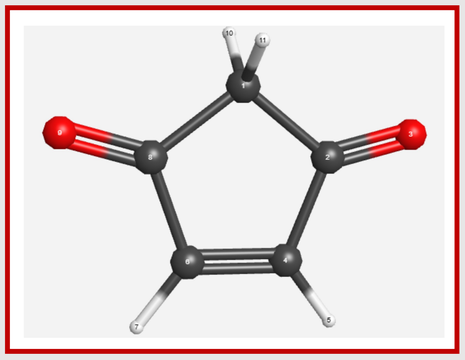
Introduction

The ability to compute the properties of a molecule in an electronically excited state is critical for understanding and predicting the behavior of photochemical processes. This project focuses on using quantum-chemical methods to investigate the excited-state properties of 4-cyclopentene-1,3-dione (4CPD). Our calculations will characterize vibrational frequencies in the excited state, and we will compare the results to known experimental data. While this is our eventual goal, the work we have done thus far is a validation of the computational methods available for the ground state of 4CPD. A baseline knowledge of how to calculate accurate ground state properties will then allow us to apply our methods to the excited state. We are testing two computational methods: one approach combines unrestricted coupled-cluster singles and doubles (U-CCSD) with unrestricted density functional theory (U-DFT), and a second approach uses U-DFT on its own. We are assessing the performance of these methods in terms of their computational efficiency and accuracy for determining vibrational frequencies of 4CPD. This will enable investigators to make rational choices when planning calculations on similar systems.



Model of 4-cyclopentene-1,3-dione in its ground state

Computational Methods

We carried out harmonic-frequency calculations for the ground and $T_1(n, \pi^*)$ excited state of 4CPD using the CCSD and CCSD(T) methods with the cc-PVTZ and cc-pwCVTZ basis sets. We estimated anharmonic corrections through various DFT methods, namely B3LYP, PBE0, CAM-B3LYP, and B2PLYP.

We used the Q-Chem[1] computational chemistry package for initial CCSD harmonic calculations and CFOUR[2] for final CCSD(T) optimization and frequency calculations.

Approaches and Results

mode #	CCSD/cc-pVTZ	Experimental Values	Observed - calculated
1	88.01	99	10.99
2	250.24	239	-11.24
3	394.29	385	-9.29
4	443.27	424	-19.27
5	530.92	522	-8.92
6	580.83	588	7.17
7	658.42	637	-21.42
8	698.91	699	0.09
9	815.73	784	-31.73
10	839	808	-31
11	862.82	842	-20.82
12	981.94	951	-30.94
13	1021.59	1014	-7.59
14	1088.02	1057	-31.02
15	1165.23	1125	-40.23
16	1167.94	1130	-37.94
17	1266.77	1227	-39.77
18	1285.64	1242	-43.64
19	1370.19	1322	-48.19
20	1444.67	1392	-52.67
21	1654.87	1635	-19.87
22	1835.52	1786	-49.52
23	1870.22	1857	-13.22
24	3107.61	3073	-34.61
25	3157.51		
26	3241.09		
27	3263.48		

We calculated harmonic frequencies (in cm^{-1} units) for the ground state of 4CPD using the CCSD/cc-pVTZ method and compared to experimental[3] values. As shown in the table at left, the computed harmonic frequencies are generally larger than observed. This is because the harmonic model does not account for the anharmonicity found naturally in chemical bonds. Therefore, anharmonic corrections must be made so that our calculations can achieve optimum agreement with experiment.

We also completed harmonic-frequencies using DFT and included DFT anharmonic corrections. The frequencies from four different methods are shown in the table below in cm^{-1} units. The absolute errors are obtained from the difference between the computational value and the value obtained experimentally (see table above for experimental values). Because anharmonic corrections are made in the case of the DFT calculations, the computed frequencies values more closely match experimental values.

mode #	B3LYP	Abs. Error	PBE0	Abs. Error	CAM-B3LYP	Abs. Error	B2PYLP	Abs. Error
1	96.038	2.962	120.906	21.906	98.484	0.516	93.515	5.485
2	244.683	5.683	260.763	21.763	250.318	11.318	242.273	3.273
3	384.302	0.698	397.8	12.8	392.523	7.523	384.149	0.851
4	441.283	17.283	462.315	38.315	445.976	21.976	438.559	14.559
5	523.947	1.947	536.234	14.234	530.838	8.838	521.895	0.105
6	578.373	9.627	570.723	17.277	587.152	0.848	576.907	11.093
7	647.205	10.205	668.45	31.45	659.197	22.197	644.872	7.872
8	669.876	29.124	686.723	12.277	679.605	19.395	696.948	2.052
9	791.089	7.089	817.754	33.754	797.538	13.538	794.108	10.108
10	794.539	13.461	825.051	17.051	814.94	6.94	802.646	5.354
11	824.303	17.697	851.929	9.929	841.981	0.019	829.239	12.761
12	949.976	1.024	969.857	18.857	964.462	13.462	950.118	0.882
13	997.414	16.586	1029.018	15.018	1015.491	1.491	997.244	16.756
14	1060.721	3.721	1079.732	22.732	1070.208	13.208	1062.774	5.774
15	1098.558	26.442	1135.934	10.934	1122.386	2.614	1109.47	15.53
16	1109.653	20.347	1135.01	5.01	1127.079	2.921	1132.962	2.962
17	1216.639	10.361	1247.886	20.886	1238.613	11.613	1219.364	7.636
18	1221.979	20.021	1265.671	23.671	1255.042	13.042	1236.364	5.636
19	1315.076	6.924	1342.93	20.93	1332.324	10.324	1320.862	1.138
20	1374.349	17.651	1392.421	0.421	1386.156	5.844	1398.524	6.524
21	1600.303	34.697	1615.181	19.819	1643.088	8.088	1572.228	62.772
22	1756.166	29.834	1802.672	16.672	1806.816	20.816	1726.185	59.815
23	1802.794	54.206	1842.416	14.584	1850.494	6.506	1756.385	100.615
24	2941.515	131.485	2974.63	98.37	2973.979	99.021	2960.293	112.707
25	2959.94		3008.626		3002.315		2986.599	
26	3075.096		3108.74		3105.242		3093.33	
27	3078.531		3116.732		3110.77		3090.063	
Mean Abs. Error		20.378125		21.610833		13.4190833		19.6775

We alternatively made DFT anharmonic corrections to the CCSD/cc-pVTZ calculation, bringing its absolute error down by about 9 cm^{-1}, compared to purely harmonic results. Anharmonic frequencies (cm^{-1}) are shown below.

B3LYP	Abs. Error	PBE0	Abs. Error	CAM-B3LYP	Abs. Error	B2PYLP	Abs. Error
93.876	5.124	92.445	6.555	92.816	6.184	91.694	7.306
247.278	8.278	248.989	9.989	245.961	6.961	246.606	7.606
391.384	6.384	391.808	6.808	391.758	6.758	391.412	6.412
443.376	19.376	440.314	16.314	441.833	17.833	441.351	17.351
527.542	5.542	528.121	6.121	527.934	5.934	527.812	5.812
581.409	6.591	581.746	6.254	581.69	6.31	580.947	7.053
652.467	15.467	652.719	15.719	652.39	15.39	652.215	15.215
675.676	23.324	674.758	24.242	674.419	24.581	674.549	24.451
798.663	14.663	798.113	14.113	797.823	13.823	797.212	13.212
822.995	14.995	822.875	14.875	823.322	15.322	822.348	14.348
843.999	1.999	842.719	0.719	843.809	1.809	842.916	0.916
962.836	11.836	962.856	11.856	962.618	11.618	962.645	11.645
996.719	17.281	999.213	14.787	993.756	20.244	998.973	15.027
1072.316	15.316	1073.187	16.187	1073.206	16.206	1071.55	14.55
1133.695	8.695	1134.694	9.694	1134.994	9.994	1133.22	8.22
1146.2	16.2	1145.362	15.362	1146.934	16.934	1144.555	14.555
1244.387	17.387	1243.662	16.662	1245.039	18.039	1242.43	15.43
1263.738	21.738	1263.573	21.573	1264.157	22.157	1262.312	20.312
1338.221	16.221	1338.202	16.202	1338.864	16.864	1337.82	15.82
1418.252	26.252	1415.019	23.019	1417.305	25.305	1415.603	23.603
1622.234	12.766	1621.382	13.618	1622.396	12.604	1620.032	14.968
1811.1	25.1	1809.532	23.532	1810.15	24.15	1809.703	23.703
1853.152	3.848	1851.779	5.221	1852.674	4.326	1851.395	5.605
2983.845	89.155	2983.646	89.354	2986.491	86.509	2981.25	91.75
3014.967		3014.591		3018.229		3013.263	
3117.683		3117.434		3119.82		3114.731	
3127.3		3126.647		3129.493		3124.122	
Mean Abs. Error	16.81408333		16.615667		16.910625		16.452917

While some of the pure DFT approaches have a lower absolute error than the hybrid methods above, we predict that this will change as the accuracy of the harmonic calculation is increased. We will increase the ordinal value of the coupled-cluster method for calculating electron correlation and extrapolate to the complete basis set limit. When we have done this and corrected the results for anharmonicity using a DFT method, we expect that our results will be closer to the experimental values than pure DFT methods. By contrast, there is no way to increase the accuracy of the harmonic component of pure DFT calculations.

We are now using CFOUR instead of Q-Chem to prepare for the transition from CCSD calculations to CCSD(T) calculations. We reran the CCSD/cc-pVTZ harmonic calculation as a parallelized finite-difference frequency calculation to confirm that it saves time but provides the same results as those obtained using Q-Chem. Now that this is confirmed, we can begin calculations at a higher level of theory using CCSD(T).

Future Work

The ground-state calculations reported here serve as a solid foundation from which to build our excited state calculations. The long-term goal is to work up the accuracy of excited state calculations in the same way as we have the ground state. The ability to compute the properties of molecular excited states is important for predicting photochemistry, especially because it is difficult to characterize the excited states experimentally. Accurate computational results will increase the knowledge of excited-states properties in a feasible and sustainable way.

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