

Photochemical dynamics of E-methylfurylfulgide — Kinematic effects in photorelaxation dynamics of furylfulgides — Electronic supplementary information

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1 Calculation of the spectra

1.1 Simulation of static spectra

The comparison with experimental spectra is the essential part of the validation of the presented simulations, thus although the process of calculation of the static spectra is exceedingly simple we will give a brief explanation for reasons of completeness. At each time step of the thermalization runs, the transition dipole moments of the ground state with the first five excited state were calculated. These were squared and multiplied with the corresponding transition frequencies, thus creating a measure for the absorption cross-section. By summation over the time steps, thus neglecting the time information, and over the set of trajectories we then created the static spectrum of the ground-state ensemble.

1.2 Simulation of transient spectra

As part of the validation against experiment, in this work we present a comparison of simulated and experimental transient spectra. Basically, the simulation of the transient spectra is a straightforward process, nevertheless some explanation is needed. An experimental transient absorption is measured as the difference UV/Vis spectrum of an excited volume of sample at a given time and an unexcited reference volume of the same sample. This gives the time-dependent spectrum as the difference in optical density between excited transient and static UV/Vis spectrum (ΔOD). To simulate the transient spectrum *in silico*, we computed all relevant transition frequencies and squared transition dipole moments along the photo-excited trajectories at each time step of our simulation, covering all possible transitions from the currently populated state. The squared transition dipole moment was taken to be positive in the case of absorption, and negative in the case of stimulated emission. This procedure effectively yielded a UV/Vis absorption spectrum for the whole swath of trajectories at each given time step. The resulting spectrum was divided by the number of trajectories for normalisation, and the transient spectrum at each time step was then obtained by subtracting the (also normalised) static spectrum of the reactant (calculated from the thermalisation runs without keeping the time information).

2 Details of the used active space

As detailed in the main body of the article, the active space was chosen to consist of the 9 occupied and 8 unoccupied orbitals with the highest π -character with respect to the 14 atoms of the conjugated π -system. Here we depict an exemplary active space that was used at the Franck-Condon point, which in turn is discussed in the following section.

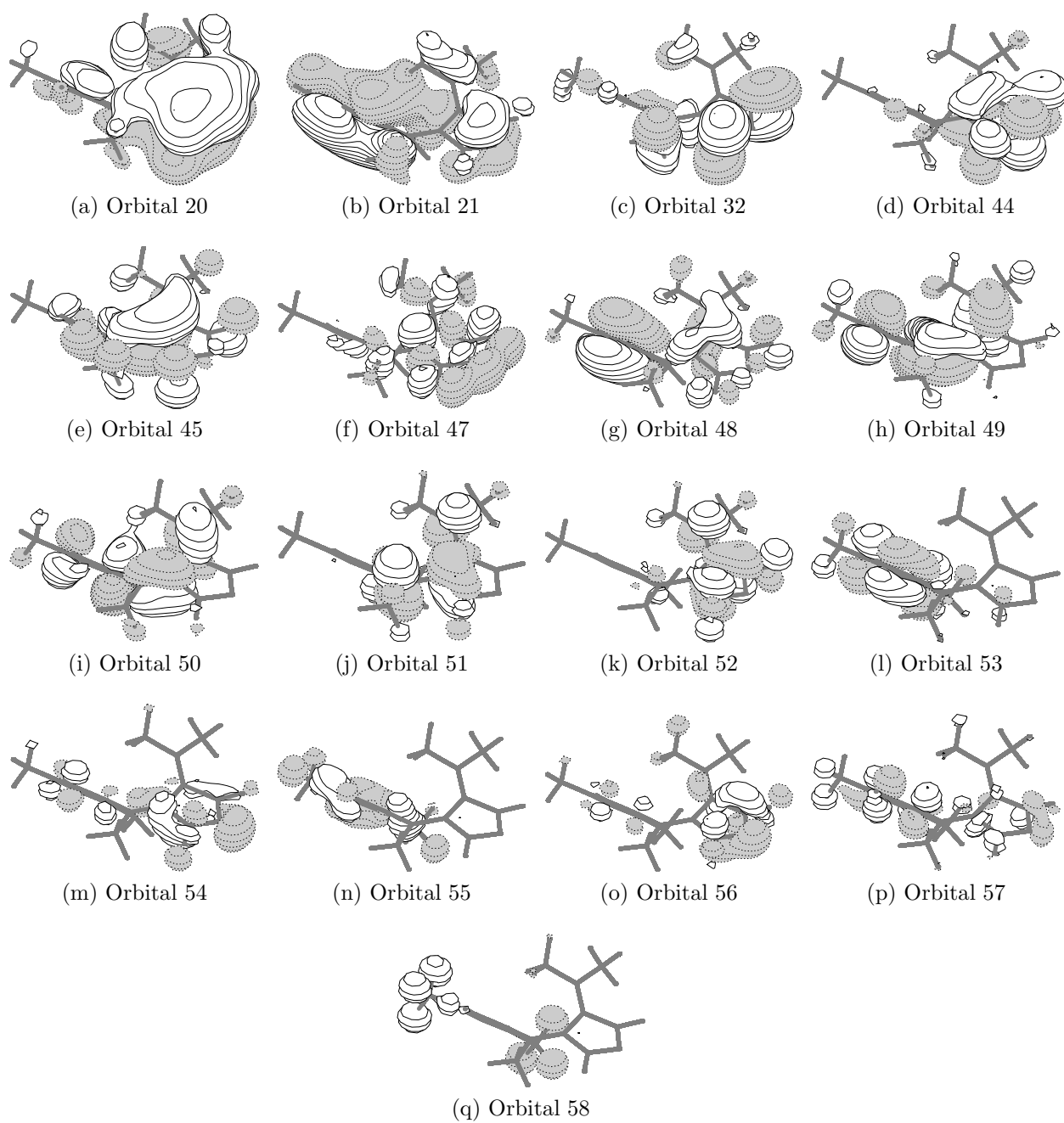


Figure 1: Active orbitals in the MRCI treatment at the optimized Franck-Condon point.

3 Comparison of static minimum geometries

For verification of the applied semiempirical model, the ground state geometries of the α -isomers were optimized on the TPSS/cc-pVTZ, MP2/cc-pVTZ and OM3-MR-CI levels of theory. The minima were confirmed to be minima by frequency calculations. For the MP2 geometry this was done for a pre-optimized MP2/cc-pVDZ geometry on that level, which was then re-optimized with MP2/cc-pVTZ, without a following frequency calculation. The geometries are depicted in Fig. 2; explicit values for the three coordinates used are given in Table 1. The data clearly shows two things: Firstly, the semiempirical model is in reasonable agreement with both other models, as its coordinate values usually are somewhere in-between those of DFT and MP2. Secondly, the pre-orientational effect observed in methylfurylfulgide is absent in the optimized structures. Thus this effect has to be attributed to the thermal sampling.

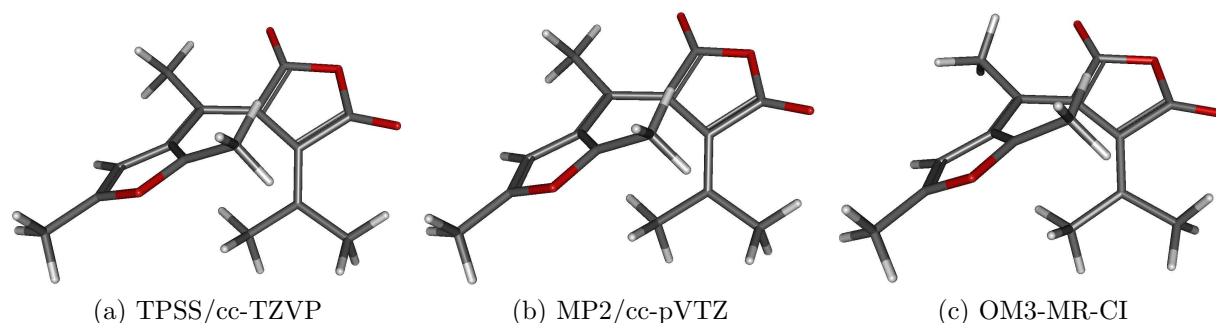


Figure 2: Optimized structures of the α -isomer of methylfurylfulgide, optimized on three different levels.

Table 1: Comparison of the structure of the α -isomer minimum structure on DFT, *ab-initio* and OM3/MR-CI levels. The coordinates are the ones defined in the main article.

molecule	method	$r1/\text{\AA}$	$\phi1/^\circ$	$\phi2/^\circ$
methyl	OM3/MR-CI	3.44	12	11
	TPSS/cc-pVTZ	3.52	19	12
	MP2/cc-pVTZ	3.35	17	11
isopropyl	OM3/MR-CI	3.44	10	8
	TPSS/cc-pVTZ	3.52	17	13
	MP2/cc-pVTZ	3.34	14	12

4 Comparison of state energies along points encountered during the dynamics

To verify that the accuracy of the used OM3-MRCI method for methylfurylfulgide is comparable to the accuracy for isopropylfurylfulgide, we calculated state energies at various points along three arbitrarily picked trajectories. The energies were calculated for the four energetically lowest electronic states on OM3-MRCI, SA-CASSCF(14,12)/app-TZ (see [3] for details on the used basis set and active space) and MS-CASPT2(14,12)/appTZ levels of theory at four points along each trajectory. The points were chosen to be in the beginning of the relaxation (70 fs), in the middle (140 fs) and after the electronic relaxation (210 fs), additionally the point of the actual surface transition of the trajectory was picked. The resulting evolution of energies for the three trajectories is depicted in the three panels (a), (b) and (c) of Fig 3. The energetically lowest point on the S_0 surface within the 12 treated points was set to zero for each level of theory. For Figs. 3a and 3b it is obvious that although there are quantitative differences between the three models, the CASPT2 (blue) and OM3-MRCI (red) data follow the same trend. In the beginning of the trajectory, the energy gap between S_1 and S_0 gets smaller until a region of a very small energy gap is reached where the surface hop occurs. From there on the energy gap increases again. For the S_2 - S_1 energy gap both models show — albeit less pronounced than for the S_1 - S_0 gap — an opposite progression with an increasing gap toward the CoIn region and a decreasing afterwards. This is also true for the S_3 - S_1 energy gap. In CASSCF the evolution of the energy gap is very different. Basically the S_1 -state energy behaves similar to the S_3 - and S_4 -states and never reaches a region with a small energy gap for the S_1 - S_0 energy difference. This is in stark contrast to the dynamically correlated CASPT2 model. For Fig. 3c the situation is less clear (the first point of the CASPT2 graph is missing for the reason that a level shift of 0.2 is not sufficient to solve the intruder state problem at that point). Still the right-hand part of the OM3-MRCI data is closer to the CASPT2 data than CASSCF is. In total, the presented data shows that the OM3-MRCI model provides a reasonable picture, qualitatively comparable to MS-CASPT2(14,12)/appTZ data, as already predicted from the favorable comparison shown for isopropylfurylfulgide [3]. In this comparison it performs significantly better than SA-CASSCF(14,12)/appTZ does.

5 Excited state lifetimes

In this section, we will give a brief comparison with observed time constants in the quoted literature [1,2]. In the older studies, the Temps group reported absorption decay times of approximately 0.10 and 0.25 ps [1], which were refined to 0.11(2) and 0.33(2) ps in the later study [2]. It is important to note, however, that many different processes are contributing to these decay times and that it is not possible to disentangle all of them experimentally. In particular, starting both from S_0 and S_1 , absorption processes to a multitude of highly excited states occur. Some of these are responsible for the experimental signals visible as “white areas” in Fig.3 of the main article.

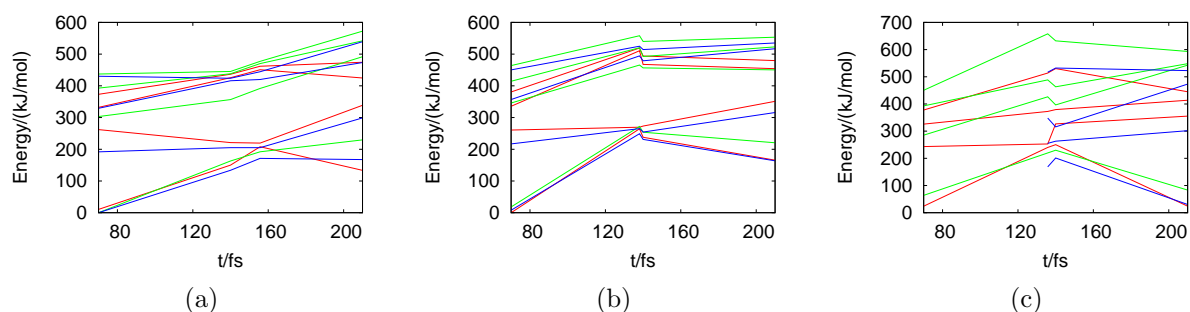


Figure 3: State energies for the 4 lowest electronic states of methylfurylfulgide along three simulated trajectories. The level of theory used for the simulation is color-coded: red: OM3-MRCI, green: CASSCF(14,12)/appTZ, blue: CASPT2(14,12)/appTZ.

Hence, to cover all this in a simulation, a large number of highly excited electronic states would have to be included, at a sufficient level of accuracy. For molecules of this size, this cannot be done at present, with any kind of approach. As discussed in the corresponding text portion of the main article, we only include a limited number of excited states in our simulations, and hence (among other things) we are not able to include the processes leading to signals in these “white areas”.

As a corollary, we cannot directly model all the processes entering into those decay times. Hence, for any timings we extract from our simulations, we cannot expect more than a qualitative agreement with experimental decay times.

In our simulations, we observe an average lifetime on the excited state of 166 fs over the total of the trajectories. This average can be separated into an average lifetime of 158 fs for the α - and 180 fs for the β -isomer. The lifetime of the α -isomer can be further broken down to an average of 160 fs for the ones most closely resembling the zwitterionic pathway and 151 fs for the ones resembling the central ethylenic path. These numbers are in qualitative agreement with the experimental decay times.

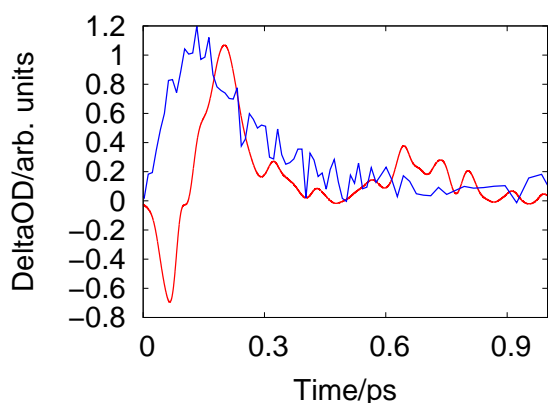
Based on our data, the most likely interpretation for the two different decay times in methylfurylfulgide lies in the two isomers discussed. In the earlier experimental discussion [1] the two different decay times were also attributed to the de-excitation of the two isomers, but this was also based on the observation that the hot ground-state absorption rises slower for the *Z*-isomer. The formation of the *Z*-isomer was at that time discussed to be solely caused by the de-excitation of the β -isomer, therefore the slower rise of the hot ground-state absorption supported this. Today the strict separation “ α -isomer forms *C*-isomer” and “ β -isomer forms *Z*-isomer” is agreed not to be true [2,3]. However, the basic interpretation for the decay times in methylfurylfulgide is still used, and since the central ethylenic direction is the only one open to the β -isomer, a major part of the *Z*-isomer that is formed in solvent is very likely attributable to that isomer. This would be in agreement with our assumptions about the solvent effects and the simulated life times.

6 Comparison of spectral cuts

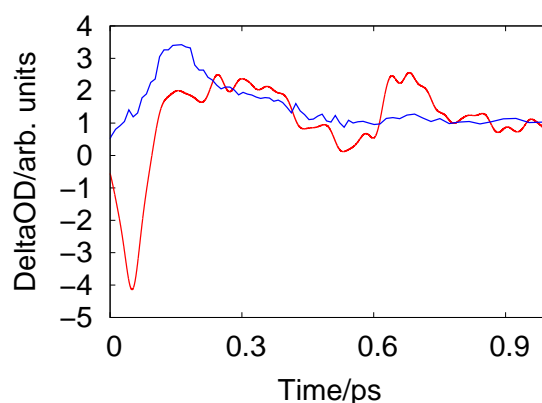
In this section, we show a comparison of spectral cuts through both the experimental and simulated data. Before we go into the detailed comparison, we want to stress several important caveats. In the presented study we discuss results from a total of 223 trajectories covering the de-excitation of methylfurylfulgide. At every time step, each of these trajectories creates 5 absorption signals if on the ground state or 4 absorption and 1 emission signals if on the excited state, since 6 electronic states were treated in total. Thus, for every step in time there are about 1000 signals forming the spectrum, which covers a range of nearly 200 nm already at thermal equilibrium and significantly more during de-excitation. For this reason, the sampling for a specific wavelength over the full simulation time can be expected to be insufficient. When comparing spectral cuts this becomes more obvious than when looking at the two-dimensional data, which is why we present the latter in the main text. Thus, the agreement of one-dimensional spectral cuts cannot be expected to be more than qualitative, in particular, the simulated spectrum is expected to show artifacts due to insufficient sampling. This has to be seen on top of the restrictions that already apply to the two-dimensional comparison, as explained in the main text. Also note that the zero point in time is a fit parameter in the experiment and is not completely identical to the zero point in time in the simulation, which also becomes more obvious in the spectral cuts. In Fig. 4 we show two different comparisons of theoretical and experimental spectral cuts. At first glance some similarities and some differences become obvious which will be discussed here. In Fig. 4a we see that the experimental data starts with a broad signal that decays to approximately zero within about 0.5 ps. The simulated spectrum reaches values close to zero on a similar time scale, but the signal in the beginning is of different shape. In the beginning, the simulation shows a negative contribution, which is due to stimulated emission. The simulated cut then goes through zero and reaches a maximum at about 250 fs due to the hot ground state absorption of the de-excited molecules returning to the region of their respective Franck-Condon points. As explained in the main body of the article, we cannot properly simulate the excited state absorption due to lack of excited states beyond S_5 . For this reason, the discrepancy in signs between simulation and experiment is expected, and it is likely that we would simulate a positive signal in the beginning of the cut if we were able to simulate higher excited states. Thus the most important comparable feature is the width of the positive signal in the experiment and the overall width of the simulated negative and positive signal, which fits very well. Based on our simulation, we therefore attribute the experimental signal to a combination of two different processes: the excited state absorption of the electronically excited ensemble and, partially overlapping with this, the absorption of the rather freshly de-excited molecules on their way to the products or the reactant.

For the cut in Fig. 4b the agreement is less good. Although the time scale for the decay of the intensity in the spectral cut is in good agreement (the peak around 0.7 ps is due to strongly vibrating ground-state molecules that are not sufficiently damped due to a lack of solvent as laid out in the main body of the manuscript), the first 250 fs are rather different. There are various imaginable reasons for the differences. The most likely explanation in

our opinion is that the significant stimulated emission in this region, which is evident in our simulation, overlaps with excited state absorption in the experiment (which is not present in the simulation for previously explained reasons). This would be an explanation for the rather slow and late (compared for example to Fig. 4a) ascend over the first about 150 fs in the experiment. This is not sufficient to explain the different relative heights of the maxima at 150 fs. A possible reason might be the different excitation scheme. We used vertical excitations, while in the experiment the excitation is caused by a laser pulse of some ten femtoseconds, which broadens the excited state ensemble in time. For this reason it is possible that a significant part of the experimental signal at 150 fs stems from excited-state absorption of still excited molecules while some are already on the ground state.



(a) simulation: 550 nm, experiment: 590 nm



(b) simulation: 430 nm, experiment: 460 nm

Figure 4: Spectral cuts through the transient data for methylfurylfulgide. The simulated data is plotted in red, the experimental in blue. The experimental data was obtained from the authors of [2].

7 Coordinate files

The following section lists the coordinates of the optimized minima in xyz-format. All coordinates are given in Ångstrom.

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om3 Franck–Condon point

C	2.2509118135	1.5996364869	-0.5092805076
C	0.9897123677	0.7974713640	-0.4137302212
C	1.4074082354	-0.6065282284	-0.4565910328
C	2.8867821027	-0.5887810200	-0.2090991785
O	3.3543124037	0.7349837308	-0.3288927084
C	-0.2247312995	1.3822971431	-0.1835122204
C	-0.4103224371	2.8666263710	-0.2754145294
C	0.7488953477	-1.7341264377	-0.8730985548
C	1.4169026731	-3.0738138514	-0.8658261669
O	3.6835715092	-1.4995694896	0.0127355721
O	2.4478040782	2.8037111237	-0.6318072463
C	-1.4045391744	0.6459823396	0.2676315550
C	-2.7701724960	0.8346849701	-0.2126397119
C	-3.5711113431	-0.0099678703	0.5444057321
O	-2.8029333767	-0.6871941867	1.4863968623
C	-1.4859645746	-0.2862806519	1.3087187968
C	-5.0222682362	-0.3167555847	0.5568899796
H	-3.0757646853	1.4927071384	-1.0152360809
H	-0.2180127307	3.1763408341	-1.3112348519
H	-1.4360708943	3.1619537264	0.0040677895
H	0.2828146059	3.3750825208	0.4020770327
H	2.0737734621	-3.1610257224	-1.7470104315
H	2.0384753746	-3.2063661423	0.0318022543
H	0.6703709294	-3.8855018034	-0.8994755570
H	-5.5280812294	0.2537137743	-0.2382189379
H	-5.1705061860	-1.3974186824	0.3861058147
H	-5.4470889686	-0.0432891004	1.5342039948
C	-0.6263574193	-1.6853716213	-1.4527770946
H	-1.3686324895	-1.8995030783	-0.6636122240
H	-0.8518269975	-0.6991533295	-1.8886343546
H	-0.7349264368	-2.4414570366	-2.2457005229
H	-0.1694952790	-1.8553638600	1.8925319106
C	-0.4964638615	-0.8633717220	2.2468784521
H	-0.9467336427	-0.9710485435	3.2528088037
H	0.3791662623	-0.1962858336	2.3301674460

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mp2/cc-pVTZ Franck-Condon point

C	2.357934	1.573606	-0.056418
C	1.078552	0.837076	-0.232171
C	1.445606	-0.576456	-0.229165
C	2.795031	-0.631528	0.388653
O	3.310689	0.660899	0.391328
C	-0.145552	1.441227	-0.190953
C	-0.326964	2.924370	-0.339688
C	0.881182	-1.623391	-0.883909
C	1.441875	-3.011498	-0.847786
O	3.444698	-1.542392	0.823857
O	2.651891	2.728922	-0.196875
C	-1.369930	0.698203	0.053624
C	-2.650748	0.935273	-0.545770
C	-3.523808	0.052192	0.017222
O	-2.872704	-0.698618	0.955801
C	-1.566820	-0.304970	0.980128
C	-4.965277	-0.229942	-0.175739
H	-2.888719	1.648665	-1.316107
H	0.617741	3.451038	-0.398833
H	-0.890826	3.120430	-1.254519
H	-0.922881	3.310657	0.487126
H	1.737727	-3.310870	-1.855431
H	2.286200	-3.112638	-0.177519
H	0.654277	-3.703815	-0.540443
H	-5.366307	0.435653	-0.935751
H	-5.126168	-1.258489	-0.496809
H	-5.521317	-0.075367	0.748256
C	-0.332319	-1.460317	-1.738465
H	-1.237148	-1.723166	-1.181700
H	-0.455430	-0.437658	-2.088262
H	-0.266130	-2.133750	-2.593418
H	-0.303033	-1.910337	1.614515
C	-0.699262	-0.960555	1.981721
H	-1.261447	-1.150238	2.894622
H	0.149871	-0.320346	2.213687

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tpss/cc-pVTZ Franck-Condon point

C	2.278939	1.661505	-0.026294
C	1.058350	0.836017	-0.231437
C	1.524540	-0.560348	-0.208587
C	2.872458	-0.525048	0.418572
O	3.297857	0.809851	0.435585
C	-0.205090	1.375143	-0.244455
C	-0.443774	2.849605	-0.476786
C	1.050781	-1.654126	-0.870384
C	1.716096	-3.002764	-0.820722
O	3.597457	-1.388289	0.846954
O	2.505100	2.840940	-0.138935
C	-1.423300	0.609373	0.012516
C	-2.711698	0.832716	-0.605745
C	-3.602917	0.002328	-0.005776
O	-2.959253	-0.714189	0.986100
C	-1.638234	-0.338844	0.991386
C	-5.051061	-0.279319	-0.191038
H	-2.927196	1.512683	-1.417422
H	0.482976	3.418535	-0.492339
H	-0.945092	2.979936	-1.445613
H	-1.121668	3.249948	0.284239
H	2.041325	-3.288542	-1.829913
H	2.564594	-3.037702	-0.141628
H	0.978436	-3.757343	-0.515079
H	-5.451616	0.359897	-0.980640
H	-5.222288	-1.325033	-0.471720
H	-5.613250	-0.087363	0.729896
C	-0.154093	-1.590086	-1.763503
H	-1.059607	-1.900434	-1.224604
H	-0.335439	-0.582419	-2.143277
H	-0.025822	-2.279250	-2.605058
H	-0.401869	-1.921717	1.760766
C	-0.797789	-0.941941	2.057277
H	-1.387173	-1.076906	2.968804
H	0.055159	-0.296057	2.275816

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