Table 1 Comparison between ADC(2) excitation energies with different basis sets. Basis sets with additional diffuse functions are marked with a + sign.

State	aug-cc -pVDZ	aug-cc -pVDZ+	cc -pVTZ+	aug-cc -pVTZ	aug-cc -pVTZ+	aug-cc -pVQZ	def2- TZVPD
$A_2(\pi\sigma^*)$	5.13	5.10	5.33	5.30	5.29	5.37	5.61
	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$B_1(\pi\sigma^*)$	5.75	5.72	5.95	5.95	5.93	6.01	6.27
	0.013	0.008	0.016	0.008	0.009	0.009	0.004
$A_2(\pi Ryd)$	5.86	5.78	5.99	6.03	5.99	6.09	6.50
	0.000	0.000	0.000	0.000	0.000	0.000	0.000
$B_1(\pi Ryd)$	5.89	5.82	6.03	6.07	6.04	6.13	6.54
	0.031	0.027	0.020	0.034	0.027	0.031	0.055
$B_2(\pi\pi^*)$	6.35	5.93	6.16	6.36	6.11	6.34	6.75
	0.214	0.072	0.064	0.20	0.095	0.18	0.202
$A_1(\pi\pi^*)$	6.49	/	6.63	6.47	6.47	6.47	/
	0.000	/	0.004	0.002	0.002	0.003	/

Table 2 Comparison between TDDFT excitation energies with different basis sets. Basis sets with additional diffuse functions are marked with a + sign.

State	def2- TZVPD	def2- QZVPPD	cc- pVTZ+	aug-cc- pVTZ	def2- QZVP(-f,-g)
$A_2(\pi\sigma^*)$	4.99	4.86	4.69	4.68	5.22
	0.000	0.000	0.000	0.000	0.000
$B_1(\pi\sigma^*)$	5.87	5.73	5.38	5.46	6.06
	0.013	0.022	0.026	0.026	0.000
$A_2(\pi Ryd)$	5.89	5.76	5.37	5.44	6.44
	0.000	0.000	0.000	0.000	0.000
$B_1(\pi Ryd)$	5.95	5.80	5.59	5.60	6.51
	0.026	0.013	0.003	0.012	0.030
$B_2(\pi\pi^*)$	6.32	6.26	5.61	5.89	6.31
	0.174	0.186	0.061	0.153	0.173
$A_1(\pi\pi^*)$	6.47	6.45	6.24	6.39	6.48
	0.001	0.000	0.025	0.009	0.001

Table 3 Exponents (multiplied by 10^3) and coefficients of the diffuse functions added to the basis sets marked with a + sign.

s		p		d	
Exponents	Coefficients	Exponents	Coefficients	Exponents	Coefficients
5.85838	3.57009	9.98821	1.83410	14.20440	1.50054
3.34597	-7.03242	5.68936	-2.60999	8.07659	-1.97912
2.04842	9.06092	3.47568	4.65587	4.92719	3.88517
1.32364	-6.42858	2.24206	-6.53099	3.17481	-5.39074
0.89310	-0.41753	1.51064	7.16231	2.13712	6.08170
0.62431	5.70765	1.05475	-5.65978	1.49102	-4.99771
0.44950	-5.00403	0.75866	2.81845	1.07174	2.61858
0.33184	1.52601	0.55958	-0.65406	0.79007	-0.64550

Table 4 Vibrational normal modes calculated at the MP2/aug-cc-pVTZ level along with the corresponding wavenumbers and Boltzmann factors (BF).

Mode	Symmetry	Wavenumber (cm^{-1})	BF (100K)	BF (293K)
1	b_1	520	0.640	0.249
2	a_2	623	0.147	0.150
3	b_1	648	0.101	0.132
4	a_2	685	0.060	0.111
5	b_1	731	0.031	0.088
6	b_1	830	0.007	0.054
7	b_2	871	0.004	0.045
8	a_2	872	0.004	0.044
9	a_1	891	0.003	0.040
10	a_1	1043		0.019
11	b_2	1065		0.017
12	a_1	1104		0.014
13	b_2	1170		0.010
14	a_1	1176		0.010
15	b_2	1313		0.005
16	a_1	1434		0.003
17	b_2	1483		0.002
18	a_1	1505		0.002
19	b_2	1558		0.002
20	b_2	3274		
21	a_1	3285		
22	b_2	3299		
23	a_1	3305		
24	a_1	3691		

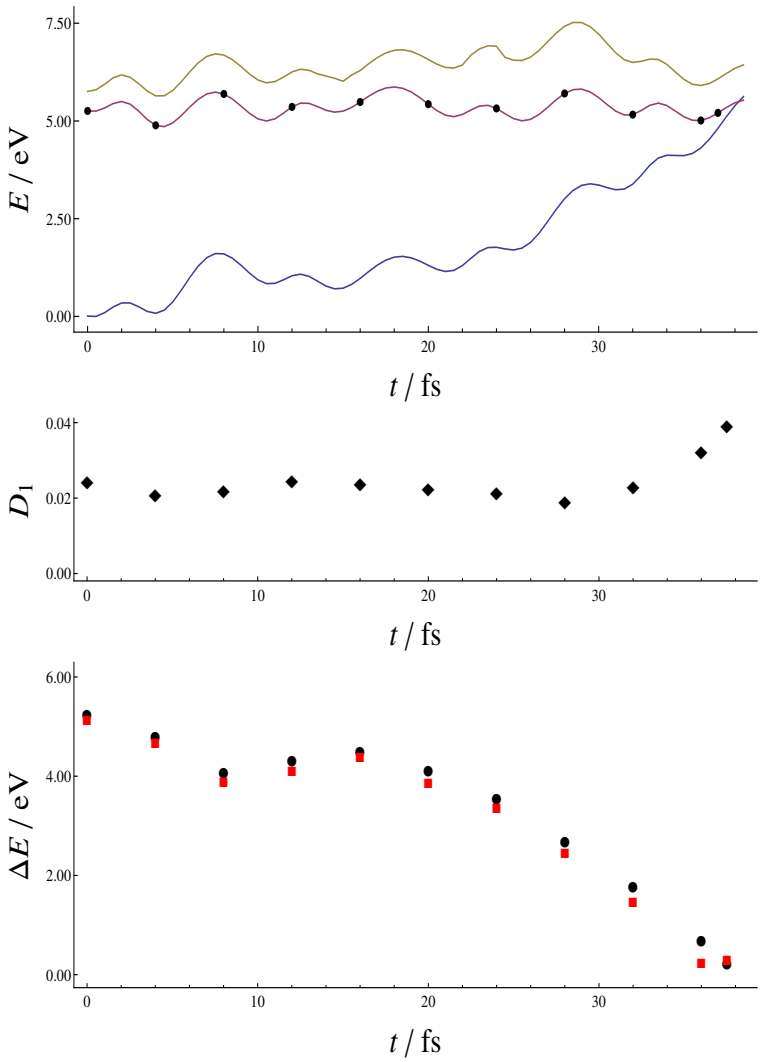

Figure 1 Characteristic trajectory for the dynamics initiated in the $A_2(\pi\sigma^*)$ state at the ADC(2)/aug-cc-pVDZ level. (Top) Potential energies of the ground and first two excited states along the trajectory (lines), and geometries for which further analysis was performed (black circles). (Middle) The D_1 diagnostic of the ground state at selected geometries along the trajectory. (Bottom) Excitation energies of the current electronic state at the ADC(2)/aug-cc-pVDZ (black circles) and CASPT2/aug-cc-pVDZ (red squares) levels.

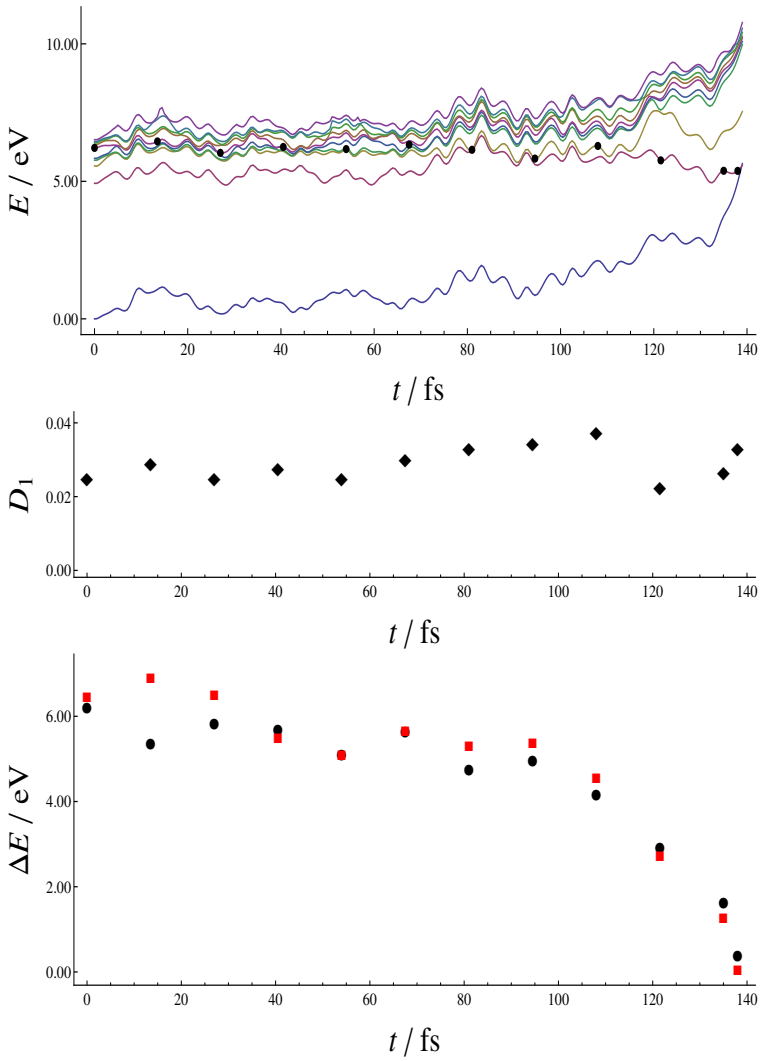

Figure 2 Representative trajectory for the dynamics from the $B_2(\pi\pi^*)$ state at the ADC(2)/aug-cc-pVDZ level. (Top) The energies of the ground and first nine excited states along the trajectory (lines). Geometries for which further analysis was performed are indicated by black circles. (Middle) The D_1 diagnostic of the ground state at selected geometries along the trajectory. (Bottom) Excitation energies of the current electronic state during the dynamics at the ADC(2)/aug-cc-pVDZ (black circles) and CASPT2/aug-cc-pVDZ (red squares) levels.

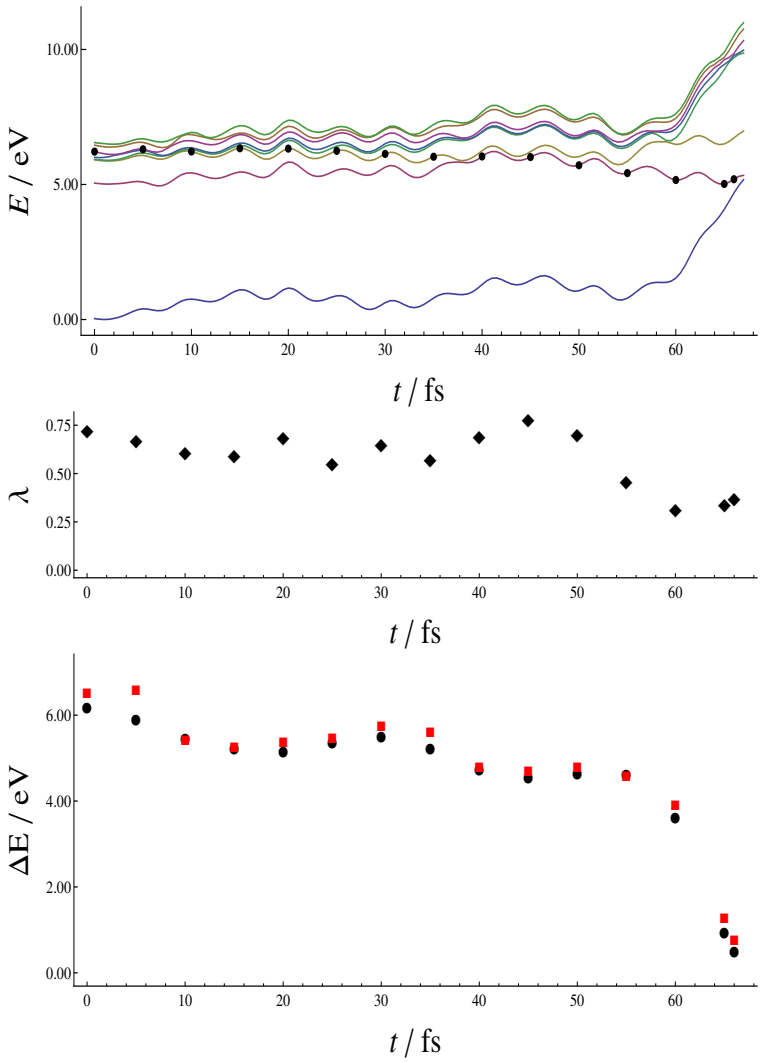

Figure 3 Representative trajectory for the dynamics from the $B_2(\pi\pi^*)$ state at the TD-B3LYP/def2-TZVPD level. (Top) The energies of the ground and first seven excited states along the trajectory (lines), and geometries for which further analysis was performed (black circles). (Middle) The λ diagnostic of the current state at selected geometries along the trajectory. (Bottom) Excitation energies of the current electronic state during the dynamics at the TD-B3LYP (black circles) and CASPT2 (red squares) levels.