

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

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## ABSTRACT

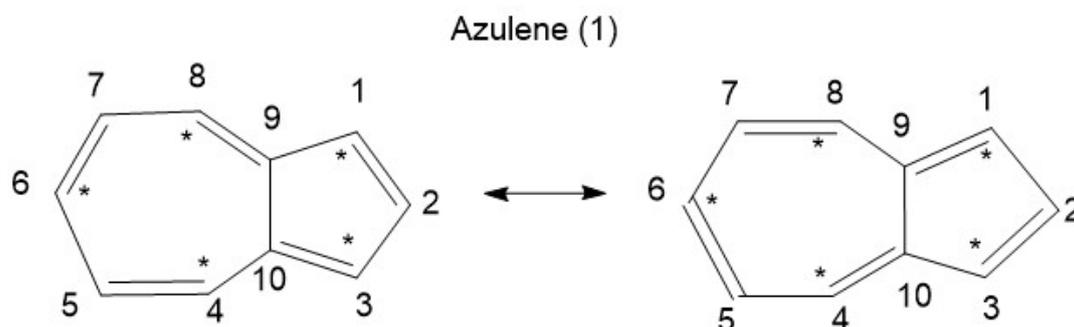
A new vacuum ultraviolet absorption (VUV) spectrum of azulene vapour has been obtained by using a synchrotron radiation source. The onset of the ultraviolet spectrum, previously reported by Sidman et al has been analysed in detail by Franck-Condon (FC) and Herzberg-Teller (HT) methods. The photoelectron spectral profile identifies the 3px-Rydberg state  $0^0$  band to be  $131\text{ cm}^{-1}$  from the VUV maximum. Excited state energy levels were calculated by three independent methods: the wide scan VUV spectrum was correlated with symmetry adapted cluster configuration interaction (SAC-CI) calculations. The low energy portion of the spectrum was studied by both time dependent density functional theoretical methods (TDDFT) and multi-reference multi-root CI (MRD-CI). Equilibrium structures were determined for valence states at the TDDFT level. Rydberg states were determined by both TDDFT and MRD-CI. The FC+HT analyses were performed on the TDDFT wave-functions. The HT intensity profiles are generally low in intensity, relative to the FC ones; however, HT is dominant in the second singlet state ( $S_2$ ,  $1^1A_1$ ). As a result, numerous non-symmetric modes, their

overtone and combination bands show considerable intensity in that band. Energies obtained from use of extremely diffuse s-, p-, d- or f-character functions enabled realistic extrapolation to the  $IE_1$  for many Rydberg states (RS). The lowest RS ( $3b_13s$ ) based on  $IE_2$  lies at 4.804 eV with a quantum defect of 0.714. Differentiation between valence and RS is readily made using the second moments of the charge distribution.

## I. INTRODUCTION

Recently, we reported synchrotron based, vacuum ultraviolet (VUV) absorption and high-resolution photoelectron spectra (PES) spectra for some multiply conjugated molecules, including cyclooctatetraene (COT),<sup>1,2</sup> cycloheptatriene (CHT)<sup>3,4</sup> and norbornadiene (NBD).<sup>5,6</sup> A major difference from preceding work for these high profile molecules, is that we have offered interpretations of the vibrational structure observed in their spectra. We now report a related UV and VUV study of azulene (*I*), another fully conjugated molecule, shown in Figure 1; recently we analysed the vibrational aspects of its PES spectrum.<sup>7</sup> Azulene is isomeric with naphthalene; these two substances played an important part, both in the development and the acceptance of, molecular orbital (MO) theory in the 1940s onwards, and have been the topic of many historical studies.<sup>8,9,10,11,12,13</sup>

**Figure 1. Azulene (1), as the name implies, is bright blue, an unusual hydrocarbon property. The non-alternant hydrocarbon skeleton is shown by the starred atoms; two adjacent starred or un-starred atoms must arise from the 5+7 membered ring atoms. In this study, the axis through  $C_2C_6$  and parallel to  $C_9C_{10}$  are z- and y-axes respectively; the x-axis ( $\pi$ ) lies perpendicular to both.**



The 5 visible and ultraviolet band systems found in azulene correspond, with respect to vibrational structure, intensity, and sequence, to the 5 found in naphthalene, except that the former are shifted to

lower frequencies by  $\sim 9000\text{ cm}^{-1}$ . The lowest band is shifted even more,  $\sim 17,000\text{ cm}^{-1}$ , and its absorption gives azulene its blue colour (hence the name). Early molecular orbital calculations for the excited  $\pi\pi^*$ -states of azulene were based on the Hückel molecular orbital procedure (HMO) which included all singles configuration interaction (CI), a considerable advance to the theoretical procedures available at that time.<sup>14</sup> We now consider the valence and Rydberg states of azulene separately.

### A. Valence states.

Microwave spectral (MW) studies of the ground  $X^1A_1$  state of azulene show a planar structure with  $C_{2v}$  symmetry.<sup>15,16</sup> For the purposes of the present paper, the molecule is oriented with the long, transverse and out-of-plane axes as z,y,x respectively; several early papers transposed y and x,<sup>14</sup> we have relabelled their  $B_1$  states as  $B_2$  in the present paper. The spectroscopy of azulene (up to February 1985) was critically reviewed by Robin.<sup>17,18</sup> Five main bands present in the absorption spectrum have onsets at 1.770 ( $^1B_2, S_1$ ), 3.565 ( $^1A_1, S_2$ ), 4.229 ( $^1B_2, S_3$ ), 4.392 ( $^1A_1, S_4$ ), 5.166 eV ( $^1B_2, S_5$ ),<sup>19,20,21</sup> all attributed to  $\pi\pi^*$ -valence states; minor variations on these values are reported by other authors.<sup>17,18</sup> The relative oscillator strengths for these lowest bands are 0.01, 0.06, 0.4, 1.0, and  $\sim 0.0$  respectively. Both  $^1A_1$  and  $^1B_2$  transitions are optically allowed with electric dipole transition moments along the z-and y-axes.

The HMO calculations above,<sup>14</sup> gave a reasonable interpretation of the  $\pi\pi^*$ -states, both for energy and intensity. The lowest energy one ( $S_1$ ), responsible for the blue-violet colour ( $\lambda_{\text{max}} 700\text{ nm}$ )<sup>14</sup> continues to 450 nm (2.755 eV). The absorption and emission spectra of azulene studied as a solid solution in naphthalene at 20 K show very high resolution.<sup>22,23</sup> The spectra are both polarized and sharp, with 0-0 bands for the two lowest excited states at 1.817 and 3.478 eV (14652 and 28050  $\text{cm}^{-1}$ ). Absorption spectra of jet-cooled azulene for the range up to 2.1 eV provides the highest resolution of the onset ( $S_0 \rightarrow S_1$ ).<sup>24,25</sup> Fluorinated hydrocarbon solutions of azulene enable differentiation of Rydberg from valence states.<sup>26, 27,28</sup> Azulene exhibits fluorescence,<sup>29,30,31,32,33</sup> but contrary to most examples, where emission proceeds to the ground state from the lowest singlet or triplet state (Kasha's

Rule), there is practically no  $S_1$  fluorescence, while strong emission occurs from  $S_2$ .<sup>34</sup> This significant deviation from the rule was first attributed to the large gap between  $S_1$  and  $S_2$ , which allows more internal conversion and vibrational relaxation. A CASSCF study of the  $S_0$  and  $S_1$  surfaces of azulene, by Bearpark et al,<sup>35</sup> showed an  $S_1/S_0$  conical intersection. This crossing established how relaxation, observed by ultrafast  $S_1$  femtosecond decay using laser and spectroscopic line width measurements, occurred. The  $S_0 \rightarrow S_1 \rightarrow S_2$  excitation pathway has recently been studied by 2-dimensional electronic spectroscopy.<sup>36</sup> Fluorescence excitation and dispersed spectra from the  $S_2$ ,  $S_3$  and  $S_4$  states, when jet-cooled, only show extensive vibrational structure for the  $S_2$  state.<sup>34</sup>

## B. Rydberg states.

The presence of Rydberg series (RS) in the VUV spectrum of azulene has been widely observed.<sup>37,38,39,40</sup> The lowest ionized state of azulene ( $X^2A_2$ ), energy 7.431(6) eV;<sup>7</sup> was first evaluated by energy extrapolation from these RS<sup>38</sup> as discussed below; direct measurement using He(I) irradiation (584 Å) gave 7.42(5) eV.<sup>41</sup> Two series of VUV RS, also with a limit at 7.431 eV ( $59940\text{cm}^{-1}$ ),<sup>38</sup> lead to principal quantum numbers (PQN,  $n$ ) 4 to 10 and 4 to 7, with apparent quantum defects ( $\delta$ ) 0.91 and 1.01. The same peaks,<sup>37</sup> have been analysed in terms of  $\delta = 0.88$  and 0.36, for series with  $n = 4$  to 10, and with 4 to 5. No peaks were observed in either study for  $n = 3$ ,<sup>37, 38</sup> but these would lie under the strongest band with maximum near 4.773 eV ( $38500\text{cm}^{-1}$ ), which contains the  $S_3$  and  $S_4$   $\pi\pi^*$ -valence states, as discussed below. Robin<sup>17,18</sup> assigned these two RS as  $nD$ , with overall  $\delta = -0.09$  and  $-0.12$  respectively; negative  $\delta$  values were noted as consistent with those for naphthalene. These assignments were attributed to the processes:  $2a_2 \rightarrow nd_{XY}$  ( $X^1A_1 \rightarrow ^1A_1$ ) and  $2a_2 \rightarrow nd_{XZ}$  ( $X^1A_1 \rightarrow ^1B_2$ ).<sup>39,40</sup>

Rydberg states have also been directly obtained by both single and multi-photon excitation (MPI).<sup>42,43</sup> A variation is to use 3-photon laser ionization, to generate azulene super-excited states; these undergo internal conversion, i.e. relaxation, to generate Rydberg states, which were observed using a further laser.<sup>42</sup> Using these MPI methods various Rydberg states, identified by their quantum defects, were obtained for both azulene and naphthalene with  $n = 4, 5$  and  $6$ .<sup>42,43</sup> These methods do not involve the

IE directly, so that the Rydberg state energies are relative to the IE, and described as binding energies. Another pump-probe photoionization of azulene showed the ionization process to be more complex, but led to six new Rydberg states in the energy range 4.72 to 6.33 eV;<sup>44</sup> the  $\delta$ -values for these new states were assigned to  $3p_x$ ,  $3p_y$ ,  $3d_{xy}$ ,  $3d_{xz}$ ,  $4p_x$  and  $4p_y$ .

Some previous authors<sup>43</sup> had assigned the states with highest  $\delta$  (e.g. 0.83) as  $4s$ , but given that  $IE_1$  is  $X^2A_2$ , that last assignment appears to be incorrect, since these  $ns$ -Rydberg states are forbidden. These results suggest a photoionization process which is driven by an unstable electronic state, possibly a doubly excited state below the ionization potential.<sup>44</sup> The  $S_2$ ,  $S_3$  and  $S_4$  excited states have very short lifetimes, and undergo rapid internal conversion to high vibrationally excited levels of the electronic ground state ( $S_0^*$ ).<sup>45</sup>

The lowest singlet states of azulene ( $S_n$ , where  $n = 1$  to  $5$ ), were initially measured directly as  $S_0 \rightarrow S_n$  processes by Mann et al.<sup>46</sup> Two-photon absorption in the range 4.067 to 5.207 eV then led to the consecutive excitation processes  $S_0 \rightarrow S_1 \rightarrow S_n$  ( $n > 1$ ).<sup>47</sup> Synchronous nitrogen and dye laser excitation gave energies from the  $S_1$  to  $S_3$  and  $S_4$ .<sup>48</sup> The excitation energies for all of the  $S_n$  series ( $n = 1$  to  $5$ ) are comparatively close to the earliest calculations by Pariser.<sup>14</sup>

Ground state vibrational analyses of azulene have been reported, using density functional methods (DFT) and basis sets of similar quality to the present study.<sup>49,50,51,52</sup> Several analyses of the vibrational structure for excited singlet states of azulene both by fluorescence and absorption have been reported.<sup>23</sup> Some others include prominent vibrations for the  $S_2$ ,  $S_3$  and  $S_4$  states of azulene itself, in hydrocarbon solutions at low temperature.<sup>53,54,55</sup>

The main focus of this paper is to offer a detailed analysis of the spectral bands using both Franck-Condon (FC) or Herzberg-Teller (HT) procedures; none have been reported previously for azulene. Our high-level theoretical studies include symmetry adapted cluster (SAC-CI) calculations, time dependent density functional theoretical methods (TDDFT) procedures and multi-reference multi-root CI (MRD-CI) studies, as described below. We conclude by showing how very diffuse gaussian

type orbitals can be used to generate short Rydberg series, which in turn can be extrapolated to generate realistic ionization energies.

## II. METHODS

The azulene sample, CAS registry number 275-51-4, was used without further purification; its  $^1\text{H}$  NMR study showed  $> 99\%$  purity.

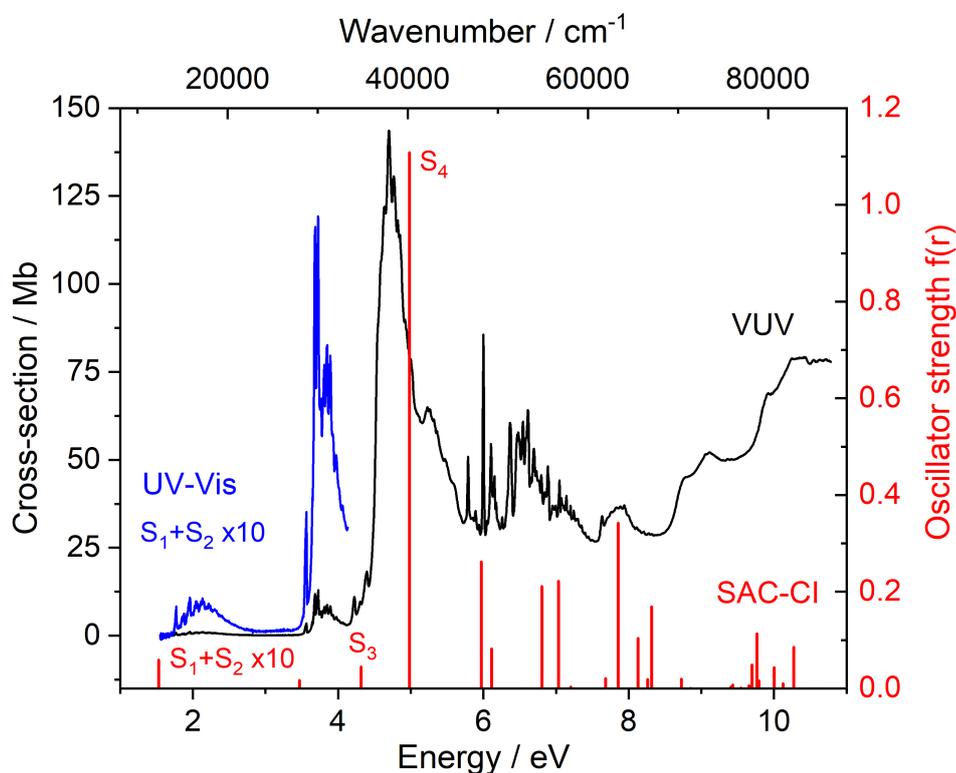
### A. The UV-visible (UV-Vis) and VUV absorption spectrum of azulene

The UV-Vis spectral onset was accessed in two ways. Solid azulene, in a 10 cm path-length quartz cell within a Thermo Unicam UV340 instrument, was allowed to equilibrate at room temperature for 48h before the gas phase measurements commenced. The bandpass and data intervals were 1 and 0.5 nm respectively, with a scan rate 30 nm/minute. Alternatively, we obtained the UV spectrum using a Thermo Evolution 300 spectrometer with a purpose built heated holder, also for a 10 cm quartz cell. The spectrum obtained at 50°C gave an improved signal to noise ratio over the room temperature data, while still keeping the temperature of the body of the cell low; this avoided azulene condensation on the end windows of the cell. These data were recorded in the spectral range from 800 nm to 300 nm with a band pass of 0.5 nm intervals, at a scan rate of 30 nm/minute.

The spectral range from 340 nm (3.647 eV) to 115 nm (10.781 eV) was collected on the AU-UV beamline of ASTRID2 (Aarhus, Denmark) at 35°C; at this temperature, the highest sample pressure achievable was 0.02 Torr.<sup>4,6</sup> Data were recorded in steps of 0.05 or 0.1 nm, depending on the level of fine detail in the spectrum. The total energy range was covered by 3131 data points. It is effectively identical to that of Bouler et al<sup>39</sup> over the common energy range 5.50 to 7.50 eV, but the much higher cross-section has allowed us to expand sections by greater amounts. The combined UV (in blue) + VUV (black) spectra are superimposed on the VUV spectrum and symmetry-adapted cluster configuration interaction (SAC-CI) calculations, in Figure 2.

A more detailed comparison with the jet-cooled 2-colour multi-photon ionization spectrum (MPI)<sup>24</sup> is shown in the supplementary material (SM) as Figure SM1. Many of the principal bands are similar, but our UV340 results are limited to a small number of scans, involving manual collection, and by the very low sample vapour pressure.

**Figure 2.** The wide scan visible + ultraviolet and vacuum ultraviolet spectrum, shown in blue and black respectively, where the amplitude of the UV-Vis cross-section has been increased by a factor of 10, to improve its visibility relative to the VUV cross-section. The symmetry-adapted cluster calculations (SAC-CI), described in the text, also show a wide range of oscillator strengths, especially near the onset with states  $S_1$  and  $S_2$  and are also amplified by a factor of 10 to improve their visibility.



## B. Theoretical methods

### i. General procedures.

Several computational chemistry suites were used. Our principal choice was GAUSSIAN-16 (G-16);<sup>56</sup> this contains SAC-CI,<sup>57,58,59,60,61</sup> and the Pisa-group<sup>62,63,64</sup> software for Franck-Condon (FC) and Herzberg-Teller (HT) vibrational analyses. Input wave-functions for the FC+HT analyses were obtained by TDDFT methods;<sup>65,66,67</sup> the Becke three-parameter Lee–Yang–Parr (B3LYP) hybrid functional,<sup>68</sup> including the Coulomb-attenuating method (CAM-B3LYP),<sup>69</sup> was particularly useful. In G-16, adiabatic ionization energies (AIE) are based upon energy differences between ground and excited state *at the excited state equilibrium geometry*; spectroscopic AIE have the difference in energy between the excited state and the ground state, *each at their equilibrium structures*.

Azulene is unusual at both the Hartree-Fock and multiconfigurational wave function level<sup>50</sup> in showing a double minimum energy surface; the  $C_{2v}$  structure is a maximum, and exhibits an

imaginary vibration frequency. Density functional methods, originally designed to take into account dynamical correlation, also succeed in these circumstances by generating only positive vibration frequencies.

## ii. Rydberg states.

These were performed by two methods: TDDFT calculations with the CAM-B3LYP method, and the MRD-CI method<sup>70</sup> within GAMESS-UK.<sup>71</sup> The 6-311G(d, p)<sup>72</sup> basis set was augmented by diffuse functions on the azulene a-axis at C<sub>2</sub> thereby maintaining C<sub>2v</sub> symmetry; this requirement is non-ideal, but G-16 does not allow optimization and frequency determination when functions are on non-atomic centres. The diffuse Gaussian exponents, (0.021, 0.008 and 0.00267) together with s-, p-, d- and f-spherical harmonics, were as used in our previous Rydberg state determinations. The basis functions were positioned at the centre of the C<sub>9</sub>C<sub>10</sub> bond when using GAMESS-UK.<sup>71</sup>

## III. RESULTS and DISCUSSION

**General points.** Following Pariser,<sup>14</sup> many early papers used the convention that molecules with C<sub>2v</sub> symmetry lay in the x,z-plane; this later changed to the y,z-plane. Here, azulene has out-of-plane  $\pi$ -molecular orbitals (MOs) in the x-axis; similarly,  $\pi\pi^*$  electronic states, previously of A<sub>1</sub> + B<sub>1</sub> symmetry, here are A<sub>1</sub> + B<sub>2</sub>. Early published assignments have been transposed to the present convention. In summary, the azulene molecule is oriented with rotational constants (A, B, C) in coordinate axes: A(z), B(y) and C(x).

The doubly occupied MOs are:  $\sigma$ -MOs:  $17a_1 + 12b_2$ , and  $\pi$ -MOs:  $3b_1 + 2a_2$ . The C<sub>1s</sub> core orbitals,  $6a_1 + 4b_2$  although included in all calculations, are ignored in the valence shell labelling system used here, which consists of:  $11a_1 + 8b_2 + 3b_1 + 2a_2$ . Azulene has 48 fundamental vibrations:  $17a_1 + 6a_2 + 9b_1 + 16b_2$ .

We concentrate on the 4-lowest singlet valence states (VS), S<sub>1</sub> to S<sub>4</sub>; their polarization gave previous assignments as  $1^1B_2$ ,  $1^1A_1$ ,  $2^1B_2$  and  $2^1A_1$  respectively. We use single excitation configuration interaction (SCI) in TDDFT, with the CAM-B3LYP functional in the FC + HT analyses. These analyses were performed by the Pisa software, as noted in Section IIB(i) above.<sup>62,63,64</sup>

All calculated Rydberg states are preceded in the state singlet manifold by  $S_1$  to  $S_4$ ; the leading configurations of these are shown in Equations 1. All of these states are  $\pi\pi^*$  rather than  $\sigma\sigma^*$  excitations and are permutations of the two highest occupied and lowest unoccupied MOs (HOMOs and LUMOs respectively). Judicious selection of the reference configurations enabled these VS to be de-selected from the CI state expansions using MRD-CI, since these behave as intruder states.

**Equations 1. Leading term densities at the  $X^1A_1$  equilibrium structure, using valence shell numbering and listed by increasing binding energy. These include all the  $\pi\pi^*$ -states making significant contributions to the cross-section of the VUV absorption spectrum; an optically forbidden state in FC terms,  $1^1A_2$  state is included to demonstrate its relatively low position in the sequence.**

$$S_1 (1^1B_2): 0.702 (2a_24b_1^*) + 0.122 (3b_13a_2^*).$$

$$S_2 (1^1A_1): 0.586 (2a_23a_2^*) + 0.394 (3b_14b_1^*)$$

$$S_3 (2^1B_2): 0.651 (3b_13a_2^*) + 0.243 (1a_24b_1^*)$$

$$S_4 (2^1A_1): 0.584 (3b_14b_1^*) - 0.396 (2a_23a_2^*)$$

$$S_5 (3^1B_2): 0.649 (1a_24b_1^*) - 0.204 (3b_13a_2^*) + 0.139 (2a_25b_1^*)$$

$$S_6 (1^1A_2): 0.646 (2a_25b_1^*) - 0.193 (2a_213a_1^*)$$

$$S_9 (3^1A_1): 0.600 (1a_23a_2^*) - 0.311 (2b_14b_1^*) + 0.120 (3b_14b_1^*)$$

#### A. The wide scan VUV spectrum and SAC-CI assignment.

We have amplified the spectral cross-sections and their calculated oscillator strengths  $f(r)$  for the two lowest lying states by a factor of 10; all higher energy calculated results in Figure 2 have intensities shown in the Figure axes. By far the highest cross-section is  $S_4$ ; some of its vibrational structure is associated with the very weak  $S_3$  band, close to 4.3 eV. The relatively sharp set of bands between 5.8 and 7.8 eV are all Rydberg state structure and are discussed separately below.

**Table I. The lowest group of SAC-CI singlet state energy levels, as depicted in Figure 2, together with the state properties such as transition dipole moment and direction, and oscillator strength. The  $X^1A_1$  ground state has calculated dipole moment (+)0.4893 (z) a.u. (1.2444 D).**

Energy /eV	Transition Dipole / a.u.	Oscillator strength	Symmetry	Energy /eV	Transition Dipole / a.u.	Oscillator strength	Symmetry
1.532	0.3979 (y)	0.0059	$^1B_2$	6.566	0.0089(x)	0.0	$^1B_1$
3.469	0.1434(z)	0.0017	$^1A_1$	6.804	1.1246(y)	0.2108	$^1B_2$
4.314	-0.6483(y)	0.0444	$^1B_2$	7.035	1.1340(z)	0.2216	$^1A_1$
4.980	3.0138(z)	1.1081	$^1A_1$	7.203	0.1271(x)	0.0029	$^1B_1$
5.969	-1.3387(y)	0.2621	$^1B_2$	7.681	0.3344(x)	0.0210	$^1B_1$

6.115	0.7383(z)	0.0817	$^1A_1$	7.857	-1.3333(y)	0.3422	$^1B_2$
6.548	-0.0187(x)	0.0001	$^1B_1$	8.131	-0.7204(z)	0.1034	$^1A_1$

The lowest SAC-CI singlet (vertical excitation) states, shown in Table I, are determined at the equilibrium geometry of the  $X^1A_1$  ground state. The full set of calculated singlet state energy levels, as depicted in Figure 2, are shown in the SM as Table SM2. The changes in signs of the transition dipole direction are apparent in Table I. The  $^1B_1$  states have non-zero  $f(r)$  but most are very small;  $^1A_2$  states have  $f(r) = 0$ ; the  $\pi\sigma^*$ ,  $\sigma\pi^*$  states have little influence. This leads to the VUV absorption spectrum being largely dominated by the  $^1A_1$  and  $^1B_2$  states.

### B. The wide scan experimental UV + VUV spectrum.

The black curve in Figure 2 presents the full photoabsorption spectrum of azulene in the range 1.55 to 10.78 eV; the UV onset region (in blue) intensity was scaled, as above. The absorbance data measured using the benchtop UV spectrometer have been scaled to the AU-UV beamline intensities in the 3.65 to 4.13 eV overlap region, in order to present their cross-sections in Mb. This spectrum covers the largest energy range with associated absolute cross-sections for azulene. Robin<sup>17,18</sup> reviewed many azulene Rydberg states (RS), as stated above. The lowest observed RS, term value 1.549 eV and  $f(r)$  0.024, was assigned to an unspecified  $2a_23d$  state, since  $3s$  states are forbidden.  $3p$ -RS are  $\sim 4.339$  eV,<sup>39,40</sup> close to the intense  $\pi\pi^*$ -valence state at 4.711 eV. Two further RS<sup>37,38</sup> also converge on the lowest IE at 7.420 eV, but with  $\delta = 0.36$  and 0.88; the latter, too high to be an  $np$ -Rydberg state, was attributed to a  $d$ -series, with higher PQN.<sup>17,18</sup> Higher valence states underlying these Rydberg states are exposed by hydrocarbon solutions, and have broad maxima close to 5.976, 6.509 and 6.980 eV respectively;<sup>17,18</sup> these energies are very close to those for valence states determined by the SAC-CI method shown in Figure 2; they correspond to  $3^1B_2$ ,  $4^1B_2$  and  $4^1A_1$  with energies 5.943, 6.670 and 7.010 eV respectively. The peaks to either side of the 8 eV VUV maximum then correspond to  $5^1B_2$  and  $6^1B_2$ . It was impractical to compute more than 15 roots in SAC-CI for each irreducible representation owing to facility limitations. The group of relatively intense VUV

peaks calculated circa 10 eV, are probably too high in energy, and relate to the observed band between 8.74 and 9.08 eV.

### C. Ground state vibrational frequencies.

The results from a resonance Raman (RR) study<sup>28</sup> of azulene-H<sub>8</sub> and azulene-D<sub>8</sub>, are widely used, after minor corrections,<sup>50</sup> to provide the ground state fundamentals. These give a close correlation with the present X<sup>1</sup>A<sub>1</sub> results at the CAM-B3LYP level. After re-designation of b<sub>1</sub> and b<sub>2</sub> vibrations, we find  $\nu_{\text{calc}} = 1.056(9)\nu_{\text{RR}} - 15(14) \text{ cm}^{-1}$ ; the correlation coefficient (CC) is 0.997, and the standard errors (SE) are in parentheses. This correlation line lies very close to the origin, since its intercept is only slightly larger than its SE. These ground state frequencies are similar to both the experimental values<sup>28,52</sup> and DFT theoretical ones,<sup>50,51</sup> and are shown in the SM as SM3.

### D. Singlet excited state structures.

A comparison between the microwave study<sup>15,16</sup> of the azulene X<sup>1</sup>A<sub>1</sub> molecular structure, and that from our largest basis set, Def2TZVP, is shown in the SM as SM4. Equilibrium structures, followed by vibrational frequency determinations, were obtained for several low-lying singlet states, including 1<sup>1</sup>A<sub>1</sub>, 2<sup>1</sup>A<sub>1</sub>, 1<sup>1</sup>B<sub>2</sub>, 2<sup>1</sup>B<sub>2</sub>, 1<sup>1</sup>A<sub>2</sub>, 2<sup>1</sup>A<sub>2</sub>, 1<sup>1</sup>B<sub>1</sub>, and 2<sup>1</sup>B<sub>1</sub>. These were obtained by use of the TDDFT procedure, where the symmetry and root of interest are user selected. The vibrational structure for these states is discussed below. As expected for a rigid molecular system, the variations with structure are relatively small; most bonds vary by less than 0.07 Å and most angles by less than 4°. The C<sub>9</sub>C<sub>10</sub> bond is typical, varying from 1.392 to 1.508 Å. Further details of the actual structures are given in the SM as SM5.

### E. Comparison of the theoretical absorption manifold of azulene with experiment.

The harmonic frequencies for the 1<sup>1</sup>B<sub>2</sub> state at 1.817 eV, using the CAM-B3LYP method with the 6-311G(d,p) basis set, is shown in Table II. The systematic nomenclature for vibrational spectroscopy has mode sequence numbers: a<sub>1</sub> < a<sub>2</sub> < b<sub>1</sub> < b<sub>2</sub>, and are high to low frequency in each representation. G-16, including the Pisa software,<sup>62,63,64</sup> labels modes in ascending frequency rather than the spectroscopic sequence above; for simplicity, both sets of labels are shown in Table II. This binary system of labels applies to all other calculated vibrational states described below. All vibrational

modes are in  $\text{cm}^{-1}$ , while intensity units are molar absorption coefficient ( $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ). All vibrational states with up to 8 simultaneous excitations are included in our calculations. Many of these states have low intensity, but their considerable number ( $> 10^5$ ) allow these to make a significant contribution to the overall intensity.

Similarity of the vibrational frequencies for  $S_2 \rightarrow S_1$  fluorescence with those from the  $S_0 \rightarrow S_1$  absorption for azulene in a naphthalene mixed crystal at 4.2 K<sup>33</sup>, led Gillispie and Lim to assignments for their  $a_1$  and  $b_2$  frequencies. A comparison of the present calculated data in Table II, over 20 ( $a_1 + b_2$ ) vibrations, yields a linear correlation  $v_{\text{CAM-B3LYP}} = 1.044 (14)v_{\text{Gillispie}} - 3.2 (168) \text{ cm}^{-1}$ , with standard errors (SE) in parentheses and a correlation coefficient (CC) of 0.996; a similar correlation is found for comparison of our results with other studies.<sup>77 73</sup> These correlations give confidence that the present harmonic frequencies are close to the experimental results.

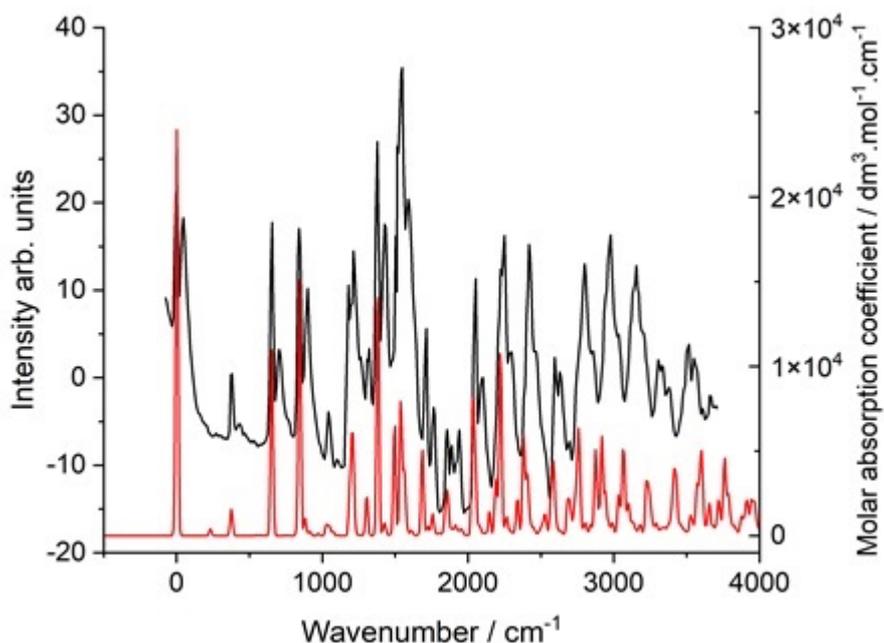
**i. The lowest singlet state ( $1^1B_2$ ,  $S_1$ ) at 1.817 eV.**

We describe this state, in detail since this explains our approach. Solution spectra of azulene show 4 peaks in the 700 to 500 nm range, with separations of  $\sim 750 \text{ cm}^{-1}$ . The highest resolution spectra for this state are in two jet-cooled studies using either 2-colour double resonance spectroscopy,<sup>24</sup> or a cavity ring-down (CRD) absorption spectrum.<sup>25</sup> Both groups<sup>24, 25</sup> propose spectral analyses which include symmetric and non-symmetric vibrations.<sup>73,74</sup> A comparison of our onset with the CRD spectrum, in the SM as SM1, shows that the principal features are reproduced in both spectra. However, it appears that Figure 1 of Suzuki et al<sup>24</sup> with energy axis labelled as wavenumber, is in fact non-linear, and should correctly be labelled wavelength; for example  $14500 \text{ cm}^{-1}$  should be 145 nm. This scale change yields good agreement between the Figure 1 of both Suzuki et al<sup>24</sup> and Ruth et al<sup>25</sup> with the present study.

The colour of azulene allowed its absorption and emission spectra to be determined as a very dilute solid solution in the host naphthalene at 20K, by Sidman and McClure (S&M).<sup>22,23</sup> Using earlier gas phase data,<sup>75</sup> they estimated the shift of the 0-0 band as  $703 \text{ cm}^{-1}$  to the red on solid solution formation; we found a slightly smaller shift of  $633 \text{ cm}^{-1}$  would correlate the S&M and present spectral results.

The S&M absorption spectrum leads to a much more detailed picture than that generated by conventional methods.<sup>75</sup> This is reproduced in Figure 3, where the base-line has been flattened by subtraction of a sigmoid function from the reported<sup>23</sup> signal in their Figure 1. It is strongly polarized across the transverse-axis. Many of the spectral peaks in Figure 3 are doublets, which become closer and merge as the energy increases. S&M suggest that the sharpness and polarization of the spectra indicate that azulene molecules occupy two lattice positions with almost identical environments in the naphthalene unit cell. An alternative assignment for the jet-cooled azulene spectra by Suzuki et al<sup>24</sup> and Ruth et al<sup>25</sup> for the  $S_0 \rightarrow S_1$  for azulene, is included in the SM as Table SM1.

**Figure 3.**The Sidman and McClure (S&M) onset band at  $14652 \text{ cm}^{-1}$  after flattening of the baseline by subtraction of a best fit sigmoid function (black curve); the peaks in red are the Franck-Condon profile for this band, as described in the text. These have been aligned for the 0-0 bands to the lowest S&M peak; the alternative to the higher origin of S&M is equally possible, and leads to little change in correlation.



Our TDDFT calculated  $1^1B_2$  state using the CAM-B3LYP functional, is a  $\pi\pi^*$ -excitation with two leading configurations, as shown in Equations 1. The FC profile is superimposed on the S&M spectrum in Figure 3. Our calculated 0-0 band onset is at  $16773 \text{ cm}^{-1}$  (excitation energy 2.358 eV, with  $f(r)$  0.0117). The observed band origin is at  $14652 \text{ cm}^{-1}$  (1.817 eV),<sup>23,26</sup> and our profile has been shifted to 0-0 superposition.

S&M<sup>23</sup> identified three symmetric ( $a_1$ ) frequencies, 384, 664 and 857  $\text{cm}^{-1}$ , for this state; these clearly correlate with the 3 lowest  $a_1$  vibrations of the present study at 394, 686 and 886  $\text{cm}^{-1}$ , since there are no other  $a_1$  modes close to these values. Their higher  $a_1$  bands<sup>23</sup> at 1191, 1386 and 1554  $\text{cm}^{-1}$ , correlate with our 1251 ( $11a_1$ ), 1453 ( $9a_1$ ) and 1619  $\text{cm}^{-1}$  ( $7a_1$ ) values. These six pairs of data lead to a linear correlation:  $v_{\text{CAM-B3LYP}} = 1.053(61) * v_{\text{Sidman}} - 11.1(6)$ , with an CC of 0.99983 and SE in parentheses. Thus, the calculated frequencies are 5.3% high, with a very low intercept (i.e. correction) of only 11.1  $\text{cm}^{-1}$ . These corrections were then applied to all calculated Franck-Condon (FC) and Hertzberg-Teller (HT) data for this state, enabling the calculated profiles to be superimposed on the spectrum.

The FC profile (Table III) of this band shows that many  $a_1$  fundamental modes and binary combinations are excited, but with the 0-0 band having by far the highest intensity. The C-H stretching frequencies have negligible intensity. Those shown in Table III are where modes 5( $17a_1$ ), 10( $16a_1$ ) and 18( $15a_1$ ) are prominent. A set of vibrational states showing the range of vibrational types occurring close to the onset is shown in the SM as SM6.

The HT vibrational states calculated for the  $1^1B_2$  band have intensities  $\sim 20$  times weaker than the FC states, and hence will have little impact on the profile of the combined set when compared with experiment; these are shown in Table IV. The calculated onset shows several non-symmetric modes with even quanta and relatively high intensity.

**Table II. The harmonic frequencies ( $\text{cm}^{-1}$ ) for the lowest excited ( $1^1B_2$ ) state, determined by single excitation CI. The sequence numbers 1 to 48 apply for the vibrations excited by FC and/or HT processes.**

1	2	3	4	5	6
32b <sub>1</sub>	23a <sub>2</sub>	31b <sub>1</sub>	48b <sub>2</sub>	17a <sub>1</sub>	22a <sub>2</sub>
120	194	286	338	394	407
7	8	9	10	11	12
30b <sub>1</sub>	47b <sub>2</sub>	29b <sub>1</sub>	16a <sub>1</sub>	28b <sub>1</sub>	21a <sub>2</sub>
510	512	582	686	691	708
13	14	15	16	17	18
27b <sub>1</sub>	20a <sub>2</sub>	46b <sub>2</sub>	26b <sub>1</sub>	19a <sub>2</sub>	15a <sub>1</sub>
741	771	781	823	881	887
19	20	21	22	23	24
25b <sub>1</sub>	14a <sub>1</sub>	13a <sub>1</sub>	24b <sub>1</sub>	18a <sub>2</sub>	45b <sub>2</sub>
905	927	957	996	1003	1055

25	26	27	28	29	30
44b <sub>2</sub>	12a <sub>1</sub>	43b <sub>2</sub>	11a <sub>1</sub>	42b <sub>2</sub>	10a <sub>1</sub>
1100	1102	1185	1251	1254	1268
31	32	33	34	35	36
41b <sub>2</sub>	40b <sub>2</sub>	39b <sub>2</sub>	9a <sub>1</sub>	38b <sub>2</sub>	8a <sub>1</sub>
1286	1371	1421	1453	1480	1500
37	38	39	40	41	42
37b <sub>2</sub>	7a <sub>1</sub>	6a <sub>1</sub>	36b <sub>2</sub>	5a <sub>1</sub>	35b <sub>2</sub>
1571	1619	1643	1925	3156	3160
43	44	45	46	47	48
4a <sub>1</sub>	34b <sub>2</sub>	3a <sub>1</sub>	2a <sub>1</sub>	33b <sub>2</sub>	1a <sub>1</sub>
3189	3191	3201	3227	3231	3262

**Table III.** A selection of the most intense vibrational states, especially fundamentals, 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  $\text{cm}^{-1}$ . Intensity units are molar absorption coefficient ( $\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ).

Position / $\text{cm}^{-1}$	Intensity	Vibration	Fundamental
0	2995	0 <sup>0</sup>	
394	187	5 <sup>1</sup>	17
686	1077	10 <sup>1</sup>	16
887	1363	18 <sup>1</sup>	15
927	80	20 <sup>1</sup>	14
957	20	21 <sup>1</sup>	13
1080	79	10 <sup>1</sup> 5 <sup>1</sup>	
1102	59	26 <sup>1</sup>	12
1251	331	28 <sup>1</sup>	11
1268	631	30 <sup>1</sup>	10
1281	128	18 <sup>1</sup> 5 <sup>1</sup>	
1372	270	10 <sup>2</sup>	
1453	1897	34 <sup>1</sup>	9
1500	73	36 <sup>1</sup>	8
1573	717	18 <sup>1</sup> ;10 <sup>1</sup>	
1613	53	20 <sup>1</sup> ;10 <sup>1</sup>	
1619	928	38 <sup>1</sup>	7
1643	408	39 <sup>1</sup>	6
3156	2.4	41 <sup>1</sup>	5
3189	0.6	43 <sup>1</sup>	4
3201	2.3	45 <sup>1</sup>	3
3227	0.9	46 <sup>1</sup>	2
3262	1.6	48 <sup>1</sup>	1

**Table IV.** The complete onset 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  $\text{cm}^{-1}$ . Intensity units are the molar absorption coefficient ( $\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ).

Position / $\text{cm}^{-1}$	Intensity	Vibration	Position / $\text{cm}^{-1}$	Intensity	Vibration
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0	121.4	0	927	0.9	10 <sup>11</sup> 2
241	2.1	1 <sup>2</sup>	965	0.4	14 <sup>12</sup> 1
338	4.7	4 <sup>1</sup>	1020	0.6	7 <sup>2</sup>
388	0.3	2 <sup>2</sup>	1025	2.3	10 <sup>14</sup> 1
394	7.7	5 <sup>1</sup>	1055	0.7	24 <sup>1</sup>
512	13.7	8 <sup>1</sup>	1080	4.0	10 <sup>15</sup> 1
686	53.4	10 <sup>1</sup>	1100	27.5	25 <sup>1</sup>
708	3.4	12 <sup>1</sup>	1102	4.3	26 <sup>1</sup>
733	0.3	5 <sup>1</sup> 4 <sup>1</sup>	1128	1.1	18 <sup>11</sup> 2
752	0.4	8 <sup>1</sup> 1 <sup>2</sup>	1176	0.3	15 <sup>15</sup> 1
771	0.8	14 <sup>1</sup>	1185	2.7	27 <sup>1</sup>
781	6.6	15 <sup>1</sup>	1198	7.6	10 <sup>18</sup> 1
881	1.6	17 <sup>1</sup>	1225	3.1	18 <sup>14</sup> 1
887	66.0	18 <sup>1</sup>	1251	27.2	28 <sup>1</sup>
906	1.3	8 <sup>1</sup> 5 <sup>1</sup>	1254	19.1	29 <sup>1</sup>
927	0.5	20 <sup>1</sup>	1268	56.8	30 <sup>1</sup>

**ii. The singlet state ( $1^1A_1$ ,  $S_2$ ) at 3.478 eV.**

This excited state has band origin at 28050 cm<sup>-1</sup> (3.478 eV), and is polarized along the long z-axis, according to S&M.<sup>23</sup> Their observed frequencies from this absorption band differed significantly from the onset  $S_1$  absorption, and a series of possible assignments were offered in FC terms (i.e. only  $a_1$  vibrations), which are discussed below.<sup>23</sup> The harmonic frequencies for the  $1^1A_1$  state, the generally assumed assignment, are shown in Table V; C-H stretching frequencies are excluded from later discussion; none appear to contribute. We will see that the S&M frequencies do not match with the calculated values in Tables VI and VII below. The similarity between the rotational constants for the  $S_2$  and  $S_0$  states by microwave spectroscopy indicates that  $S_2$  has an equilibrium structure similar to that of the ground electronic state.<sup>76</sup> This indicates that our calculated frequencies should be accurate. Our UV-Vis spectrum for  $S_2$  in this region, shown in Figure 2, is a higher resolution version of the absorption in 3-methylpentane solution at 77 K.<sup>41</sup> However, it shows only a general similarity to the 28050 cm<sup>-1</sup> band of S&M, with considerable differences in groupings and balance. It appears that the polarized ultraviolet absorption system of azulene in naphthalene shown by S&M (their Figure 3) is not directly comparable to the gas phase UV spectrum.

**Table V. The harmonic frequencies (cm<sup>-1</sup>) for the  $1^1A_1$  state, determined by single excitation CI. The sequence numbers 1 to 48 apply for the vibrations excited by FC and/or HT processes.**

1	2	3	4	5	6
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32b <sub>1</sub>	23a <sub>2</sub>	31b <sub>1</sub>	48b <sub>2</sub>	22a <sub>2</sub>	17a <sub>1</sub>
144	146	301	335	351	390
7	8	9	10	11	12
47b <sub>2</sub>	30b <sub>1</sub>	29b <sub>1</sub>	28b <sub>1</sub>	21a <sub>2</sub>	16a <sub>1</sub>
495	530	545	675	679	688
13	14	15	16	17	18
27b <sub>1</sub>	46b <sub>2</sub>	20a <sub>2</sub>	19a <sub>2</sub>	15a <sub>1</sub>	26b <sub>1</sub>
738	747	750	824	853	891
19	20	21	22	23	24
14a <sub>1</sub>	18a <sub>2</sub>	24b <sub>1</sub>	13a <sub>1</sub>	25b <sub>1</sub>	12a <sub>1</sub>
918	922	922	957	971	1017
25	26	27	28	29	30
45b <sub>2</sub>	44b <sub>2</sub>	11a <sub>1</sub>	43b <sub>2</sub>	42b <sub>2</sub>	10a <sub>1</sub>
1057	1072	1172	1175	1233	1254
31	32	33	34	35	36
41b <sub>2</sub>	9a <sub>1</sub>	40b <sub>2</sub>	39b <sub>2</sub>	8a <sub>1</sub>	38b <sub>2</sub>
1270	1349	1373	1421	1428	1458
37	38	39	40	41	42
37b <sub>2</sub>	7a <sub>1</sub>	6a <sub>1</sub>	36b <sub>2</sub>	5a <sub>1</sub>	35b <sub>2</sub>
1484	1595	1564	1614	3164	3172
43	44	45	46	47	48
4a <sub>1</sub>	34b <sub>2</sub>	3a <sub>1</sub>	2a <sub>1</sub>	33b <sub>2</sub>	1a <sub>1</sub>
3176	3191	3199	3251	3246	3255

We compare our FC and HT data in Figure 4, after subtraction of a ramp to flatten the axes of the experiment to enable comparison. The FC data in Table VI show an onset which is dominated by the  $0^0$  band; this profile cannot provide an explanation for the UV spectrum. The HT profile contrasts with the FC one in almost all details, through a wide range of fundamentals, overtones and combination bands having high intensity in the HT profile, while the  $0^0$  band is weak. Comparison of the combined FC + HT theoretical values with the observed spectra is an improvement on either separately. The comparison is far from ideal, since the balance of intensities is poor around the principal doublet close to  $30000\text{ cm}^{-1}$ , and there is insufficient intensity in the spectral tail. However,  $S_2$  clearly differs greatly from  $S_1$ , in its FC and HT balance.

**Table VI . The calculated Franck-Condon onset to the  $S_2$  state ( $1^1A_1$ ), determined by the CAM-B3LYP method with the 6-311G(d,p) basis set. Energy of the 0-0 transition is  $29430\text{ cm}^{-1}$ . Intensity units are the molar absorption coefficient ( $\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ).**

Position / $\text{cm}^{-1}$	Intensity	Vibration and quanta	Position / $\text{cm}^{-1}$	Intensity	Vibration and quanta
0	27570	$0^0$	846	11	$9^13^1$
287	92	$1^2$	853	967	$17^1$

292	45	2 <sup>2</sup>	918	30	19 <sup>1</sup>
390	293	6 <sup>1</sup>	957	946	22 <sup>1</sup>
444	42	3 <sup>1</sup> 1 <sup>1</sup>	970	5	16 <sup>1</sup> 2 <sup>1</sup>
497	2	5 <sup>1</sup> 2 <sup>1</sup>	975	18	12 <sup>1</sup> 1 <sup>2</sup>
574	1	1 <sup>4</sup>	980	9	12 <sup>1</sup> 2 <sup>2</sup>
601	13	3 <sup>2</sup>	1018	28	24 <sup>1</sup>
670	1	4 <sup>2</sup>	1541	166	17 <sup>1</sup> 12 <sup>1</sup>
674	21	8 <sup>1</sup> 1 <sup>1</sup>	1645	180	22 <sup>1</sup> 12 <sup>1</sup>
677	1	6 <sup>1</sup> 1 <sup>2</sup>	1860	173	27 <sup>1</sup> 12 <sup>1</sup>
688	5507	12 <sup>1</sup>	2281	143	35 <sup>1</sup> 17 <sup>1</sup>
703	124	5 <sup>2</sup>	2385	129	35 <sup>1</sup> 22 <sup>1</sup>
779	7	6 <sup>2</sup>	2521	138	32 <sup>1</sup> 27 <sup>1</sup>
819	2	10 <sup>1</sup> 1 <sup>1</sup>	2600	111	35 <sup>1</sup> 27 <sup>1</sup>
825	66	11 <sup>1</sup> 2 <sup>1</sup>	2843	135	34 <sup>2</sup>
831	6	8 <sup>1</sup> 3 <sup>1</sup>	2856	117	35 <sup>2</sup>

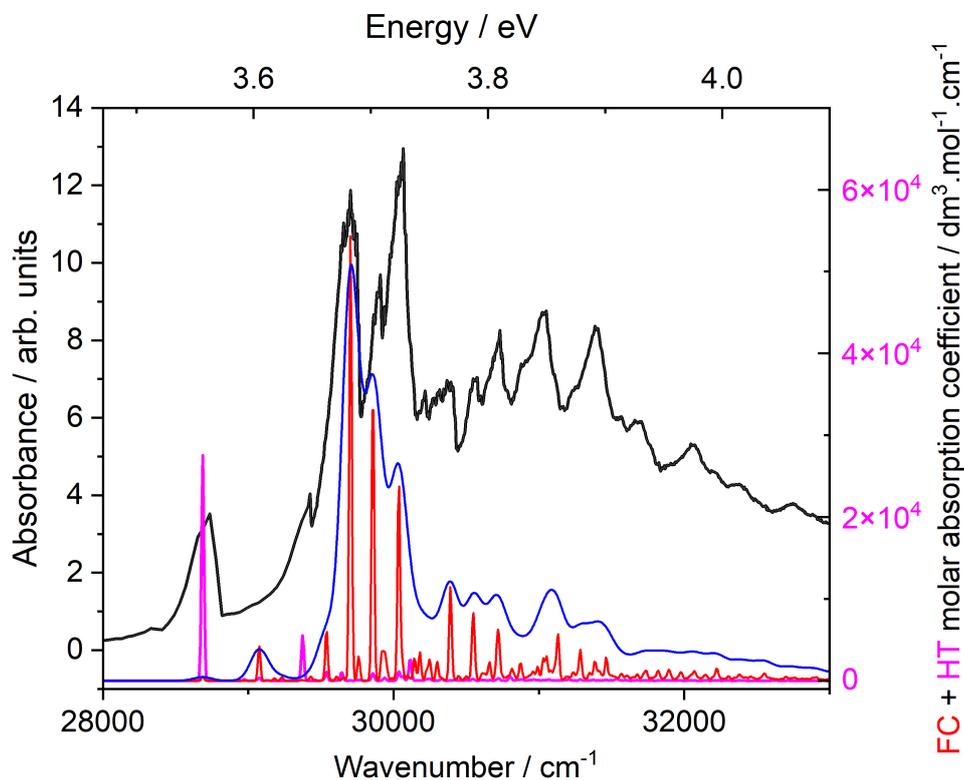
Returning to the S&M analysis of S<sub>2</sub>, we find considerable similarity with many of their a<sub>1</sub> proposed assignments, but not all, since too many were proposed. Our descending sequence of 11 a<sub>1</sub> symmetry members, from 1581 to 408 cm<sup>-1</sup>, is to be compared with their 14 members from 1568 to 336 cm<sup>-1</sup>. The higher frequency members are well spaced in both series and a correlation seems clear. The relation between the a<sub>1</sub> fundamentals for the 1<sup>1</sup>A<sub>1</sub> state is  $v_{\text{Calc}} = 0.986 (26) v_{\text{S\&M}} + 67 (28) \text{ cm}^{-1}$ , with a CC of 0.993, and SD in parentheses. When this correlation is extended to the lower frequencies, then it is clear that the S&M values 336, 804 and 856 cm<sup>-1</sup> do not fit, and hence the tentative assignment of these as a<sub>1</sub> fundamentals is unlikely.

**Table VII. The calculated Herzberg-Teller fundamentals for the S<sub>2</sub> state (1<sup>1</sup>A<sub>1</sub>), determined by the CAM-B3LYP method with the 6-311G(d,p) basis set. Energy of the 0-0 transition: 29431 cm<sup>-1</sup>. Intensity units are the molar absorption coefficient (dm<sup>3</sup>.mol<sup>-1</sup>.cm<sup>-1</sup>).**

Position /cm <sup>-1</sup>	Intensity	Vibration and quanta	Position /cm <sup>-1</sup>	Intensity	Vibration and quanta
0	536	0 <sup>0</sup>	1175	730	28 <sup>1</sup>
144	5	1 <sup>1</sup>	1183	43	12 <sup>1</sup> 7 <sup>1</sup>
287	2	1 <sup>2</sup>	1233	3054	29 <sup>1</sup>
301	7	3 <sup>1</sup>	1233	87	12 <sup>1</sup> 9 <sup>1</sup>
335	15	4 <sup>1</sup>	1242	462	17 <sup>1</sup> 6 <sup>1</sup>
390	3578	6 <sup>1</sup>	1254	2417	30 <sup>1</sup>
495	219	7 <sup>1</sup>	1270	901	31 <sup>1</sup>
530	5	8 <sup>1</sup>	1305	264	24 <sup>1</sup> 1 <sup>2</sup>
545	437	9 <sup>1</sup>	1310	82	24 <sup>1</sup> 2 <sup>2</sup>
688	68	12 <sup>1</sup>	1346	138	22 <sup>1</sup> 6 <sup>1</sup>
738	110	13 <sup>1</sup>	1349	20260	32 <sup>1</sup>

747	433	14 <sup>1</sup>	1373	2022	33 <sup>1</sup>
779	93	6 <sup>2</sup>	1407	409	24 <sup>1</sup> 6 <sup>1</sup>
853	5492	17 <sup>1</sup>	1421	169	34 <sup>1</sup>
891	56	18 <sup>1</sup>	1458	2394	36 <sup>1</sup>
918	80	19 <sup>1</sup>	1459	161	27 <sup>1</sup> 1 <sup>2</sup>
922	421	20 <sup>1</sup>	1495	2536	38 <sup>1</sup>
957	52	22 <sup>1</sup>	1541	1052	17 <sup>1</sup> 12 <sup>1</sup>
971	405	23 <sup>1</sup>	1561	1080	27 <sup>1</sup> 6 <sup>1</sup>
1018	54320	24 <sup>1</sup>	1564	1354	39 <sup>1</sup>
1057	15	25 <sup>1</sup>	1614	1671	40 <sup>1</sup>
1072	2285	26 <sup>1</sup>	1706	491	17 <sup>2</sup>
1172	32320	27 <sup>1</sup>	1706	10840	24 <sup>1</sup> 12 <sup>1</sup>

**Figure 4.** The S<sub>2</sub> state (1<sup>1</sup>A<sub>1</sub> in black) after subtraction of a ramp to give a horizontal axis. The Franck-Condon (magenta) and Herzberg-Teller (red and blue) profiles are shown where the Half-Widths at Half-Maximum are 10 (red) and 70 (blue) cm<sup>-1</sup>. No scaling of the results for best fit has been performed.



In the discussion of the higher singlet states of azulene, the pattern of Tables are similar to the above for the two lowest states. For brevity, most of these higher singlet state Tables have been transferred to the supplementary material.

### iii. The S<sub>3</sub> singlet state (2<sup>1</sup>B<sub>2</sub>) at 4.219 eV.

It has been claimed that this region has never been satisfactorily explained.<sup>40</sup> Most of the intensity of this region is the rise of the strongest S<sub>4</sub> band at higher energy. The calculated profile of S<sub>4</sub> shows a

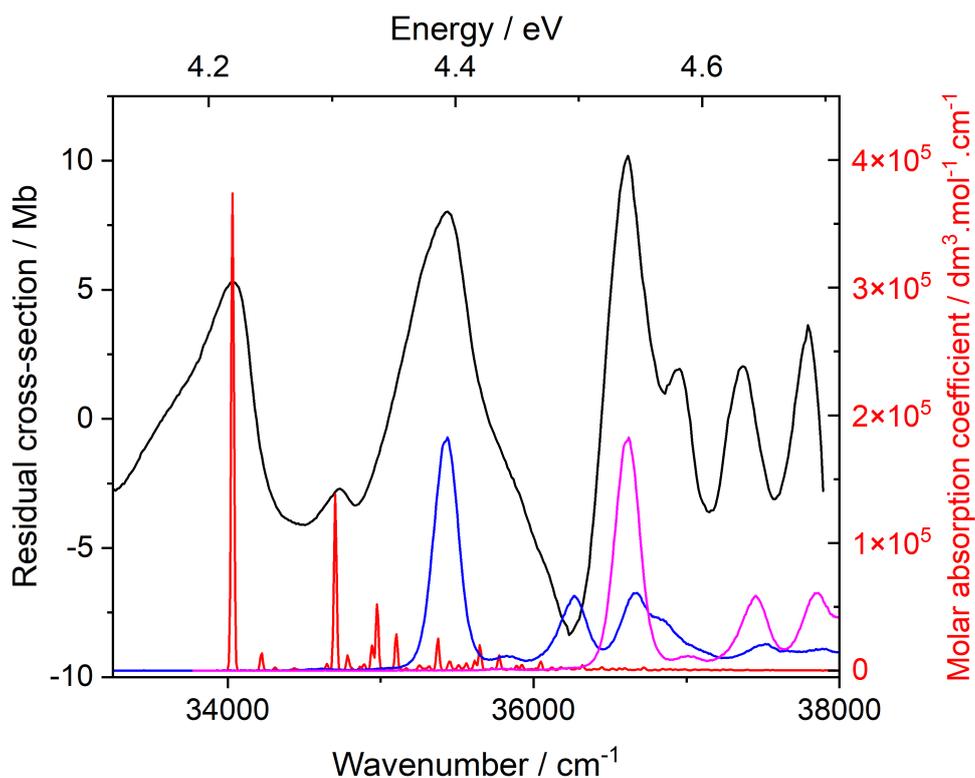
very intense 0-0 band; minor undulations on the leading edge of  $S_4$  in Figure 2 do not give the appearance of hot-bands for  $S_4$ . We separate these minor peaks from the rise of  $S_4$  by subtracting a 7<sup>th</sup> order polynomial, the lowest power to give a close fit to the  $S_4$  spectrum; the resultant regular residuals, are shown in Figure 5.

The FC envelope for  $S_3$ , shown in the SM as Table SM7, using ascending frequency listing, demonstrates that the calculated 0-0 band is dominant, but fundamentals,  $7^1$ ,  $13^1$ ,  $20^1$ ,  $22^1$  and  $25^1$ , have relatively high intensities. However, the state shows numerous vibrational states where the non-symmetric fundamental is raised to even numbers of quanta; examples of overtones are  $4^2$  and  $6^2$ ; similar binary and higher combination bands (such as  $6^12^1$ ) also occur.

The  $0^0$  band of the HT onset, as shown in the SM as Table SM8, is 30 times less intense than that of the FC profile. Non-symmetric modes occur widely. The most intense vibrational band in the HT profile is the fundamental  $32^1$ . We conclude that  $S_3$  is narrow as a result of domination by low-frequency modes both in the FC and HT models.

The structure above 4.39 eV in Figure 5 is similar to the  $IE_1$  ionic state shown in magenta,<sup>7</sup> leading to assignment as a Rydberg state. McGlynn et al<sup>39,40</sup> previously suggested that the lowest-energy p-Rydberg  $2a_23p$  transitions must occur in the vicinity of  $S_3$ . A further member of the  $3p$  set may occur on the side of the principal  $\pi\pi^*$  absorption as shown in the blue curve. These bands close to  $36000\text{ cm}^{-1}$  disappear in solution,<sup>41</sup> another indication of their Rydberg state character. Higher Rydberg states, lying in the range  $51000$  to  $47000\text{ cm}^{-1}$  ( $5.703$  to  $6.623\text{ eV}$ ) show this same profile.<sup>39</sup>

**Figure 5. The  $S_3$  band and calculated FC profile (in red) together with structure of two Rydberg states (in blue and magenta) at higher energy, as discussed in the text.**



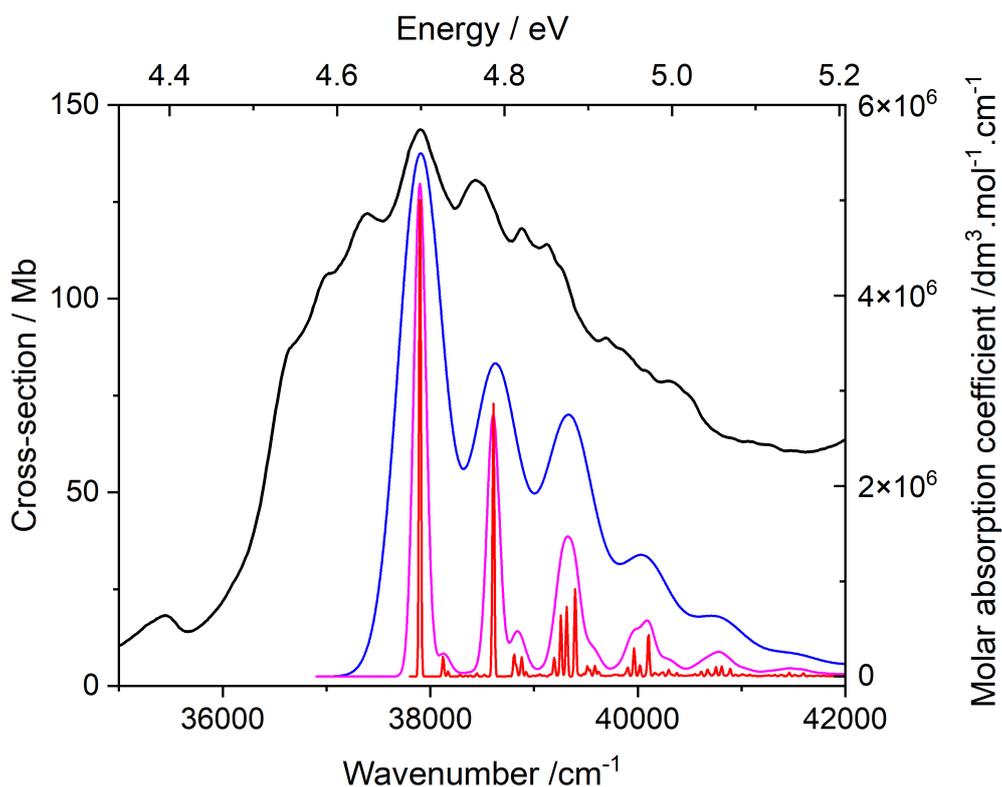
**iv. The  $S_4$  singlet state ( $2^1A_1$ ) with peak maximum at 4.700 eV.**

This is the most intense absorption by far. Its overlap with the tail of the very weak  $S_3$  ( $2^1B_2$ ) band discussed above, is clearly demonstrated in Figure 6. A list of the principal vibrational states for  $S_4$ , shown in the SM as Tables SM9 to SM11, are relatively simple. Since the theoretical calculations for both  $S_3$  and  $S_4$  are performed independently, interaction between them is impossible, and thus the calculations represent the unperturbed bands. The FC profile for  $S_4$  is dominated by the 0-0 band and several fundamentals with frequencies below  $1100\text{ cm}^{-1}$ . The HT profile has a very low 0-0 band, but is also dominated by low frequency vibrations. The theoretical vibrational states for  $S_4$  included in Figure 6, are simulated by means of Gaussian functions with several band broadening functions, indicated by different colours. The sharpest peaks (shown in red) have Half-Widths at Half-Maximum (HWHM) of  $10\text{ cm}^{-1}$ , with those in magenta ( $70\text{ cm}^{-1}$ , which are usually suitable to reproduce the width of an isolated vibrational peak), and  $250\text{ cm}^{-1}$  (in blue). Taken together, these show consolidation of several vibrational states into broad maxima. Even that largest HWHM is insufficient to account for the small local bands observed; we have previously shown that when two (ionic) states

overlap in this way, the necessary HWHM to account for the width observed can be  $400\text{ cm}^{-1}$  or more. Similar considerations occur here.

Both Blanchet et al<sup>44</sup> and Lewis et al<sup>40</sup> assign a  $3p_x$  Rydberg state to the vicinity of the peak maximum for  $S_4$ ; this RS has binding energy (BE)  $\sim 2.69\text{ eV}$ , and hence electronic energy (EE)  $4.72\text{ eV}$ . Although close to the peak maximum,  $S_4$  is clearly not an RS; its high calculated oscillator strength and spectral cross-section make this impossible. The MPI methods used<sup>40, 44</sup> must focus upon either a close or under-lying weak band. Their pump probe at  $4.626\text{ eV}$  ( $268\text{ nm}$ ) lies very close to the VUV absorption maximum. A 2<sup>nd</sup> Blanchet et al<sup>44</sup> MPI RS, with BE  $2.22\text{ eV}$  and hence EE  $5.19\text{ eV}$ , was correlated with a state having BE  $2.16\text{ eV}$  and EE  $5.15\text{ eV}$  previously assigned to a  $3p$ -RS by Kuthirummal and Weber in a further MPI study.<sup>43</sup> That work is supported by the observation of several RS with PQN 3 or 4, and in particular, the twin  $nd$  series of Kitagawa et al.<sup>37</sup>

**Figure 6. The principal maximum of the azulene VUV spectrum,  $S_4$ , with the Franck-Condon profile superimposed. There is a very clear overlap with the preceding very weak  $S_3$  state, and the weak sub-structure around  $37000\text{ cm}^{-1}$  is one or more Rydberg states rather than  $S_4$ , since the 0-0 band of  $S_4$  is predicted to be the highest intensity of the band.**

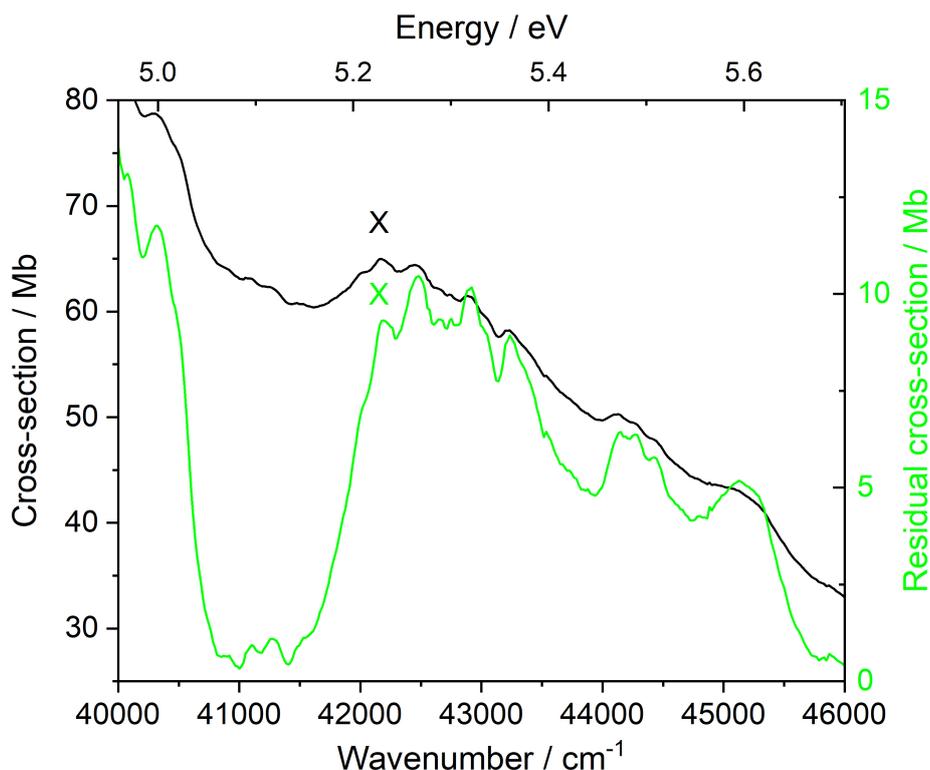


#### v. The $S_5$ singlet state ( $3^1B_2$ ).

This has been reported to lie on the tail of  $S_4$  at 5.166 eV.<sup>19</sup> Mann et al<sup>46</sup> compared the UV + VUV spectra of azulene with naphthalene; their 4<sup>th</sup> band with onset 40300  $\text{cm}^{-1}$  and peak maximum at 42300  $\text{cm}^{-1}$ , is featureless; this is our 5<sup>th</sup> band, since  $S_3$  was not observed by them. This 5<sup>th</sup> calculated singlet state is  $3^1B_2$  using the CAM-B3LYP functional in the TDDFT method. Since its oscillator strength is 0.251, it is expected to make a significant contribution to the experimental cross-section. The structure of  $S_4$  and its theoretical interpretation were shown in Figure 6; we believe that the profile for  $S_4$  is basically complete by 5.2 eV, and that absorption to higher energy/wavenumber must be either  $S_5$  and/or Rydberg in nature.

The VUV spectrum from 5.08 to 5.70 eV shows a nearly linear decline in cross-section with increasing energy, but with several relatively weak peaks superimposed. Subtraction of a ramp from the cross-section then leads to Figure 7. The first main peak at 5.231 eV is very close to the 3p state identified by Kuthirummal and Weber.<sup>43</sup> Our spectrum in Figure 7 is much more complex, and does not present the profile of one or more Rydberg states.

**Figure 7. The 41000 to 46000  $\text{cm}^{-1}$  region of the VUV spectrum of azulene, after flattening of the sloping baseline to horizontal, by removal of a ramp. The first main peak marked X, at 5.231 eV, is very close to the 3p state identified by Kuthirummal and Weber, J. Molec. Struct., 787, 163 (2006).**



### F. The spectral Rydberg states of azulene.

These have been reported by several groups, especially in the energy region 5.579 to 7.439 eV,<sup>37,38,40,41</sup> two RS series were successfully extrapolated to yield a relatively accurate value for the  $IE_1$  for azulene. The two lowest ionization energies for azulene are: 7.409 ( $X^2A_2$ ) and 8.598 eV ( $A^2B_1$ ), an energy difference between  $IE_1$  and  $IE_2$  of 1.189 eV. Profiles of the  $X^2A_2$  and  $A^2B_1$  ionic states are compared in the SM as SM12; both are dominated by 0-0 bands, with relatively similar vibronic structure. This makes RS identification based on  $IE_2$  difficult, and currently no such states have been claimed. The adiabatic  $IE_3$  for  $B^2A_2$  at 9.93 eV is well defined, but the main structure of the band is complex; this is a result of many overlapping low frequency vibrations. There is currently no prospect of identifying RS leading to  $IE_3$  for that reason.

The relationship between the RS energy ( $E_n$ ) and the ionization energy is shown in Equation 2; other terms are the principal quantum numbers (PQN,  $n$ ) and quantum defect ( $\delta$ ). Conventional values for  $\delta$  are  $\sim 0.9$  (s-states),  $\sim 0.3$  to  $0.6$  (p-states),  $\sim 0.1$  (d-states), and  $\sim 0.0$  (f-states), while the PQN start at 1s, 2p, 3d and 4f.<sup>17,18</sup>

**Equation 2. The relationship between ionization energy (IE) and Rydberg state energy ( $E_n$ )**

$$E_n = IE - 13.61/(n-\delta)^2$$

As noted above,  $IE_1$  for azulene has leading configuration  $2a_2^{-1}$ , and  $2a_2ns$  Rydberg states are optically forbidden; <sup>40</sup> Robin<sup>17,18</sup> reassigned earlier  $2a_2ns$  results, <sup>37,38,40,41</sup> to  $2a_2nd$ , where  $\delta = -0.09$  or  $-0.12$  respectively. Negative quantum defects had already been proposed for the naphthalene  $nd$  series.<sup>17</sup> The detailed symmetry in  $C_{2v}$  for these d-type states has not been reported, and the question of whether the lowest observed are 3d or 4d is also unanswered to date.

McGlynn et al<sup>46,47</sup> studied azulene absorption from 5.951 eV to 11.271. Their results<sup>40,41</sup> for two series ‘A’ and ‘B’ in the 5.951 to 7.438 eV region are very similar to those of Kitagawa,<sup>37</sup> but measured to higher precision. These gave effective (i.e. non-integral) principal quantum numbers (EPQN,  $n-\delta$ ) from 3.10 to 8.83. If their measured peaks are simultaneously fitted to the Rydberg equation, we find that the extrapolated  $IE_1$  and  $\delta$  are effectively identical with A-series: 7.404(2) and -0.111(5) and B-series: 7.415(9) and -0.117 (17) respectively. Lack of vibrational structure at the high energy end of the range, potentially leading to  $IE_2$  ( $A^2B_1$ ), was ascribed<sup>40,41</sup> to autoionization followed by collapse to  $IE_1$ . Super-excited state MPI processes<sup>26</sup> have added to the overall RS information; three RS with  $n = 4$  were obtained with  $\delta = 0.57, 0.41$  and  $0.23$ ; these are presumably two  $4p$ -states and a  $4d$ -state. Although similar values were obtained for naphthalene, the spectral profiles are quite different.<sup>42</sup> Results obtained by these MPI methods have been assessed by Blanchet et al,<sup>44</sup> and are discussed below in relation to our calculated RS.

The overall profile of our Rydberg state region shows a marked increase in signal to noise than previous studies, and is shown in the SM as SM13. We have electronically fitted 36 of the peaks in this spectrum, using the ‘peak-pick’ method in Origin 2021b; the peak energies ( $E(x)$  in eV), and relative intensities (Mb) are shown in the supplementary material as SM14. Although our VUV spectrum does not show major new features, when compared with earlier spectra, the very high cross-section and the electronically measured peak positions, makes the Rydberg state features much higher in intensity than surrounding noise, and allows magnification, as in Figures 4 to 7, to be more reliable.

As expected, portions of the profiles for VUV absorption and photoionization for azulene are very similar;<sup>40,41</sup> the VUV spectral RS yielded 3 vibrations, 440, 849 and 1230  $\text{cm}^{-1}$ , which were compared with 4 vibrations, 830, 1130, 1340 and 1990  $\text{cm}^{-1}$  (all  $\pm 70 \text{ cm}^{-1}$ ) in early PES of azulene.<sup>77</sup> Our recent re-analysis<sup>7</sup> of the azulene PES concluded that the two main vibrational peaks above the 0-0 band are actually doublets, 410 and 696  $\text{cm}^{-1}$  (modes  $6^1$  and  $10^1$  respectively), and 859 and 911  $\text{cm}^{-1}$  (modes  $15^1$  and  $17^1$ ) respectively; a higher vibration occurred at 1275  $\text{cm}^{-1}$  (mode  $30^1$ ). Thus the frequencies given by these early studies are (accidentally) relatively close to our current values.

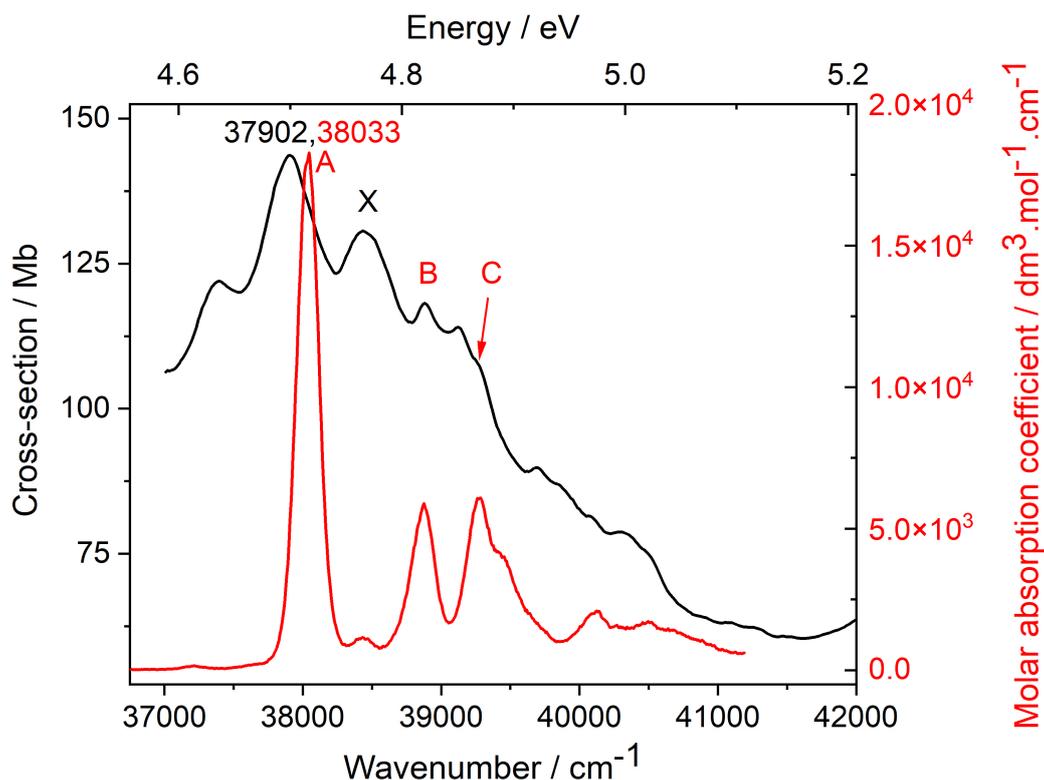
We now consider separate regions of the VUV spectrum, especially in the light of our calculated Rydberg state energies. The energy region above  $S_4$  is more complex than the theoretical profile presented in Figure 6 above. The VUV region from 37000 to 42000  $\text{cm}^{-1}$  is shown in Figure 8, with the leading part of the PES shifted to lower energy to best fit the VUV profile of a RS. In order to fit the leading doublet of the PES to the VUV profile, it is necessary to shift the PES peak maximum to 38033  $\text{cm}^{-1}$  rather than to the maximum of the VUV at 37902, a difference of 131  $\text{cm}^{-1}$ . Blanchet et al<sup>44</sup> give 38070  $\text{cm}^{-1}$  and Lewis et al<sup>41</sup> give 37,989  $\text{cm}^{-1}$  for a 3p-RS, and these are clearly identical to the assignment shown in Figure 8; this is the first assignment of a 3p-RS from a VUV spectrum.

The peak X between A and B in Figure 8, could be part of the  $S_4$  structure described above, and it certainly does not correlate with any of the RS collected in Blanchet et al,<sup>44</sup> since its apparent BE is 2.605 eV. However, using our  $A^2B_1$  state energy 8.598 eV, this BE would give  $n - \delta = 2.286 \text{ eV}$ , and hence a realistic value for a 3s RS based on  $IE_2$  with  $\delta = 0.714$ ; we believe this conclusion is correct.

There remain several state binding energies listed by Blanchet et al<sup>44</sup> where future assignments are awaited. These include apparently significant differences occurring in measured BE between alternative authors for the same state; also 4s RS levels apparently leading to  $X^2A_2$  are given, which appear to be FC forbidden.

**Figure 8. The 37000 to 42000  $\text{cm}^{-1}$  region of the VUV spectrum of azulene, where the leading profile of the  $X^2A_2$  state (peaks A, B and C) of the photoelectron spectrum, after a shift to lower energy by 21722  $\text{cm}^{-1}$  (2.6931 eV), has been superimposed in red. The two peak maxima of the**

PES and VUV shown are separated by  $131\text{ cm}^{-1}$  to allow for better alignment of the leading doublet B + C.



### G. Calculated Rydberg state energies.

Using the MRD-CI method,<sup>70,71</sup> identification of the leading configurations as either valence or Rydberg, is immediately obvious from the second moments of the charge distribution (SECMOM); examples are shown in the SM as SM15. The orbital energies of the very diffuse GTOs representing Rydberg functions lie immediately above the zero energy level, i.e. at positive energy, but much closer to zero than the valence virtual orbitals (VMOs). At the CI level, valence states (VS) often lie within the calculated energy range for the  $n = 3$  to 5 lowest RS. These VS behave as intruder states; that is, the states have the desired symmetry, but incorrect leading configurations. When close to a calculated RS, they perturb it, and potentially lead to linear combinations of  $VS \pm RS$ , since all belong to the same irreducible representation. Here we note that in MRD-CI the full CI matrix is separated into separate sub-matrices of  ${}^1A_1$ ,  ${}^1B_1$ ,  ${}^1B_2$  and  ${}^1A_2$  symmetry. These include both occupied and virtual orbitals, so that the VS and RS have sequential root numbers. Thus the  $a_1$  doubly occupied MOs (DOMOs) have sequence numbers 1 to 11, and the s-Rydberg orbitals, also of  $a_1$  symmetry, follow

immediately with sequence numbers 12, 13 and 14. Each electronic state is described by one or more configuration state functions (CSFs), shown in Equations 1.

The principal RS results using either the TDDFT method with the CAM-B3LYP functional, or the MRD-CI method at the Hartree-Fock level, are shown in the SM as Table SM16. Rydberg states and their ionic limits share a common vibrational envelope, implying that their structures are similar, at least to first order. The RS in MRD-CI behave as a group, since the same set of reference configurations are diagonalised simultaneously to generate the set of roots with their vertical excitation energies (VEE). In TDDFT, because of the structural similarity of individual RS of same symmetry, optimization of the lowest state, generates its adiabatic excitation energy (AEE); the relative energies of higher RS of same symmetry are determined at the same time; these can also be treated as a group.

**i. The optically forbidden theoretical  $ns$ -Rydberg states.**

The lowest IE,  $X^2A_2$  is dominated by  $2a_2^{-1}$ , and presents the simplest situation relating to VS and RS interaction in VUV absorption. The TDDFT results fitted to the Rydberg state equation leads to  $AIE_{1A_2} = 6.802$  eV and  $\delta = 0.309$ , with standard errors (SE) 0.4 or 9%; our previous  $IE_1$  is 7.409 eV;<sup>7</sup> this is acceptable since extrapolation from calculated values for  $n = 3, 4$  and  $5$  to infinity cannot be expected to be precise. The MRD-CI values offer additional flexibility, when an intervening VS close to the RS with  $n = 5$ , is included or excluded; for (inclusive)  $IE_1$  and its  $\delta$  are 6.898 eV and 0.478 and 7.170 for the excluded value; the SE are at 2% and 24% in both cases. The intruder VS is  $2a_217a_1^*$  which lies immediately above the three Rydberg VMOs in the orbital energy sequence.

The corresponding values for the excitation process  $3b_1ns$  are also shown in the SM as Table SM16; the higher energy of the states makes the effect of the corresponding intruder state  $3b_117a_1^*$  less important. The extrapolated  $VIE_2$  using the MRD-CI method are 8.144 (1%) and with  $\delta$  0.656 (9%) for the included intruder state, and 8.353 eV (2%) with  $\delta$  0.621 (23%) for the VS excluded state. These are to be compared with our recent PES study<sup>7</sup> of  $VIE_2$  8.598(1) eV ( $A^2B_1$ ). It is usual for CI estimations of IE to lie at lower energies than experiment, since there is an inability of the method to

balance the degrees of electron correlation between the ground state (a relatively small number of CSF) with the excited (or ionized) state with a very much larger number of CSF. In the discussion above, it is uncertain whether any of these states have been observed experimentally in the UV+VUV spectrum. The TDDFT method predicts the 3s- and 3p-Rydberg state ( $^1B_2$ ), shown in the SM as Table SM15, with  $\delta$  0.740 (17) and 0.398 (21) respectively. Only two  $2a_23p$ -states are allowed.

### ii. The calculated $np$ -Rydberg states.

Addition of a set of  $np$ -Rydberg functions to the 6-311G(d,p) basis set, adds extra CI roots, with orbital symmetries  $a_1$ ,  $b_1$  and  $b_2$  respectively. In most of our TDDFT studies using the CAM-B3LYP functional, the RS roots are preceded by the 4 lowest valence states in Equations 1 as roots 1 to 4 respectively. Optimization of the next 3 Rydberg states leads to the adiabatic excitation energies:  $1^1B_1$  (5.287 eV with  $f(r)$  0.0018),  $1^1A_2$  (5.291 eV,  $f(r)$  0.0) and  $3^1B_2$  (5.518 eV,  $f(r)$  0.0022); these are  $3py$ ,  $3pz$  and  $3px$  respectively. Thus the  $2a_23py$  excitation lies at marginally lower energy than the other members of the group. Extrapolation of the three lowest RS member energies, shown in the SM as Table SM16, gives the theoretical  $IE_1$  of 7.172 eV (2.7%) with  $\delta$  0.338, but a higher SE uncertainty of 64%; however, these results are similar to the theoretical  $2a_2ns \pi\sigma^*$ -excitation above. Here SE are expressed as % errors rather than absolute errors. The  $2a_23py$  excitations ( $^1B_1$ ) again give reasonable values after extrapolation, giving  $IE_1$  7.170 eV (2.7%) and  $\delta$  0.337 (64%). Finally, the  $2a_2npx$  series yield  $IE_1$  7.246 eV, with a lower  $\delta$  of 0.241.

### iii. The calculated $nd$ - and $nf$ -Rydberg states.

Having noted that the symmetry of the previously reported  $2a_2nd$ -Rydberg series is currently unknown, we have calculated the energies of several of the lowest Rydberg states, concentrating on the  $nd$ -series. Processing of the  $nd$ - and  $nf$ -states in MRD-CI are routine, where we use the 6d- and 7f-cartesian versions of the spherical harmonics; these simplify the mixing with the  $C_{2v}$  state of the azulene carrier.

The lowest excited state of azulene, the  $1^1B_2$  state, is shown in Equations 1. In order to generate  $2a_2nd$  states of  $^1B_2$  symmetry from the input reference configurations, we needed to suppress the VS terms. The Rydberg basis set results in the lowest  $1^1B_2$  state being perturbed, to the higher excitation energy,

2.937 eV, compared with the unperturbed excitation energy of 2.358 eV discussed above. The following roots are 3d, 4d and 5d-RS with energies 5.461, 6.119 and 6.926 eV. The projected  $IE_1$  for this  ${}^1B_2$  series is 7.388 eV (4.1%) with  $\delta$  0.380 (84.9%), where standard errors are in parentheses, to be compared with the PES  $IE_1$  at 7.409 eV; this projection is close to experiment. Based on these calculated  $2a_{2nd}$  Rydberg states, we extrapolated to generate comparable data to the seven states ( $n = 3$  to 8) observed by Bouler et al<sup>39</sup> for azulene. The spacing is very close, but a graph (not shown) has a considerable slope and intercept. The correlation is  $v_{Bouler} = 1.247 v_{2a_{2nd}} - 13967 \text{ cm}^{-1}$ , with adjacent  $R^2$  0.9984. The intercept may be an indicator that the Bouler et al<sup>39</sup> data should have their EPQN as:  $n = 3.10$  to 9.83.

Two alternative determinations of the 3d, 4d and 5d-RS were within the  ${}^1B_1$  and  ${}^1A_1$  manifolds;  ${}^1B_1$  is simpler, since there are no low-lying VS of this symmetry. A fit of the calculated RS with values 5.489, 6.159 and 7.167 eV gives the projected  $IE_1$  as 7.5936 eV (5%) and  $\delta$  0.501 (77%).. The  ${}^1A_1$  sequence has an intruder state as the leading (lowest energy) root, easily recognised from its high  $f(r)$  and low SECMOM relative to roots 2 to 4. The 3d, 4d and 5d-RS have energies 5.473, 6.482 and 6.953 eV, which when fitted to the Rydberg equation give  $IE_1$  7.599 (0.4%) and  $\delta$  0.473 (6%); these values are slightly higher than the  ${}^1B_1$  and  ${}^1B_2$  nd states, but there is no requirement for degeneracy. The simplest optically allowed f-Rydberg states are the  ${}^1B_1$  series; but the lowest f-RS appears to be the  $2a_{2nf} ({}^1A_2)$  series with  $n$  4, 5 and 6, as shown in the SM as Table SM16. The extrapolated  $IE_1$  is 7.149 eV (5.8%), but the calculated  $\delta$  is unexpectedly large at -0.449. These f-RS are particularly simple to calculate using MRD-CI, since the method is focussed upon the desired symmetry only, and states of other symmetry are ignored.

#### IV. CONCLUSIONS

All of the calculated singlet valence states  $S_1$  to  $S_4$  have two leading configurations, the most prominent involve excitations from the two HOMOs to the two lowest LUMOs. All of these states are  $\pi\pi^*$  rather than  $\sigma\sigma^*$  excitations. Although the calculated  ${}^1B_1$  states ( $\pi\sigma^*$ ,  $\sigma\pi^*$ ) have non-zero oscillator strengths, most are very weak; this leads to the VUV absorption spectrum being dominated

by the  $^1A_1$  and  $^1B_2$  states. Generally the valence portions of the spectrum are well represented by the energy profile generated from the high level coupled cluster (SACC-CI) calculations. The wide scan spectrum from 1.5 to 11 eV shows valence states at both the onset and high energy regions, but the mid-energy region is dominated by Rydberg states.

The present TDDFT level calculations allow the vibrational coupling within several of the singlet states to be evaluated using the Pisa Group software. The onset  $S_1$  state of Sidman and McClure in Figure 3 is closely reproduced by our calculations at the Franck-Condon level. However, some of the apparent doublets given are not identified by Herzberg-Teller study, and these may be a result of more than one crystal site for the solid solution spectra. The HT vibrations appearing in this  $^1B_2$  band mostly have intensities  $\sim 20$  times weaker than the FC states, and hence will have little impact on the profile of the combined set, when compared with experiment. Many fundamental modes are excited, but with a very wide range of intensities. Numerous binary combinations occur, in which modes 5 ( $17a_1$ ), 10 ( $16a_1$ ) and 18 ( $15a_1$ ) are prominent.

It appears that the polarized ultraviolet absorption system of  $S_2$  azulene in naphthalene shown by S&M (their Figure 3) is different from the gas phase UV spectrum. Our FC data show an onset, dominated by the  $0^0$  band, with little vibrational intensity from any of the fundamentals, overtones or combination bands; this profile cannot provide an explanation for the  $S_2$  spectrum. The situation is improved when the HT profile is included, since this contrasts with the FC one, with a wide range of fundamentals, overtones and combination bands. The HT  $0^0$  band is weak, while ascending sequence modes 24 ( $24b_1$ ), 27 ( $11a_1$ ) and 32 ( $9a_1$ ) are extremely intense. None of these are prominent in the FC profile. Combination of the FC+HT profiles, gives a closer match to the experimental spectrum in main groupings, but  $S_2$  clearly differs greatly from  $S_1$ , in its FC and HT balance.

Most of its intensity for the  $S_3$  state lies on the rise of the strongest  $S_4$  band at higher energy. After removal of the slope associated with  $S_4$ , much of the residual structure above  $S_3$  is similar to the  $IE_1$  ionic state. This leads directly to assignment as Rydberg states, in agreement with earlier studies. We propose that two  $2a_23p$  Rydberg state of the  $3p$  set occur here. Much of the intensity of the VUV

spectrum between 4.4 and 5.2 eV is the S<sub>4</sub> band, where we find that the FC profile provides a realistic interpretation. The energy region above S<sub>4</sub> is more complex than the theoretical profile presented in Figure 6 above. In order to fit a PES profile for the 3px-Rydberg state in the VUV region from 37000 to 42000 cm<sup>-1</sup>, it is necessary to place the PES peak maximum to 38033 cm<sup>-1</sup> rather than at the maximum of the VUV at 37902, a difference of 131 cm<sup>-1</sup>. Blanchet et al<sup>44</sup> give 38070 cm<sup>-1</sup> and Lewis et al<sup>40</sup> give 37,989 cm<sup>-1</sup> for this Rydberg state, but do not appear to differentiate the valence state maximum from the PES one.

The Rydberg state region of the VUV spectrum, between 5.75 and 7 eV, shows no additional information to that extracted by earlier workers, so that our principal contribution here lies in the theoretical RS determinations. We find that the use of very diffuse GTOs allows straightforward determination of s-, p-, d- and f-RS, especially using the MRD-CI system within GAMESS-UK. The higher members of these states lie high up in the singlet state manifold. This makes the TDDFT method more difficult to use, since all 4 representations of C<sub>2v</sub> are treated simultaneously; MRD-CI treats each representation separately. There is little comparison with the  $n = 3$  to  $8$  nd-RS previously reported, since we can only cover the range  $n = 3$  to  $5$ ; the extrapolated energies of these calculated states are generally close to our recent re-determination of the lowest X<sup>2</sup>A<sub>2</sub> ionic state energy. The same procedure was applied to RS leading to the A<sup>2</sup>B<sub>1</sub> state, where no experimental RS have yet been observed.

Extrapolation to infinity using Equation 2 for the low-lying members of RS which have PQN 3 to 5; inevitably produces uncertainties in the values obtained. The standard errors for the IE, are generally small in absolute energy terms, and just a few percentage points; this is the principal reason for the projection. Errors for the quantum defect are markedly higher. An early graphical procedure for determining  $(n - \delta)$  directly from three successive members of the RS, purely in terms of the energies of the three states has been given;<sup>78</sup> such a method should produce lower errors than our projection used here, but apparently generates other uncertainties,<sup>78</sup> and we were unable to exploit the principle.

## SUPPLEMENTARY MATERIAL

See the supplementary material for additional information on each of the following:

The onset of the azulene UV spectrum, recorded using a Unicam UV340 spectrometer, compared with the multi-photon ionization spectrum of Suzuki and Ito, *J. Phys. Chem.* 1987, 91, 3537-3542. (Figure SM1). An alternative assignment for the jet-cooled azulene spectra by Suzuki et al (Table SM1). 2. The full set of SACCI singlet state energy levels as depicted in Figure 2, and state properties (Table SM2). 3. The harmonic frequencies for the  $X^1A_1$  state of azulene ( $\text{cm}^{-1}$ ) (Table SM3). 4. The azulene equilibrium structure at the Hartree-Fock level with the Def2-TZVPPD basis set (Figure SM4). 5. The singlet state structures of azulene compared with the parent molecule using the CAM-B3LYP method with the 6-311G(d,p) basis set (Figure SM5). 6. 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 (Table SM6a). 7. 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 (Table SM6b). 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 (Table SM6c). 7. Table SM7. The calculated Franck-Condon fundamentals for the  $S_3$  state ( $2^1B_2$ ). 8. Table SM8. The calculated Herzberg-Teller fundamentals for the  $S_3$  state ( $2^1B_2$ ). 9. Table SM9. Harmonic frequencies for the  $S_4$  state. 10. Table SM10. Principal fundamental and combination band vibrational states, at the Franck-Condon level, based on intensity, for  $S_4$  in azulene,  $2^1A_1$  11. Table SM11. The vibrational structure of the onset of the Herzberg-Teller structure to the 4<sup>th</sup> excited state ( $S_4$ ,  $2^1A_1$ ) state. 12. Profiles of the  $X^2A_2$  and  $A^2B_1$  lowest ionic states compared, by lowering the energy of the latter by  $8735 \text{ cm}^{-1}$  (Figure SM12). 13. The principal Rydberg state region of the VUV spectrum of azulene between  $42000$  to  $61000 \text{ cm}^{-1}$  (Figure SM13). 14. The peak energies, measured in wave-numbers with relative intensities (Mb) for the principal Rydberg state region of azulene between  $46000$  and  $61000 \text{ cm}^{-1}$  (Table SM14). 15. Dipole and second moments of the charge distribution (Table SM15). 16. Table SM16. The calculated Rydberg states for azulene using either the CAM-B3LYP functional under TDDFT, or Hartree-Fock with MRD-CI.

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#### DATA AVAILABILITY OF ARTICLE OR SUPPLEMENTARY MATERIAL.

The data that support the findings of this study, including its supplementary material, will be available from the corresponding author upon reasonable request.

**AUTHOR DECLARATIONS** The authors have no conflicts to disclose.

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