SUPPLEMENTARY MATERIAL for:

The excited states of azulene; a study of the vibrational energy levels for the lower ππ*-valence states by configuration interaction and density functional calculations, and theoretical studies of the Rydberg states.

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1. Supplementary Material SM1[SVH1].

Figure SM1. The onset of the azulene UV spectrum, recorded using a Unicam UV340 spectrometer, compared with Cavity ring-down (CRD) spectrum of Ruth, Kim and Hese, Phys. Chem. Chem. Phys. 1999, 1, 5121–5128. The comparison shows that the principal features of the CRD spectrum are reproduced. In contrast, the spectrum of a 2-colour double resonance spectroscopy in a supersonic jet is significantly different from both of these spectra (Suzuki and Ito, J. Phys. Chem. 1987, 91, 3537-3542).

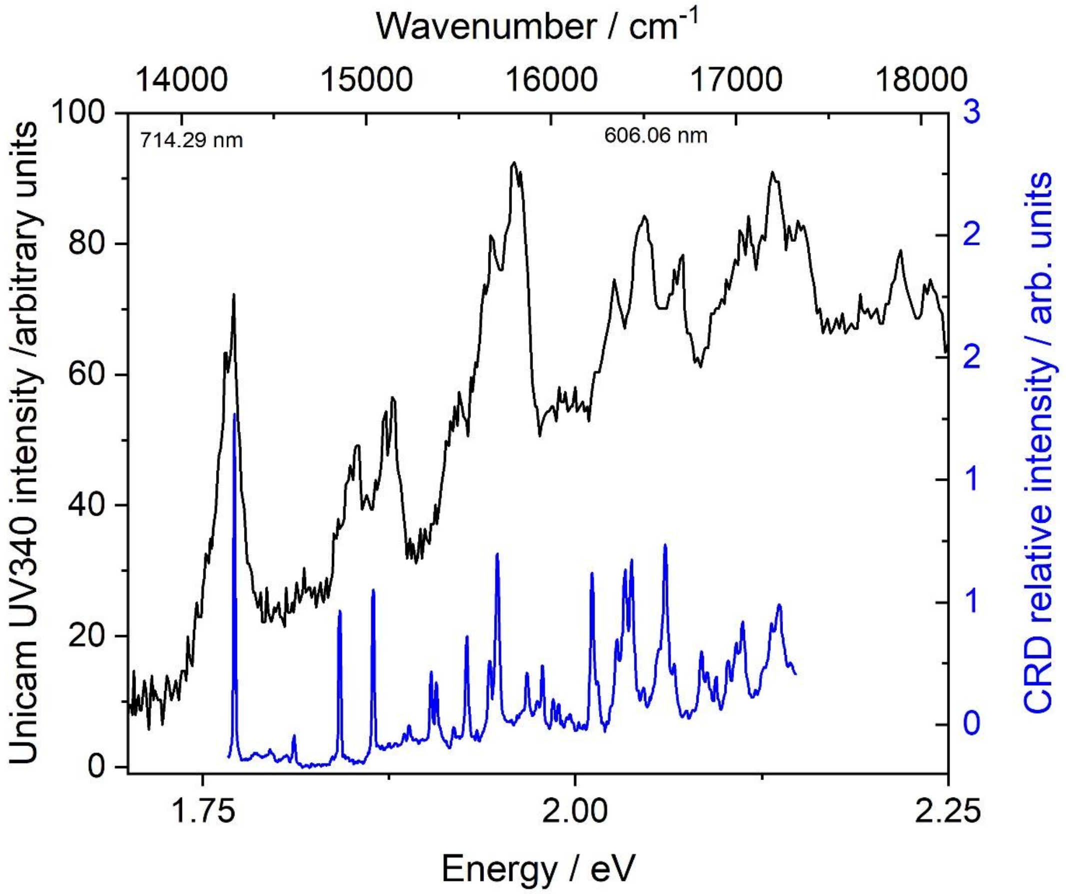


Table SM1. An alternative assignment for the jet-cooled azulene spectra by Suzuki et al,[24] who used jet-cooled azulene studied by population labelling spectroscopy, and Ruth et al[25] also using the $S_0 \rightarrow S_1$ transition of jet-cooled azulene but studied by cavity ring-down absorption spectroscopy.

24. T. Suzuki and M. Ito, J. Phys. Chem. 91, 3537–3542 (1987) https://doi.org/10.1021/j100297a015
25. A. A. Ruth, E.-K. Kim and A. Hese, Phys. Chem. Chem. Phys., 1, 5121–5128 (1999) https://doi.org/10.1039/A906344G

Ruth[25] $S_0 \rightarrow S_1$ jet-cooled azulene				Suzuki[24]		Present work	FC	HT
Peak / cm^{-1}	Relative to 0-0 / cm^{-1}	Relative intensity	Assignment	Relative to 0-0 / cm^{-1}	Assignment	Peak / cm^{-1}	State /cm^{-1}	State /cm^{-1}
14283.3	0	100	0^0	0		194		23^1
14511.3	228	4.4	39^1	230	39^1	242		32^2
14613.7	330.4		38^1	326		338		48^1
14646.9	363.6			366				
14659.9	376.6		17^1	378	17^1	389		23^2
14665.2	381.9	6.1	23^2	385	23^2	394	17^1	17^1
14779	495.7		37^1	496		481	32^4	
14890	606.7			571				
14898.6	615.3							
14944.6	661.3	40.5	16^1	664	16^1	686	16^1	16^1
15055	771.7		36^1	775		862	$27^1 32^1$	
15142	858.7	47.5	15^1	862	15^1	887	15^1	15^1
15194.1	910.8	4.3	14^1	913	14^1	927	14^1	
15232.3	949					957	13^1	
15322.6	1039.3	6.5	35^1; $17^1 16^1$	1041	$17^1 16^1$	1020	30^2	
15351.3	1068	7.5	34^1	1068		1080	$16^1 17^1$	
				1092	$15^1 39^1$	1102	12^1	12^1
15478.1	1194.8	21.9	13^1	1197	10^1	1251	$27^1 30^1$	11^1
15507.2	1223.9	9.8	12^1	1226	11^1			
15520.7	1237.4	8	33^1; $17^1 15^1$	1240	$17^1 15^1$	1268	10^1	10^1
						1281	$15^1 17^1$	$15^1 17^1$
15605.9	1322.6	7.6	16^2	1324	16^2	1372	16^2	16^2
15627.5	1344.2	5.9	32^1					
15677.4	1394.1	29.4	10^1	1399	9^1			
15688.9	1405.6	20.4	31^1					
15732.8	1449.5	7.7	30^1	1451	8^1	1453	9^1	9^1
				1490		1500	8^1	8^1
				1504		1573	16^1	37^1
15803.3	1520	23.7	15^1;16^1	1522	15^1;16^1	1613		$15^1 16^1$
				1532				
15828.3	1545	16	29^1	1545				
15842.5	1559.2	45.7	9^1					
15852.7	1569.4	25	8^1; $16^1 4^1$	1566	6^1	1619	7^1	7^1
				1602	$17^1 11^1$	1643	$13^1 16^1$	6^1
16000.8	1717.5	19.9	15^2	1719	15^2	1774	15^2	15^2

16055.4	1772.1	12.4	$15^{2}14^{1}$;$17^{1}10^{1}$	1771	$17^{1}11^{1}$	1814	$15^{1}16^{1}$	
16083.9	1800.6	23	7^{1}	1801		1847	$9^{1}17^{1}$	$9^{1}17^{1}$
16136.5	1853.2	13.9	$16^{1}13^{1}$	1855	$16^{1}10^{1}$	1895	$36^{1}5^{1}$	
16166.5	1883.2	12.6	$16^{1}12^{1}$	1886	$16^{1}11^{1}$	1925	$14^{1}15^{1}$	36^{1}
16209.1	1925.8	9.2	15^{1}; 34^{1}					
16224.5	1941.2	9.4		1937		1955	$10^{1}16^{1}$	$10^{1}16^{1}$
16335.9	2052.7	40	$15^{1}13^{1}$	2054	$15^{1}10^{1}$	2139	$9^{1}16^{1}$	$9^{1}16^{1}$
16348.5	2065.2	18.6	$16^{1}13^{1}$					
16365.4	2082.1	16.5	$15^{1}12^{1}$	2083	$15^{1}11^{1}$	2155	$10^{1}15^{1}$	$10^{1}15^{1}$
16396	2112.7	11.5	$16^{1}30^{1}$	2111	$14^{1}10^{1}$	2168	$47^{2}17^{1}$	
16460.1	2176.8	25	$17^{1}7^{1}$	2181		2259	$15^{1}16^{2}$	$15^{1}16^{2}$
16499.3	2216	36.6	$16^{1}9^{1}$	2218		2305	$7^{1}16^{1}$	
16532.9	2249.6	41.5	$15^{1}10^{1}$	2251		2329	$6^{1}16^{1}$	
16547.3	2264	22.6	$15^{1}31^{1}$	2306		2339	$9^{1}15^{1}$	
16591.7	2308.4	14.7		2379		2458	$15^{2}16^{1}$	$15^{1}37^{1}$
16665.9	2382.6	20.1		2387		2505	$7^{1}15^{1}$	$7^{1}15^{1}$
16698.6	2415.3	43.6	$15^{1}9^{1}$	2417		2530	$5^{1}15^{1}$	
16741.9	2458.6	19.1	$16^{1}7^{1}$	2456		2612		$16^{1}36^{1}$

2. Supplementary Material SM2.

Table SM2. The full set of SACCI singlet state energy levels as depicted in Figure 2, and state properties. The transition dipole direction reversal for several $^1A_1$ states is apparent. The $^1A_2$ states have zero oscillator strength, and while the $^1B_1$ states have non-zero values, all are very small. This leads to the VUV absorption spectrum being dominated by the $^1A_1$ and $^1B_2$ states.

ππ* and σσ* excitations							
Energy /e V	Transition Dipole (z) / a.u.	Oscillator strength	Symmetry	Energy /e V	Transition Dipole (y) / a.u.	Oscillator strength	Symmetry
3.469	1.1340	0.2216	$^1A_1$	1.532	0.3979	0.0059	$^1B_2$
4.980	-0.7204	1.1034	$^1A_1$	4.314	-0.6483	0.0444	$^1B_2$
6.115	-0.3039	0.0187	$^1A_1$	5.969	-1.3387	0.2621	$^1B_2$
7.035	-0.1751	0.0071	$^1A_1$	6.804	1.1246	0.2108	$^1B_2$
8.131	0.4514	0.0484	$^1A_1$	7.857	-1.3333	0.3422	$^1B_2$
8.260	0.2033	0.0103	$^1A_1$	8.315	0.9105	0.1689	$^1B_2$
9.430	0.0225	0.0001	$^1A_1$	9.407	-0.1177	0.0032	$^1B_2$
9.698	0.0771	0.0017	$^1A_1$	9.763	0.6887	0.1135	$^1B_2$
10.127	0.1639	0.0077	$^1A_1$	10.001	0.4207	0.0434	$^1B_2$
10.656	-0.0812	0.0020	$^1A_1$	10.271	-0.5819	0.0852	$^1B_2$
11.437	0.0796	0.0020	$^1A_1$	11.246	0.347	0.0332	$^1B_2$
11.770	0.1456	0.0067	$^1A_1$	11.887	0.0218	0.0001	$^1B_2$
12.423	1.134	0.2216	$^1A_1$	12.418	0.0794	0.0019	$^1B_2$
12.776	-0.7204	0.1034	$^1A_1$	12.707	0.1258	0.0049	$^1B_2$
12.834	-0.3039	0.0187	$^1A_1$	13.040	-0.0707	0.0016	$^1B_2$
πσ* and σπ* excitations							
Energy / eV	Transition dipole (x) / a.u.	Oscillator strength	Symmetry	Energy /eV	Transition dipole / a.u.	Oscillator strength	Symmetry
6.548	-0.0187	0.0001	$^1B_1$	5.958659		0	$^1A_2$
6.566	0.0089	0.0	$^1B_1$	6.879488		0	$^1A_2$
7.203	0.1271	0.0029	$^1B_1$	7.519228		0	$^1A_2$
7.681	0.3344	0.0210	$^1B_1$	7.577274		0	$^1A_2$
8.133	0.0179	0.0001	$^1B_1$	7.922578		0	$^1A_2$
8.726	0.3041	0.0198	$^1B_1$	8.409133		0	$^1A_2$
8.855	0.0561	0.0007	$^1B_1$	9.010411		0	$^1A_2$
8.974	-0.0134	0.0	$^1B_1$	9.043448		0	$^1A_2$
9.545	-0.0617	0.0009	$^1B_1$	9.089639		0	$^1A_2$
9.655	-0.1552	0.0057	$^1B_1$	9.420966		0	$^1A_2$
9.795	0.259	0.0161	$^1B_1$	9.831351		0	$^1A_2$
10.118	-0.0204	0.0001	$^1B_1$	10.004253		0	$^1A_2$
10.272	0.0341	0.0003	$^1B_1$	10.312016		0	$^1A_2$
10.498	-0.0204	0.0001	$^1B_1$	10.522840		0	$^1A_2$
10.747	0.0012	0.0	$^1B_1$	11.205496		0	$^1A_2$

3. Supplementary Material SM3.

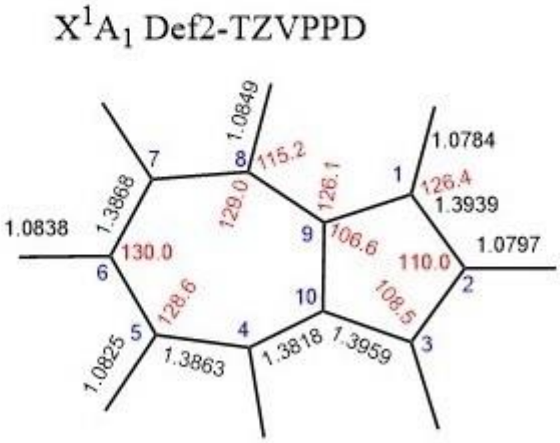
Table SM3. The harmonic frequencies for the X^{1}A$_1$ state of azulene (cm^{-1})

1	2	3	4	5	6
23a2	32b1	32b1	48b2	17a1	22a2
164	173	322	341	415	436
7	8	9	10	11	12
47b2	30b1	29b1	16a1	46b2	21a2
491	587	624	692	700	733
13	14	15	16	17	18
28b1	27b1	20a2	15a1	19a2	14a1
752	796	815	845	895	924
19	20	21	22	23	24
45b2	26b1	13a1	25b1	18a2	24b1
962	966	979	998	1018	1036
25	26	27	28	29	30
44b2	12a1	43b2	42b2	11a1	10a1
1077	1093	1185	1235	1257	1322
31	32	33	34	35	36
4b2	40b2	39b2	9a1	38b2	8a1
1328	1336	1443	1448	1508	1512
37	38	39	40	41	42
37b2	7a1	36b2	6a1	5a1	35b2
1557	1611	1677	1679	3155	3158
43	44	45	46	47	48
4a1	34b2	3a1	2a1	33b2	1a1
3165	3184	3193	3217	3236	3244

4. Supplementary Material SM4.

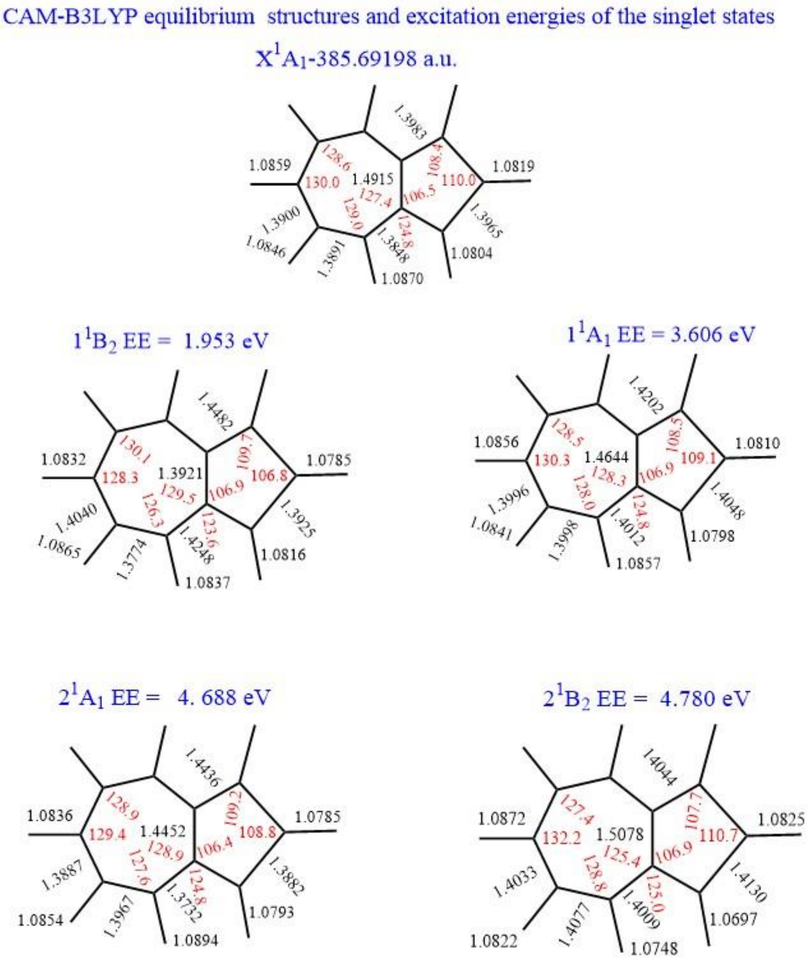
Figure SM4. The azulene equilibrium structure at the Hartree-Fock level with the Def2-TZVPPD basis set.
Microwave spectroscopy shows a relatively rigid molecule, with rotational constants (RC) A = 2841.951(24), B = 1254.8463 (10) and C = 870.7162 (8) MHz.[15,16] The X^1A_1 state equilibrium structure used in the excited state study, was determined with the 6-311G(d,p) basis set, and is shown in Figure 3; its RC are: A, 2876.829, B, 1265.900 and C, 879.075; the absolute errors when compared with the MW data are: -35 (+1.2%), +11 (-0.9%) and +8 MHz (+1.0%), are relatively close to the experimental MW data. A rather larger basis set equilibrium structure, potentially useful for comparisons with other data.

15. H. J. Tobler, A. Bauder, and Hs. H.Günthard, J. Mol. Spectrosc. **18**, 239–246 (1965). https://doi.org/10.1016/0022-2852(65)90139-6 .
16. S. Huber, G. Grassi, and A. Bauder, Mol. Phys. **103**, 1395–1409 (2005) https://doi.org/10.1080/00268970500038451.



5. Supplementary Material SM5.

Figure SM5. The singlet state structures of azulene compared with the parent molecule using the CAM-B3LYP method with the 6-311G(d,p) basis set. The ring numbering is the same as shown in Figure SM4.



6. Supplementary Material SM6.

Table SM6a. The full onset of vibrational states from the Franck-Condon profile of the lowest excited (1^1B_2) singlet state, determined by the CAM-B3LYP method with the 6-311G (d,p) basis set. The calculated 0-0 transition is at 16770 cm^{-1}. All intensity units are molar absorption coefficient / dm^3.mol-^{1}.cm^{-1}. The full list contains combinations of up to 8-simultaneous vibrations.

Position / cm^{-1}	Intensity	Vibration	Position / cm^{-1}	Intensity	Vibration
0	2680.00	0	811	0.45	11^1;1^1
241	45.12	1^2	813	0.16	3^2;1^2
388	5.26	2^2	815	1.77	6^2
394	147.80	5^1	842	0.07	6^1;2^1;1^2
407	4.68	3^1;1^1	850	1.38	8^1;4^1
481	1.13	1^4	862	5.50	13^1;1^1
573	5.46	3^2	868	5.57	9^1;3^1
601	4.46	6^1;2^1	876	0.06	5^1;1^4
629	0.14	2^2;1^2	887	1791.00	18^1
630	0.27	7^1;1^1	902	2.13	12^1;2^1
635	2.43	5^1;1^2	927	102.80	20^1
647	0.24	3^1;1^3	927	23.28	10^1;1^2
677	0.07	4^2	957	23.04	21^1
686	1358.00	10^1	965	13.24	14^1;2^1
782	0.51	5^1;2^2	967	0.33	5^1;3^2
789	2.19	5^2	977	0.36	11^1;3^1
796	0.30	7^1;3^1	996	0.24	6^1;5^1;2^1
801	0.27	5^1;3^1;1^1	--	--	

Table SM6b. The full onset of vibrational states from the Herzberg-Teller profile of the lowest excited (1^1B_2) singlet state, determined by the CAM-B3LYP method with the 6-311G(d,p) basis set. The calculated 0-0 transition is at 16770 cm^{-1}. All intensity units are: molar absorption coefficient / dm^3.mol-^{1}.cm^{-1}.

Position / cm^{-1}	Intensity	Vibration	Position / cm^{-1}	Intensity	Vibration
0	108.60	0	2883	52.31	38^1;20^1;4^1
686	67.43	10^1	2905	116.10	38^1;31^1
887	86.71	18^1	3025	61.37	40^1;25^1
1265	64.51	10^1;4^1;1^2	3067	157.20	29^1;18^1;10^1;1^2
1445	222.20	28^1;2^1	3096	65.13	36^1;18^1;12^1
1554	69.30	10^1;9^1;3^1	3174	115.30	27^1;26^1;18^1
1613	101.70	10^2;1^2	3194	213.20	36^1;34^1;1^2
1911	1106.00	18^1;10^1;4^1	3296	91.19	39^1;17^1;14^1
2138	79.65	28^1;18^1	3375	553.00	28^1;20^1;10^1;8^1
2300	57.26	26^1;10^1;8^1	3496	238.50	40^1;37^1
2313	66.12	40^1;2^2	3542	323.50	18^3;17^1
2338	110.10	14^1;10^2;2^1	3568	140.80	30^1;26^1;10^1;8^1
2505	82.09	39^1;13^1;1^1	3607	59.62	36^1;33^1;10^1
2609	352.70	30^1;25^1;1^2	3020	56.56	29^1;10^2;5^1
2718	74.17	28^1;15^1;10^1	3591	54.74	38^1;31^1;10^1
2811	706.20	30^1;14^2	--	--	

Table SM6c. The vibrational intensities contributed by the fundamentals to the Herzberg-Teller profile of the lowest excited (1^1B_2) singlet state, determined by the CAM-B3LYP method with the 6-311G(d,p) basis set. All intensity units are: molar absorption coefficient / $dm^3.mol^{-1}.cm^{-1}$.

Position / cm^{-1}	Intensity	Vibration	Position / cm^{-1}	Intensity	Vibration
0	108.6	0^0	1100	20.14	25^1
194	0.2296	2^1	1102	5.293	26^1
338	3.699	4^1	1185	2.204	27^1
394	6.076	5^1	1251	20.78	28^1
407	0.1353	6^1	1254	23.23	29^1
512	18.67	8^1	1268	64.51	30^1
686	67.43	10^1	1286	20.28	31^1
708	3.885	12^1	1371	0.0478	32^1
771	0.6090	14^1	1421	12.45	33^1
781	7.892	15^1	1453	222.2	34^1
881	1.348	17^1	1480	7.727	35^1
887	86.71	18^1	1500	5.462	36^1
927	0.6094	20^1	1571	69.30	37^1
957	0.0347	21^1	1619	101.7	38^1
1003	0.1938	23^1	1643	42.81	39^1
1055	0.9176	24^1	1925	1106	40^1

7. Supplementary Material SM7.

Table SM7. The calculated Franck-Condon fundamentals for the S_3 state (2^1B_2). determined by the CAM-B3LYP method with the 6-311G(d,p) basis set. Calculated energy of the 0-0 transition: 37921 cm^{-1}. Intensity units are the molar absorption coefficient ($dm^3.mol^{-1}.cm^{-1}$).

Position /cm^{-1}	Intensity	Vibration and quanta	Position /cm^{-1}	Intensity	Vibration and quanta
0	374100	00	662	112	6^1;3^1
189	11670	1^2	672	93750	13^1
277	2240	2^2	681	10	7^1;2^2
379	775	1^4	702	15	3^1;2^3
403	508	4^1;1^1	704	40	6^1;2^1;1^2
404	1256	7^1	710	340	10^1;1^1
425	899	3^1;2^1	752	11720	6^2
467	99	2^2;1^2	761	40	3^2;1^2
515	986	6^1;2^1	762	805	12^1;1^1
555	29	2^4	778	2047	9^1;3^1
568	52	1^6	799	170	8^1;5^1
572	944	3^2	801	179	11^1;2^1
593	62	4^1;1^3	804	2	3^1;2^1;1^4
593	53	7^1;1^2	806	178	4^2;1^2
614	27	3^1;2^1;1^2	912	19860	20^1
617	5377	4^2	946	50560	22^1
631	69	9^1;2^1	1071	21050	25^1
635	264	5^2	1343	16700	13^2

8. Supplementary Material SM8.

Table SM8. The calculated Herzberg-Teller fundamentals for the S_3 state (2^1B_2). determined by the CAM-B3LYP method with the 6-311G(d,p) basis set. Calculated energy of the 0-0 transition: 37921 cm^{-1}. Intensity units are the molar absorption coefficient (dm^3.mol^{-1}.cm^{-1}).

Position /cm^{-1}	Intensity	Vibration and quanta	Position /cm^{-1}	Intensity	Vibration and quanta
0	130	0^0	672	160	13^1
95	26	1^1	681	2	$7^1;2^2$
189	4	1^2	696	14	$5^1;1^4$
277	1	2^2	711	0.3	$4^2;1^1$
284	4	1^3	721	9	$5^1;4^1;1^1$
308	2	4^1	722	23	$7^1;5^1$
318	5086	5^1	741	13	15^1
372	0.2	$2^2;1^1$	742	12	$5^1;3^1;2^1$
379	0.3	1^4	752	4	6^2
404	196	7^1	759	44	$8^1;2^2$
425	0.3	$3^1;2^1$	762	0.3	$12^1;1^1$
474	0.4	1^5	766	10	$13^1;1^1$
482	8429	8^1	771	538	16^1
507	227	$5^1;1^2$	778	1	$9^1;3^1$
515	0.3	$6^1;2^1$	783	0.3	$7^1;1^4$
572	0.3	3^2	784	2	$5^1;2^2;1^2$
593	8	$7^1;1^2$	804	3	$10^1;1^2$
595	43	$5^1;2^2$	807	0.2	$7^1;4^1;1^1$
615	78	10^1	808	1	7^2
617	2	4^2	829	0.5	$7^1;3^1;2^1$
667	14	12^1	832	18	$6^1;5^1;2^1$
671	231	$8^1;1^2$	834	1211	17^1

9. Supplementary Material SM9.

Table SM9. Harmonic frequencies for the S_4 state of azulene (cm^{-1}).

1	2	3	4	5	6
32b1	23a2	31b1	22a2	38b2	17a1
111	134	274	349	354	420.
7	8	9	10	11	12
30b1	47b2	29b1	21a2	28b1	16a1
511	551	575	639	706	706
13	14	15	16	17	18
27b1	20a2	46b2	19a2	15a1	14a1
752	767	792	839	905	965
19	20	21	22	23	24
26b1	13a1	18a2	25b1	24b1	45b2
969	980	992	997	1045	1115
25	26	27	28	29	30
12a1	44b2	43b2	11a1	42b2	10a1
1158	1178	1273	1294	1331	1356
31	32	33	34	35	36
41b2	40b2	9a1	39b2	8a1	38b2
1387	1489	1495	1558	1571	1613
37	38	39	40	41	42
7a1	37b2	36b2	6a1	5a1	4a1
1639	1662	1945	2193	3291	3310
43	44	45	46	47	48
35b2	34b2	3a1	2a1	33b2	1a1
3312	3329	3335	3344	3362	3372

10.Supplementary Material SM10.

Table SM10. Principal fundamental and combination band vibrational states, at the Franck-Condon level, based on intensity, for S_4 in azulene, 2^1A_1 at 4.70 eV with oscillator strength f(r) = 1.1770. The calculated energy of the 0-0 transition is 42559 cm^{-1}. Intensity units are the molar absorption coefficient (dm^3.mol^{-1}.cm^{-1}).

Position / cm^{-1}	Intensity	Vibration / quanta	Position / cm^{-1}	Intensity	Vibration / quanta
0	4169000	0	1277	14060	10^2
222	173600	1^2	1294	22390	28^1
269	47250	2^2	1356	158700	30^1
385	12630	$3^1 1^1$	1403	536000	$12^1 4^2$
420	1853	6^1	1413	16820	11^2
548	28500	3^2	1413	13100	12^2
622	16130	$7^1 1^1$	1495	582900	33^1
697	40130	4^2	1535	761100	14^2
706	2000000	12^1	1578	10950	$30^1 1^2$
905	159300	17^1	1612	16250	$17^1 12^1$
928	81550	$12^1 1^2$	1634	58730	$12^2 1^2$
965	15030	18^1	1639	16610	37^1
975	22700	$12^1 2^2$	1678	33130	16^2
980	145000	20^1	1687	11060	$20^1 12^1$
1022	36420	7^2	1716	74750	$33^1 1^2$
1158	12970	25^1	1728	30240	$12^1 7^2$
1255	14060	$12^1 3^2$			

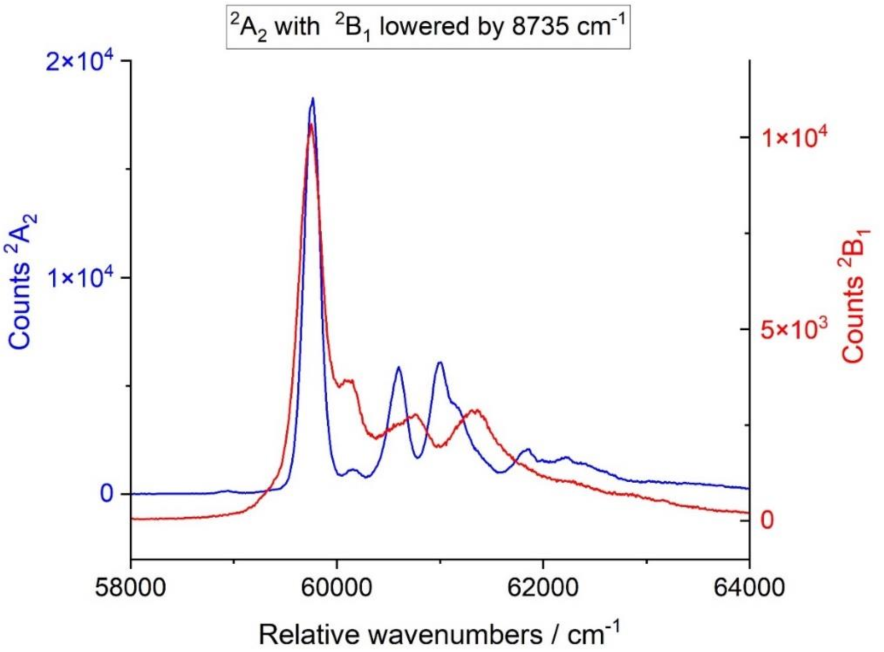
11.Supplementary Material SM11.

Table SM11. The vibrational structure of the onset of the Herzberg-Teller structure to the 4th excited state (S4, 2^1A_1) state at 4.70 eV with oscillator strength f(r) = 1.1770. The indices for the vibrations shown are as given in Table III; for example, 1^1 refers to one quantum of mode 34 (b_1) 111 cm^{-1} above the 0^0 band. All intensity units are: molar absorption coefficient / dm^3.mol-^{1}.cm^{-1}.

Position / cm^{-1}	Intensity	Vibration / quanta	Position / cm^{-1}	Intensity	Vibration / quanta
0	42.82	0	576	2.51	$5^{1}1^{2}$
111	0.02	1^{1}	607	0.02	$3^{1}1^{3}$
222	1.63	1^{2}	622	0.15	$7^{1}1^{1}$
269	0.44	2^{2}	623	0.67	$5^{1}2^{2}$
274	0.49	3^{1}	642	0.20	$6^{1}1^{2}$
354	65.95	5^{1}	659	0.00	$3^{2}1^{1}$
385	0.14	$3^{1}1^{1}$	665	0.01	1^{6}
420	5.34	6^{1}	686	0.04	$9^{1}1^{1}$
443	0.09	1^{4}	689	0.05	$6^{1}2^{2}$
483	0.08	$4^{1}2^{1}$	697	0.44	4^{2}
491	0.02	$2^{2}1^{2}$	705	0.00	$4^{1}2^{1}1^{2}$
496	0.02	$3^{1}1^{2}$	706	12.40	11^{1}
511	0.43	7^{1}	706	40.02	12^{1}
538	0.01	2^{4}	732	0.02	$7^{1}1^{2}$
543	0.01	$3^{1}2^{2}$	739	0.21	$5^{1}3^{1}1^{1}$
548	0.26	3^{2}	752	0.02	13^{1}
551	350.90	8^{1}	770	0.01	$3^{2}1^{2}$
575	0.89	9^{1}	773	0.01	$10^{1}2^{1}$

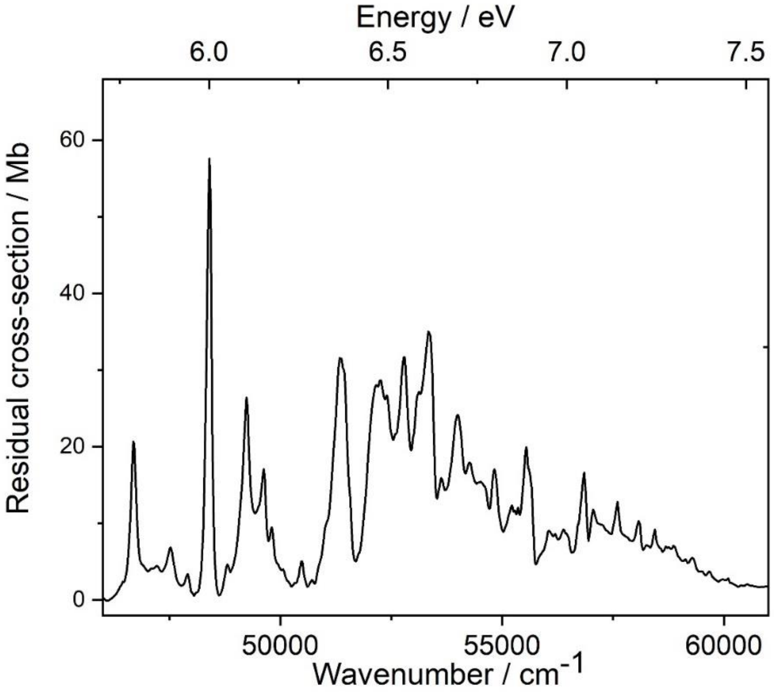
12.Supplementary Material SM12

Figure SM12. Profiles of the X^2A_2 and A^2B_1 lowest ionic states compared, by lowering the energy of the latter by 8735 cm^{-1}. The relative similarities make distinction of Rydberg states in the VUV absorption, where these are the series limits, difficult to achieve.



13.Supplementary Material SM13

Figure SM13. The principal Rydberg state region of the VUV spectrum of azulene between 42000 to 61000 cm^{-1}.



14.Supplementary Material SM14

Table SM14. The peak energies, measured in wave-numbers with relative intensities (Mb) for the principal Rydberg state region of azulene between 46000

and 61000 cm^{-1}. A peak is defined as a maximum by use of the 2nd derivative of the curve. Each contains a minimum of 5 local points in the curve, with a threshold height being set. The smoothing method is adjacent-averaging.

Wavenumber / cm^{-1}	Cross-section /Mb	Wavenumber / cm^{-1}	Cross-section /Mb	Wavenumber / cm^{-1}	Cross-section /Mb
46686	21	52785	32	56852	17
47529	7	53103	27	57053	12
47919	4	53334	35	57605	13
48404	58	53997	24	58073	10
49238	26	54256	18	58247	7
49629	17	54519	15	58446	9
49800	9	54826	17	58859	7
50481	5	55219	12	59140	5
51362	32	55541	20	59300	6
52170	28	56055	9	59687	4
52261	29	56181	9	59971	3
52398	27	56387	9	60090	3

15.Supplementary Material SM15.

Table SM15. Dipole (Debye) and second moments of the charge distribution (SECMOM, a.u.^{2}).

This is exemplified by the choice of the valence and Rydberg states of the $^1A_1$ states 2a2→nd. Note that for Rydberg states one or more terms in the SECMOM are markedly different (a large increase in the negative values).

	Nuclear	**Electronic CI**	**Total CI**
1. Molecular properties for valence state (root 1)			
dipole(z)	-0.02645818	1.97960469	1.95314651
quad(xx)	0.00000000	-51.20095569	-51.20095569
quad(yy)	370.77011025	-411.62899153	-40.85888128
quad(zz)	802.50656495	-842.92310926	-40.41654431
2. Molecular properties for Rydberg state (root 2)			
dipole(z)	-0.02645818	-2.20271811	-2.22917629
quad(xx)	0.00000000	-81.96967431	-81.96967431
quad(yy)	370.77011025	-436.34039132	-65.57028107
quad(zz)	802.50656495	-841.58101215	-39.07444720
3. Molecular properties for Rydberg state (root 3)			
dipole(z)	-0.02645818	-2.62094737	-2.64740555
quad(xx)	0.00000000	-176.82402106	-176.82402106
quad(yy)	370.77011025	-530.92606431	-160.15595406
quad(zz)	802.50656495	-872.16074317	-69.65417822
4 Molecular properties for Rydberg state (root 4)			
quad(xx)	0.00000000	-387.24662717	-387.24662717
quad(yy)	370.77011025	-741.37674311	-370.60663286
quad(zz)	802.50656495	-942.12930389	-139.62273894

16.Supplementary Material SM16

Table SM15. The calculated Rydberg states for azulene using either the CAM-B3LYP functional under TDDFT, or Hartree-Fock with MRD-CI. The latter includes or excludes VS CSF. Since the *n*s, *n*p, *n*d and *n*f states are calculated separately, the state sequences for s, p, d and f can have the same labels.

*n*s-, *n*p-, *n*d- and *n*f-Rydberg states					
MRD-CI					
VS CSF included			VS CSF excluded		
VIE Energy / eV	Rydberg state	State symmetry	VIE Energy / eV	Rydberg state	State symmetry
4.733	$2a_23$s	$^1A_2$	4.836	$2a_23$s	$^1A_2$
5.909	$2a_24$s	$^1A_2$	5.855	$2a_24$s	$^1A_2$
6.1500	$2a_25$s	$^1A_2$	6.573	$2a_25$s	$^1A_2$
5.681	$3b_13$s	$^1B_1$	5.980	$3b_13$s	$^1B_1$
6.863	$3b_14$s	$^1B_1$	7.019	$3b_14$s	$^1B_1$
7.472	$3b_15$s	$^1B_1$	7.753	$3b_15$s	$^1B_1$
5.461	$2a_23$d	$^1B_2$	6.084	$2a_23d$	$^1B_2$
6.119	$2a_24$d	$^1B_2$	6.589	$2a_24d$	$^1B_2$
6.926	$2a_25$d	$^1B_2$	7.650	$2a_25d$	$^1B_2$
5.473	$2a_23$d	$^1A_1$			
6.482	$2a_24$d	$^1A_1$			
6.953	$2a_25$d	$^1A_1$			
TDDFT					
AIE Energy / eV	Rydberg state	AIE Energy / eV	Rydberg state	AIE Energy / eV	Rydberg state
4.927	$2a_23$s	5.518	$2a_23px$	5.287	$2a_23py$
5.785	$2a_24$s	6.043	$2a_24px$	6.011	$2a_24py$
6.197	$2a_25$s	6.825	$2a_25px$	6.655	$2a_25py$
5.977	$3b_13$s	5.291	$2a_23pz$	6.083	$2a_24$f($^1A_2$)
6.805	$3b_14$s	5.906	$2a_24pz$	6.187	$2a_25$f($^1A_2$)
7.224	$3b_15$s	6.136	$2a_25pz$	6.887	$2a_26$f($^1A_2$)