

High-level studies of the singlet states of quadricyclane, including analysis of a new experimental vacuum ultraviolet absorption spectrum by configuration interaction and density functional calculations.

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ABSTRACT

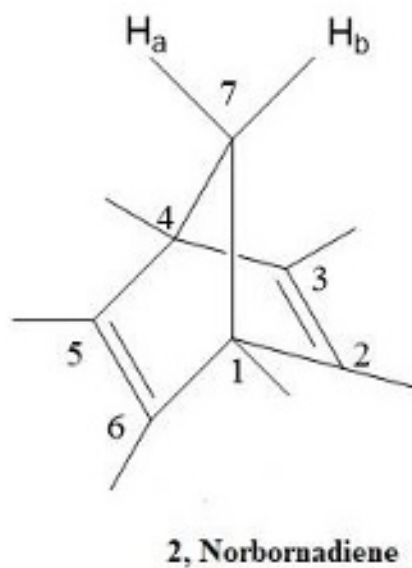
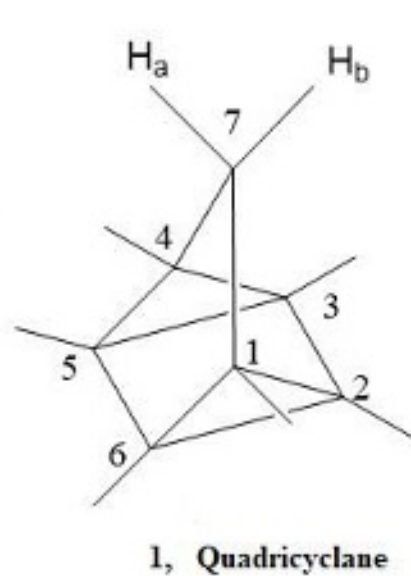
A synchrotron-based vacuum ultraviolet absorption spectrum (VUV) of quadricyclane (QC) is reported with energies up to 10.8 eV. Extensive vibrational structure has been extracted from the broad maxima by fitting short energy ranges of the VUV spectrum to high level polynomial functions and processing the regular residuals. Comparison of these data with our recent high-resolution photoelectron spectral (PES) of QC showed that this structure must be attributed to Rydberg states. Several of these appear before the valence states at higher energies. Both types of states have been calculated by configuration interaction (CI), including symmetry-adapted cluster studies (SAC-CI), and time dependent density functional theoretical methods (TDDFT). There is a close correlation between the SAC-CI vertical excitation energies (VEE) and both B3LYP and especially CAM-B3LYP determined ones. The VEE for several low-lying s-, p, d-

and f-Rydberg states (RS), have been determined by SAC-CI and adiabatic excitation energies (AEE) by TDDFT methods. Searches for equilibrium structures for $1^{1,3}A_2$, and 1^1B_1 states for QC led to rearrangement to a norbornadiene structure. Determination of the experimental 0^0 band positions, which show extremely low cross-sections, has been assisted by matching features in the spectra with Franck-Condon fits. Herzberg-Teller vibrational profiles for the Rydberg states are more intense than the FC ones, but only at high energy, and are attributed to up to ten quanta. The vibrational fine structure of the RS calculated by both FC and HT procedures, gives an easy route into generating HT profiles for ionic states, which usually require non-standard procedures.

INTRODUCTION

Recently, we reported synchrotron based, high-resolution photoelectron spectra (PES) for both quadricyclane (QC, **1**) and norbornadiene (NBD, **2**) molecules as shown in Figure 1.¹ This was followed by a vacuum ultraviolet (VUV) absorption spectral study of NBD.² The PES of **1** and **2** reveal the existence of different radical cation states ($QC^{\cdot+}$ and $NBD^{\cdot+}$).¹ Similarly, the hyperfine coupling patterns, established by the application of the chemically induced dynamic nuclear polarization (CIDNP) technique, resulted in the observation of discrete polarization patterns for these two radical cations. In contrast, matrix-isolation studies give only a single species from both QC and NBD molecules, while mass spectrometry gives identical fragmentation patterns. Both $QC^{\cdot+}$ and $NBD^{\cdot+}$ were discussed previously.¹

Figure 1. The quadricyclane (1, QC) and norbornadiene (2, NBD) structures. Classical bond switching between the two systems occurs during UV excitation. For simplicity, H atoms are unmarked for the ring system moieties.



QC and NBD have a significant joint history, in the search for methods of solar energy storage.^{3,4,5,6} Photo-absorption by NBD generates QC, in what is termed molecular solar thermal energy storage (MOST); the QC strain energy is liberated in a subsequent stage regenerating NBD. Since the main intensity of solar wavelengths lies between 300 and 700 nm, substituents are necessary on both NBD and QC moieties to shift the absorption to longer wavelengths. This is achieved by having both electron donating and accepting groups present on both the QC and the NBD units, leading to a push-pull mechanism.¹ The onset wavelength for absorption by NBD is 267 nm, but the absence of a chromophore in the structure of QC itself has resulted in no reports of its UV absorption.

The molecular structure of QC has been determined by both gas phase electron diffraction (ED)⁷ and microwave spectroscopy;⁸ the structure appears to have classical cyclopropane and other rings.^{7,8} Rydberg states are particularly important for a saturated system like QC; $\sigma\sigma^*$ -valence states are likely to lie at higher energies, than for example, $\pi\pi^*$ -states in unsaturated molecules such as NBD. Rudakov and Weber (R&W)⁹ focused on Rydberg states for the joint system QC + NBD. QC on irradiation with 208 nm photons, generates 3s and 3p Rydberg

states. Their QC spectral analysis⁹ uses a time-delayed second laser at 416 nm, which causes photoionization with excess vibrational energy. The resulting large amplitude motion allows the QC skeleton to rearrange to that of NBD. The binding energy (BE) of the electron in its Rydberg state was ionized by the third photon, and its kinetic energy measured. 3-Photon resonant multiphoton ionization (REMPI), followed by 1-colour ionization spectra with 416 nm (2.980 eV) photons, was used to observe the 3s state and the two (non-zero intensity) 3p-Rydberg states. The binding energies (BE) relative to the ionic state were 2.88, 2.29 and 2.24 eV for the 3s and two 3p states, respectively.⁹ This BE term differs from conventional usage of the ionization energy (IE) for Rydberg states as used here in Equation 1:

$$BE = IE - E = R / (n - \delta)^2 \quad \text{Equation 1.}$$

$$(n^2 - 2n\delta + \delta^2) = R / (IE - E) \quad \text{Equation 2.}$$

The BE is just the term: $R / (n - \delta)^2$ in Equation 1, where R is the Rydberg constant (13.61 eV), n is the principal quantum number and δ is the quantum defect. The IE used in both Equations 1 and 2 (where the terms have been rearranged) is strictly the adiabatic term (AIE), which is applicable when the PES vibrational structure is well determined. However, many polyatomic molecules show poorly resolved ionization spectra, so that the vertical (VIE) term is often used instead. This applied to R&W,⁹ who used an early VIE¹⁰ of 8.33 eV as their AIE. For consistency with R&W, we also use the VIE for some of our studies, but our value after 10 vibrational intervals from the onset, gave 8.363 eV, with the AIE (0-0 band) for QC at 7.671 eV.¹ This leads to the substantial difference between VIE and AIE of 0.692 eV.

We now present the first wide scan vacuum ultraviolet (VUV) absorption spectrum for QC, following our previous studies on NBD² and cycloheptatriene (CHT).¹¹ We expose detailed vibrational structure in what appears to be a relatively featureless VUV spectrum, by numerical fitting of local energy ranges of the UV and VUV spectrum to polynomial functions and processing the regular residuals. We will show, in the Results Section below, that this

vibrational structure is effectively identical to that for the ionic state of QC, and thus indicates the presence of Rydberg states at the onset of QC UV absorption.

We provide a theoretical analysis up to the coupled cluster (CC) level, which has been claimed to be both the ‘gold and platinum standard’ for electronic structure calculations.^{12,13} Thus our study allows correlation of theory with experiment at a more rigorous level than is currently available. As with CHT and NBD previously, we analyse vibrational structure in the VUV spectrum of QC in a detailed manner. Our adiabatic theoretical studies enable both Franck-Condon and Herzberg-Teller methods to be performed. Correlation of the theoretical envelopes with the experimental spectra assists identification of the 0^0 band origins, and hence adiabatic excitation energies (AEE) for the electronic states. Our study also includes generation of the theoretical vibrational structure for Rydberg states at the DFT level, having each of s-, p-, d- or f-types of excitations.

II. METHODS

QC has CAS registry number 278-06-8, with numbering as in Figure 1. It has been systematically named both as tetracyclo [2.2.1.0^{2,6}.0^{3,5}] heptane and tetracyclo [3.2.0.0^{2,7}0^{4,6}] heptane under International Union of Pure and Applied Chemistry (IUPAC) rules.

- (a) **Synthesis.** QC was prepared from NBD by irradiation, using a water-cooled 400W medium-pressure mercury discharge lamp, with acetophenone as photosensitizer; further details were given previously.¹ Although considerable care was taken to free the QC from NBD contamination, the VUV absorption samples showed about 1% NBD remained in the spectrum of QC. In practice this assisted interpretation of the onset of the QC spectrum; since both compounds show vibrational structure in the 5.5 to 6.0 eV region, but the peak maxima do not correspond. Indeed, several minima for QC match with maxima for NBD.
- (b) **The VUV absorption spectrum of QC.** This was measured in the gaseous phase at 25°C, on the AU-UV beamline of the ASTRID2 synchrotron (in Aarhus, Denmark) using methods

described previously.¹⁴ The full UV + VUV spectrum was covered by 3681 data points over the range 330nm (3.857 eV) to 116 nm (10.751 eV). These data are separated by 0.05 nm for most of the spectral range: but by 0.1 nm from 270 nm to higher wavelengths. The photon resolution is 0.08 nm over the operational range of the grating; this corresponds to 7, 3 and 1 meV at the high, mid, and low energy range.

The spectrum is discussed in detail below, but here we note that the wide scan quadricyclane VUV spectrum for the energy range up to 10.8 eV, shown in Figure 2, has a slow onset close to 5 eV with broad peaks occurring at 6.77(1), 8.62(1), 9.38(1) and 10.34(1) eV, with a point of inflexion at 8.30(1) eV. Minor undulations which occur between 6.0 and 7.2 eV, are discussed later. Throughout this study, errors are in parentheses. The spectrum, shown in Figure 2, has been corrected to remove ~1% contamination by NBD.

Figure 2 also exhibits the most rigorous theoretical vertical excitation energies from the present SAC-CI studies, which are shown in Table I. These excitation energies cannot explain the UV region shown, since the calculated onset of absorption is some 1.2 eV higher than experiment. Thus, the onset must be a result of the Rydberg states shown in Table II; this is confirmed by Figure 3, which shows the Rydberg states described below. These cover the onset energy range satisfactorily and are discussed separately. Conversely, the higher energy region of the spectrum shown must relate to the calculated valence states of Table 1. Both are discussed below.

(c) **Theoretical methods.** The Gaussian suite (G-16),¹⁵ was used for calculation of vertical and adiabatic excitation energies (VEE and AEE) for both valence and Rydberg states, as well as vibrational analysis,¹⁶⁻¹⁸ and symmetry-adapted cluster configuration interaction (SAC-CI) studies.¹⁹⁻²³ SAC-CI are our most rigorous theoretical determinations of the excited state sequence, but, in our hands, this method is an ‘excitation energy only’ procedure, since the available G-16 version of the code does not give us the facility to use the wave-functions for

vibrational or other analyses. Thus, a second method of excited state energy determination was essential; time-dependent density functional theory (TDDFT),^{24,25,26} a single excitation configuration interaction (CI) method, was particularly suitable since it enabled equilibrium structures and harmonic frequencies for both valence and Rydberg states to be determined, and AEE for several states of each symmetry. The wave-functions were directly compatible with the FC and HT software for vibrational analysis.¹⁶⁻¹⁸ The primary density functional used was a long-range-corrected version of the Becke 3-parameter hybrid functional (B3LYP),²⁷ described as the Coulomb-attenuating method (CAM-B3LYP).²⁸

Rydberg States (RS) were generated computationally by use of very diffuse Gaussian-type basis functions; exponents: 0.021, 0.008 and 0.0026 were added to the strictly valence TZVP basis set.^{30,31} Since Rydberg functions must be mounted on atomic centres in G-16, and their atomic site listed first in the geometric specification, the standard structural numbering in Figure 1 was rearranged in the Rydberg state calculations with C₇ relabelled as C₁. This is reproduced in the supplementary material as SM1.

The work described here was performed using the 6-311G (d, p) basis set.²⁹ For *nd* and *nf* states, the 5d and 7f options were implemented, thereby removing interference from the implicit s-functions through elimination of terms such as $(d_x^2 + d_y^2 + d_z^2) = d_r^2$.

We use valence shell numbering of molecular orbitals, with doubly occupied MOs up to 7a₁, 5b₂, 4b₁ and 2a₂; the core MOs, excluded from the CI studies, consist of 3a₁+2b₂+1b₁+1a₂. It is necessary to discuss the singlet state manifolds prior to use of their results in interpretation of the VUV spectrum of QC.

III. RESULTS

- (a) **The ground state bonding of the quadricyclane molecule.** Electron density plots of the highest group of the occupied MOs (23 to 25), together with the lowest virtual orbitals (VMOs, 26 to 28) are shown in the Supplementary Material as SM2. These are involved in many of the

lowest valence states for QC, including those shown in Table I. We give additional detail concerning the electron density distribution in QC, using the Atoms in Molecules (AIM) approach.³² In this procedure, integration of the electron density along all internuclear axes, and also across the centers of each ring, is performed using the QTAIM package.³³ This shows that the electron density declines to a minimum along all C-H and C-C bonds as well as at the centers of all rings. These minima, known as critical points (CP)³² are shown in the Supplementary Material under SM3. Since each CP lies much closer to the H than the C atoms, all the C-H bonds are polarized in the sense $C^{\delta-} - H^{\delta+}$. In contrast, the C-C bonds have a CP close to their midpoint. QC has a very low dipole moment,⁸ $\mu = \mu_b = 0.01989(18)$ Debye has been determined from Stark effect measurements. This must be largely attributable to the C-H polarization of the 7-CH₂ group.

(b). The theoretical singlet valence states manifold. Unexpectedly, Table I shows that the singlet states determined by the CAM-B3LYP method gave a close energy correlation with those from the (much more rigorous) coupled cluster SAC-CI method. This correlation was performed by only considering like-with-like comparisons, such as A₁ with A₁ etc, and having similar excitation type; it does not just compare two sets of ascending numbers. The two vertical excitation energy sequences by symmetry are not identical, but the differences are generally small fractions of 1 eV. Given the width associated with UV + VUV absorptions, where the lowest mode (39) for QC is 368 cm⁻¹, as discussed below, but with most modes higher than 1000 cm⁻¹, these small differences between state energy separations, will lead to many overlaps of singlet state vibrational sequences, with consequent loss of observed structure. Thus, the SAC-CI and CAM-B3LYP state energies can be used interchangeably for most purposes. In detail, the correlation shows that the CAM-B3LYP excitation energy levels are substantially lower (17%) than those of SAC-CI but offset by around 1.0 eV. The correlation is shown in the supplementary material as SM5. Subsequently it appeared that

several other DFT functionals gave related correlations,³⁴ as described in the supplementary material as SM4.

Table I. A comparison of the vertical excitation energies for the lower singlet valence states of quadricyclane using the SAC-CI coupled cluster and CAM-B3LYP density functional methods at the 6-311G (d, p) basis set level. Where more than one configuration is shown, these are in declining density. However, a single term, merely shows dominance not exclusivity. Unexpectedly, we find that there is a close correlation between these two sets of data. Using abbreviated terminology, there is a linear relationship: CAM = 0.835(28)*SAC + 1.042(271) with correlation coefficient (CC) 0.974; standard deviations (SD) are in parentheses.

State symmetry	SAC-CI /eV	CAM-B3LYP /eV	Excitation	State symmetry	SAC-CI /eV	CAM-B3LYP /eV	Excitation
1 ¹ B ₂	7.23	7.16	5b ₂ 8a ₁ *	4 ¹ A ₂	9.86	9.16	2a ₂ 9a ₁ *
1 ¹ A ₂	7.59	7.22	5b ₂ 5b ₁ *	3 ¹ B ₁	9.71	9.20	2a ₂ 6b ₂ *+ 4b ₁ 9a ₁ *
1 ¹ A ₁	8.11	7.87	5b ₂ 6b ₂ *	5 ¹ A ₂	10.01	9.36	5b ₂ 6b ₁ * + 2a ₂ 9a ₁ *
2 ¹ B ₂	8.65	8.08	5b ₂ 9a ₁ *	3 ¹ B ₁	9.94	9.41	4b ₁ 9a ₁ *- 2a ₂ 6b ₂ *
2 ¹ A ₂	8.58	8.32	5b ₂ 6b ₁ * +2a ₂ 8a ₁ *	5 ¹ B ₂	10.21	9.51	5b ₂ 11a ₁ *
2 ¹ A ₁	8.71	8.42	5b ₂ 7b ₂ *- 5b ₂ 6b ₂ *	6 ¹ A ₂	10.12	9.61	4b ₁ 6b ₂ * - 2a ₂ 10a ₁ *
3 ¹ A ₂	8.72	8.42	2a ₂ 8a ₁ *- 5b ₂ 6b ₁ *	4 ¹ B ₁	10.17	9.62	2a ₂ 7b ₂ *- 2a ₂ 6b ₂ *
3 ¹ B ₂	9.09	8.44	5b ₂ 10a ₁ * - 2a ₂ 5b ₁ *	5 ¹ A ₁	10.11	9.76	7a ₁ 11a ₁ *
1 ¹ B ₁	8.85	8.57	5b ₂ 3a ₂ *+ 4b ₁ 8a ₁ *	6 ¹ B ₂	10.71	9.79	2a ₂ 6b ₁ *+ 5b ₂ 6b ₁ *
4 ¹ B ₂	9.33	8.62	2a ₂ 5b ₁ * +5b ₂ 10a ₁ *	7 ¹ A ₂	10.43	9.81	4b ₁ 7b ₂ *+ 2a ₂ 10a ₁ *
2 ¹ B ₁	9.11	8.69	5b ₂ 3a ₂ *+ 4b ₁ 8a ₁ *	5 ¹ B ₁	10.64	9.90	7a ₁ 5b ₁ *
3 ¹ A ₁	9.39	8.84	4b ₁ 5b ₁ * - 5b ₂ 7b ₂ *	6 ¹ A ₁	10.55	9.94	2a ₂ 3a ₂ *+ 4b ₁ 6b ₁ *
4 ¹ A ₁	9.69	9.09	5b ₂ 8b ₂ *+ 4b ₁ 5b ₁ *	6 ¹ B ₁	10.86	10.21	4b ₁ 10a ₁ *

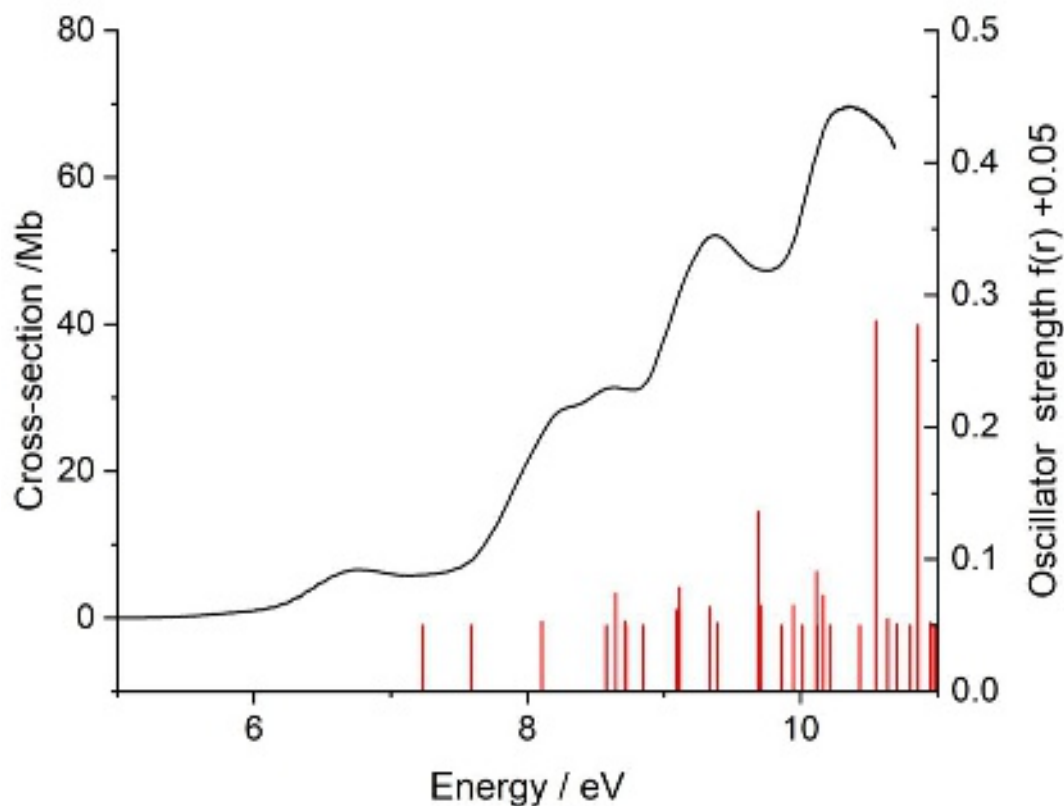
All the singlet states, shown in Table I, have several leading configurations, and these include symmetric and antisymmetric combinations. The highest occupied molecular orbital (HOMO, 5b₂), is involved as leading term in the ten lowest excited states, and some other states.

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The next two doubly occupied molecular orbitals (DOMOs), $2a_2$ and $4b_1$ also appear in groups of higher excited states; these three DOMOs and the lowest three virtual orbitals shown in SM2, cover the energy levels populated in Table I. The first leading term involving the next DOMO ($7a_1$) lies at a calculated energy close to 9.5 eV. Only 20 valence states up to 11 eV have an oscillator strength $f(r) > 0.01$ units; only 8 lie above $f(r) > 0.05$, while only 2 of these have $f(r) > 0.1$ units. The highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) excitation ($5b_28a_1^*$, X^1B_2) is typical, with an extremely low oscillator strength ($f(r)$ 0.0010). The absence of dominant peaks in the VUV spectrum is readily interpreted in these terms. Up to this stage, the theoretical determination of the excited states has all been performed at the X^1A_1 ground state equilibrium structure. In the following Sections, concerned with Rydberg states, all theoretical work was performed either at the equilibrium structure, or at the structure of the lowest ionic state X^2B_2 , as determined previously.¹ Since Rydberg and their limiting ionic state share ionic state structures, this is a suitable choice for non-optimal structures.

Figure 2. The VUV absorption spectrum of quadricyclane with SAC-CI calculated valence state energies. The energies for this theoretical series do not explain the lower onset of the spectrum, leading to the conclusion that Rydberg states are dominant especially in the low VEE energy range. This is demonstrated in Figure 3. To show the positions of the optically forbidden 1A_2 states, the oscillator strengths have been increased by 0.05 units.

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(c). Rydberg state calculations. These were performed separately with each of the SAC-CI and DFT modules. As in several of our earlier studies,^{1,2,11,14} the Rydberg basis functions populate the lowest energy group of virtual molecular orbitals (VMOs) at the Hartree-Fock level; this is relative to the corresponding valence states, whose orbitals move to higher energy positions. The 3s, 4s and 5s Rydberg states occupy VMOs 26 to 28. In all the evaluated Rydberg states, these 3s, 4s and 5s VMOs occur as linear combinations of the input gaussian orbital. Similar positions occur for p-, d- and f-Rydberg orbitals.

The Rydberg state vertical excitation energy results, performed at the equilibrium structure of the ground state, are unscaled in energy, and shown in Table II. In principle, these can be extrapolated to the VEE, but the 3 Rydberg functions can only generate states with principal quantum numbers 3, 4 and 5. Such results are shown in the Supplementary Material under SM5.

Table II. A comparison of the vertical excitation energies for the lower singlet s-Rydberg states of quadricyclane using the SAC-CI coupled cluster method at the 6-311G (d, p) basis set level. Compared with the results in Table I, energies of comparable states are lowered by ~1.2 eV, as a result of the Rydberg functions, but are still not sufficiently low to account for the spectral onset.

Symmetry	PQN sequence	Energy / eV	f(r)	Symmetry	PQN sequence	Energy / eV	f(r)
1 ¹ B ₂	3	6.009	0.001	3 ¹ B ₂	7	7.60	0.000
1 ¹ A ₂	3	6.381	0.000	1 ¹ B ₁	3	7.62	0.000
1 ¹ A ₁	3	6.469	0.003	3 ¹ B ₂	5	7.63	0.006
1 ¹ B ₂	3	6.492	0.002	2 ¹ B ₂	5	7.66	0.000
1 ¹ B ₂	4	7.070	0.000	3 ¹ A ₂	5	7.81	0.000
2 ¹ B ₂	4	7.180	0.004	3 ¹ A ₁	5	7.98	0.009
2 ¹ B ₂	4	7.215	0.002	1 ¹ A ₁	3	8.13	0.000
1 ¹ B ₂	5	7.343	0.000	3 ¹ B ₂	6	8.19	0.000
2 ¹ A ₂	4	7.349	0.000	2 ¹ A ₁	4	8.62	0.013
2 ¹ A ₁	4	7.427	0.002	2 ¹ B ₁	4	8.81	0.002
3 ¹ B ₂	5	7.455	0.000	3 ¹ A ₁	5	8.91	0.027
2 ¹ B ₂	6	7.583	0.000	3 ¹ B ₁	5	9.14	0.021

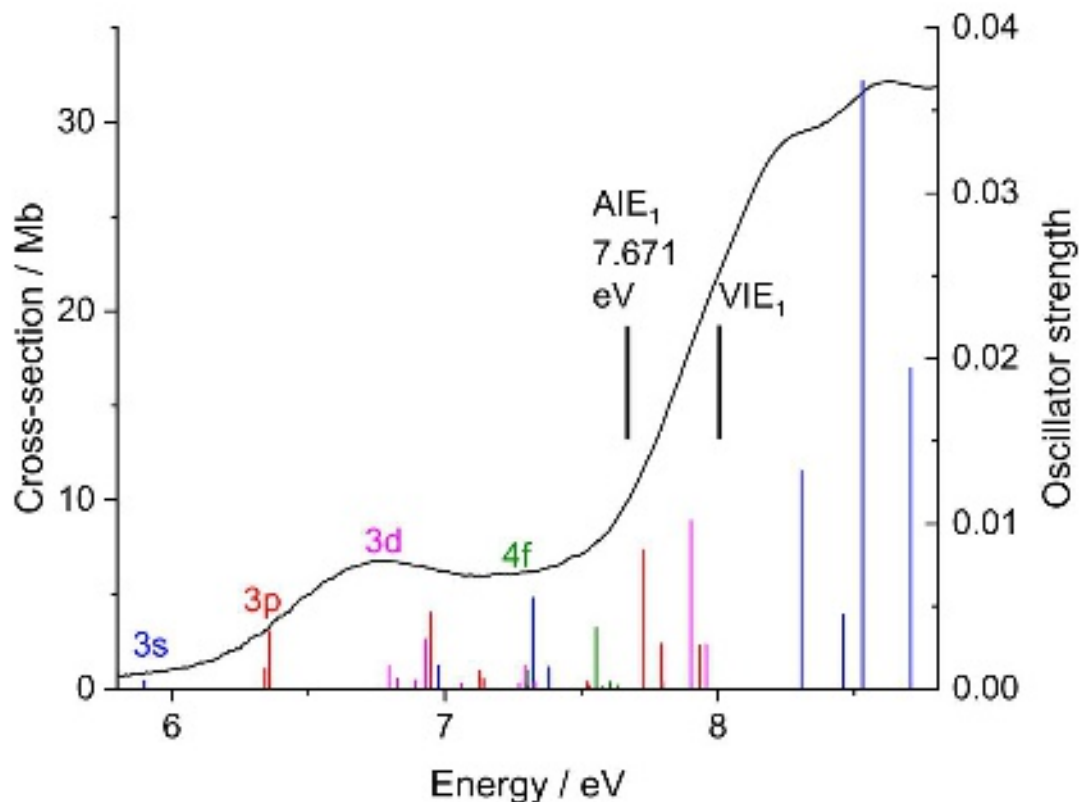
Several CAM-B3LYP calculated adiabatic excitation energy Rydberg states, are shown in Table

III. It is impracticable to determine equilibrium structures for all the lower Rydberg states; however, we have obtained equilibrium structures and harmonic frequencies for all three of the 5b₂ excitations to 3s, 4s and 5s Rydberg states; the structures are effectively identical, as are the harmonic frequencies. These structures will be almost identical to that of the lowest ionic state, as is assumed for Rydberg states. The CAM-B3LYP energies of the calculated structures are superimposed on the onset of the VUV spectrum in Figure 3. The Rydberg states for each of the Rydberg s-, p-, d-, and f-energies are displayed in distinct colours, together with our recently determined adiabatic and vertical ionization energies. The Rydberg states give an interpretation of the spectral onset. Overall, we interpret the VUV spectrum as a complex mixture, with Rydberg states at the onset, and valence states dominating the higher energy range of Figure 2. In our experience, valence states can show a wide range of intensities, while Rydberg states are universally weak, as is seen here.

Figure 3. The VUV absorption spectrum of quadricyclane with CAM-B3LYP calculated Rydberg states using very diffuse functions of s, p, d, and f symmetry. The adiabatic

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ionization energy (AIE_1) for QC is at 7.671 eV and was assigned to the X^2B_2 state in reference 1. The corresponding vertical ionization (VIE_1) was assigned to the fourth member of the progression, with vibration frequency 663 cm^{-1} , at 8.005 eV. Some higher intensity valence states appear above 8.3 eV.



The CAM-B3LYP density functional energy results, shown in Table III, were each determined by single calculations as is normal in G-16. In that suite, the excited state is correctly found, but the ground state is determined at this excited state structure. We require the normal spectroscopic convention, where both ground and excited states are determined at their equilibrium structures. This leads to essential corrections to the G-16 energies, to bring the results for the adiabatic excitation energies into alignment with spectroscopic standard usage. Each pair of ‘TDDFT’ and ‘Corrected’ energies in Table III are independently determined. But the corrected energies in Table III give a close linear correlation to the uncorrected series in this instance; this is not an automatic requirement, but merely pragmatic. We find: $E_{\text{Corrected}} = 1.017(34) * E_{\text{TDDFT}} + 1.606(194)\text{ eV}$, where the standard errors (SE) are in parentheses and the

CC is 0.987. Thus, in general, the Rydberg state energies after correction are ~ 1.61 eV higher than those initially determined. The need to make these re-evaluations is obvious.

Table III. TZVPR basis set equilibrium structures for Rydberg states with s, p, d, and f spherical harmonics.

State	Symmetry	Rydberg state energy / eV		State	Symmetry	Rydberg state energy / eV	
		TDDFT	Corrected			TDDFT	Corrected
3s	1^1B_2	4.29	5.51	3d	1^1B_1	5.24	6.99
4s	2^1B_2	5.41	6.64	4d	2^1B_1	5.80	7.56
5s	3^1B_2	5.86	7.10	5d	3^1B_1	6.48	8.25
3p	1^1B_2	4.89	5.92	4f	1^1B_1	5.72	7.46
3p	1^1A_1	4.94	5.97	5f	2^1B_1	6.07	7.82
4p	2^1A_1	5.59	6.82	6f	3^1B_1	7.08	8.80
5p	3^1A_1	6.53	7.56				

The vertical VIE for quadricyclane are: 8.199 (X^2B_2), 9.608 (1^2A_2), 9.946 (1^2B_1) and 10.914 eV (1^2A_1) using data from our previous study.¹ Comparing the data from Tables I, II and III, leads to the conclusion that the lowest Rydberg state, $5b_23s$, is lower in energy by ~ 0.4 eV than the corresponding valence state. The 3p states, shown in Figure 3, also involving $5b_2$ excitation, occur a further ~ 0.5 eV higher in energy. The full set of energies shown in Figure 3, are listed in the supplementary material as SM6.

(d) Vibrational analysis of the Rydberg states of quadricyclane under TDDFT conditions.

The full set of symmetric and non-symmetric harmonic frequencies for the lowest excited state, 1^1B_2 , are shown in Table IV, since we present both Franck-Condon (FC) and Herzberg-Teller (HT) analyses of some states below. The frequencies are listed in the standard spectroscopic mode convention where all $a_1 < a_2 < b_1 < b_2$ frequencies are given. It is important to note that the numbering used in both G-16 and the Pisa vibrational analysis software, is in ascending frequency sequence, irrespective of symmetry. For example, in Table IV, 368 cm^{-1} is mode 39 under the standard labelling, but in the ascending sequence by frequency is mode 1.

Table IV. All harmonic frequencies participating in the Franck-Condon and Herzberg-Teller modes for the 1^1B_2 state in Tables V and VI. The frequencies are labelled with the spectroscopic modes $a_1 < a_2 < b_1 < b_2$.

Mode	Symmetry a_1	Mode	Symmetry a_2	Mode	Symmetry b_1	Mode	Symmetry b_1
1	3381	13	3385	21	3389	30	3390
2	3339	14	1380	22	3294	31	3344
3	3232	15	1292	23	1449	32	1520
4	1623	16	1189	24	1202	33	1418
5	1514	17	1094	25	1077	34	1384
6	1474	18	873	26	1073	35	1126
7	1146	19	689	27	908	36	1011
8	1114	20	441	28	811	37	871
9	979			29	453	38	820
10	949					39	368
11	802						
12	693						

The FC analysis of the lowest Rydberg excited state (1^1B_2) is shown in Table V, with the corresponding HT analysis in Table VI. In these and following Tables, we give the complete onset of the vibrational envelope, to show the nature of the processes. We also show the most important combination bands in terms of intensity. In FC processes, only odd quanta of a_1 modes are stimulated, while nonsymmetric modes can only occur with even quanta. Several fundamentals occur, but with weak intensity. The most intense FC modes are overtones and multiple combinations of up to ten combination bands, which have the highest numerical intensity, and are the strongest peaks in the theoretical FC band. These show that several of the most intense combination bands, often occur at extremely high frequencies relative to the 0-0 band. The FC analysis of the (lowest) 3s Rydberg state (1^1B_2 symmetry) contains 9730 vibrational states, but only 42 have intensity with molar absorption coefficient (M) greater than $1 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$; many allowed transitions in our previous studies^{2,14} have $10^4 < M < 10^6$.

Table V. The Franck-Condon analysis of the lowest Rydberg state ($5b_23s$) using the TZVPR basis set. The modes shown in the 1st and 4th columns are the a_1 modes. The complete onset of the lowest set of vibrational states is shown in columns 1 to 3. The most intense bands are in columns 4 to 6.

Energy / cm^{-1}	Relative intensity	Modes excited + quanta	Energy / cm^{-1}	Relative intensity	Modes excited + quanta
0	0.0078	0^0	4668	1.824	$10^2 12^4$
693	0.0396	12^1	4777	1.769	$10^2 11^1 12^3$

802	0.0080	11 ¹	4924	1.811	10 ³ 12 ³
949	0.0276	10 ¹	5361	1.865	10 ² 12 ¹²
1385	0.1290	12 ²	5617	2.410	10 ³ 12 ⁴
1494	0.0376	11 ¹ 12 ¹	5873	1.798	10 ⁴ 12 ³
1641	0.1849	10 ¹ 12 ¹	6162	1.973	10 ² 11 ¹ 12 ¹²
1750	0.0247	9 ¹ 11 ¹	6419	2.393	10 ³ 11 ¹ 12 ⁴
1807	0.0209	8 ¹ 12 ¹	6732	1.758	8 ¹ 10 ³ 12 ⁴
1898	0.0643	10 ²	6840	1.518	8 ¹ 10 ³ 11 ¹ 12 ³
2063	0.0143	8 ¹ 10 ¹	7424	1.762	8 ¹ 10 ³ 12 ¹²
2078	0.1834	12 ³	8226	1.759	8 ¹ 10 ³ 11 ¹ 12 ¹²

In contrast, the HT profile in Table VI contains the lowest frequency mode 39 (368 cm⁻¹) of b₂ symmetry. The profile is mainly binary and ternary combination bands, based on the set of FC fundamentals. The whole HT spectrum is stronger than the FC spectrum. The FC profile contains several lower frequencies than the HT one, and is simpler, and hence shown in the Figures below. In both Table V and VI, the peaks occurring with extremely high frequency are the most intense of the whole spectrum, which contains many thousands of vibrational states.

Table VI. The Herzberg-Teller analysis of the 5b₂3s Rydberg state. The modes shown in columns 1 to 3 are the complete onset, as in Table V, including non-symmetric modes of a₂, b₁ and b₂ symmetry. The most intense modes are in columns 4 to 6.

Energy / cm ⁻¹	Relative intensity	Modes excited + quanta	Energy / cm ⁻¹	Relative intensity	Modes excited + quanta
0	0.0007	0 ⁰	5037	6.177	10 ² 12 ⁴ 39 ¹
1061	0.1357	5 ¹ 39 ¹	5729	6.432	10 ² 12 ¹² 39 ¹
1317	0.0941	12 ¹ 39 ¹	5985	8.293	10 ³ 12 ⁴ 39 ¹
1754	0.4454	5 ² 39 ¹	6146	6.090	10 ² 11 ¹ 12 ³ 39 ¹
1862	0.1282	6 ¹ 5 ¹ 39 ¹	6242	6.175	10 ⁴ 12 ³ 39 ¹
2010	0.6376	12 ¹ 5 ¹ 39 ¹	6293	6.114	10 ³ 12 ³ 39 ¹
2119	0.0839	12 ¹ 6 ¹ 39 ¹	6531	6.745	10 ² 11 ¹ 12 ¹² 39 ¹
2175	0.0709	18 ¹ 5 ¹ 39 ¹	6678	5.708	10 ³ 12 ¹² 39 ¹
2258	0.0943	10 ¹ 5 ²	6787	8.159	10 ³ 11 ¹ 12 ⁴ 39 ¹
2266	0.2214	12 ² 39 ¹	6838	5.873	10 ² 11 ¹ 12 ⁴ 39 ¹
2432	0.0483	18 ¹ 12 ¹ 39 ¹	6953	5.622	18 ¹ 10 ² 11 ¹ 12 ⁴ 39 ¹
2443	0.1250	12 ¹ 6 ¹ 5 ¹	7043	5.694	10 ⁴ 11 ¹ 12 ³ 39 ¹
2446	0.6223	5 ³ 39 ¹	7100	5.961	18 ¹ 10 ³ 12 ⁴ 39 ¹
2490	0.1160	5 ² 39 ³	7627	5.730	10 ⁴ 12 ¹² 39 ¹
2514	0.1349	12 ¹ 10 ¹ 5 ¹	7793	6.094	18 ¹ 12 ³ 5 ⁵ 39 ¹

2555	0.4620	$6^1 5^2 39^1$	8049	5.800	$18^1 12^4 5^4 39^1$
2664	0.0839	$6^2 5^1 39^1$	8594	6.024	$18^1 12^3 6^1 5^5 39^1$

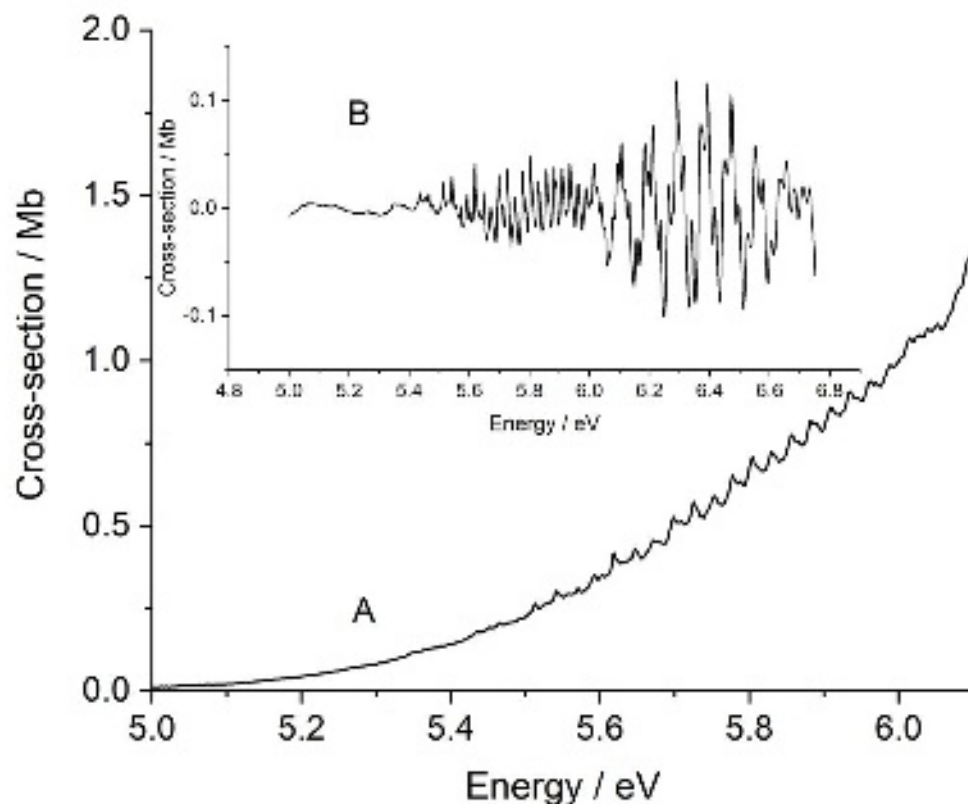
(e) **Rydberg states identified in the experimental VUV spectrum.** We believe that this is the first attempt to identify vibrational structure in the QC absorption spectrum.

We have divided the VUV range of the QC absorption spectrum over the energy range up to 8.8 eV into short sections, as shown in Figures 5, 6, 7, 8 and 9; theoretical analyses are superimposed, and are discussed below. Figure 5 shows the raw UV + VUV data as A, while the inset (B) shows the regular residuals after fitting a 9th order polynomial to the curve (A) and plotting the difference data. The full range of these residuals are shown in the supplementary material as SM6; the most prominent detail, from 5.0 to 6.8 eV, was also obtained using a 9th order polynomial as in supplementary material as SM7.

Superposition of the Franck-Condon profile for the X^1B_2 3s-Rydberg state, as shown in Figure 6, leads to a close fit to almost all the most intense peaks in the range 5.1 to 6.0 eV. The onset of UV absorption for quadricyclane, after the fit of the spectrum in Figure 6, is based on the calculated 0-0 band. This same procedure of fitting the main peaks, but using the position of the calculated 0-0 band for the spectral origin was used for the higher energy analyses. We conclude that the 3s-Rydberg state 0-0 band lies at 5.181 eV as shown in Figure 6. This is 0.26 eV higher than that given by R&W,⁹ but given the earlier assignment where their AIE was identified with an early VEE, this difference is reasonable.

Our identification of these Rydberg states is cognisant that the R&W assignment⁹ of the binding energies for the 3s and two 3p states are 2.88, 2.29 and 2.24 eV respectively; these differences are independent of the IE used. The latter pair would be expected to occur in the QC VUV spectrum ~0.6 eV higher in energy, close to 5.78 eV.

Figure 4. The raw QC absorption data shown in A; after fitting to a 9th order polynomial this gives the regular residuals shown in B. The vibrational sequence in the range 5.5 to 6.0 eV is the 3s-Rydberg state. The more complex multiplet between 6.0 and 6.8 eV is the two allowed 3p-Rydberg states.

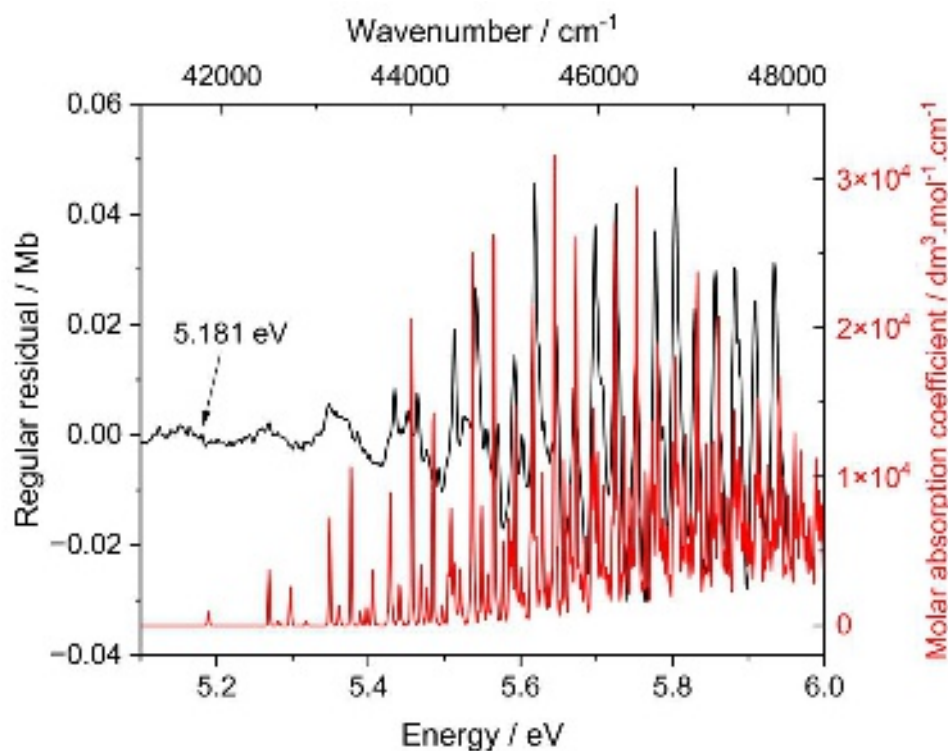


The energy range above 5.35 eV shows a set of sharp bands up to 5.95 eV, and further complex structure from 6.0 to 6.7 eV (Figure 5, inset). The region from 5.1 to 6.0 eV, shown in Figure 6, has the FC profile for the 3s Rydberg state superimposed. Almost every peak in the region is accounted for, although the FC profile does not give a good interpretation of the internal local intensities.

The set of 12 sharp peaks between 5.7 and 5.9 eV, with an average separation close to 212 cm^{-1} over 10 intervals, as seen in Figure 5, is reminiscent of the VUV spectrum of norbornadiene, where a Rydberg state occurs with similar features. However, in NBD this is spectroscopic mode 12 (368 cm^{-1}), much larger than the present QC value. Above 6.0 eV, a further set of bands with a more complex profile occurs with a maximum close to 6.290 eV as seen in Figure 7. This is the two allowed 3p Rydberg states, of 1B_2 and 1A_1 symmetries.

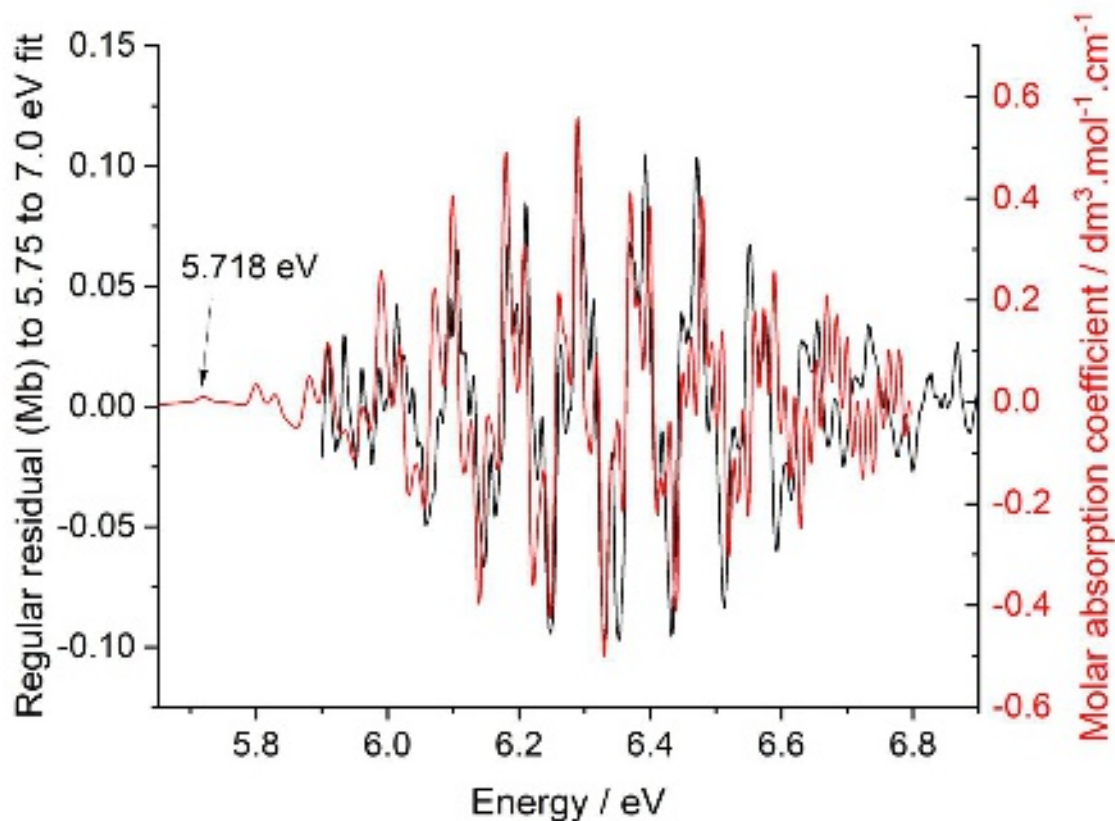
Figure 5. The onset of very weak structure in the UV absorption of quadricyclane with the Franck-Condon analysis of the 1B_2 state, which defines the lowest 3s-Rydberg state

with $n = 3$ and $\delta = 0.932$. The calculated FC have been scaled by 0.97 to bring the principal vibrational sequence into alignment. The band origin is marked with an arrow.



Similar treatment of the spectral range from 5.7 to 6.9 eV gave the black curve in Figure 7 after fitting both the calculated profile and the spectral data to a further polynomial. A series of FC fits to the region using individual peaks with various half-widths at half-maximum (HWHM) led to the choice of 70cm^{-1} , which we have often used as the width for an unperturbed state.¹⁴ The fit starting close to 5.8 eV is clearly very similar to the spectrum, but diverges slightly above 6.6 eV, which may indicate a further electronic state above that energy. Using the fit to the dense set of peaks, allows the 0-0 band of the state at 5.718 eV, to be attributed to a 3p Rydberg state.

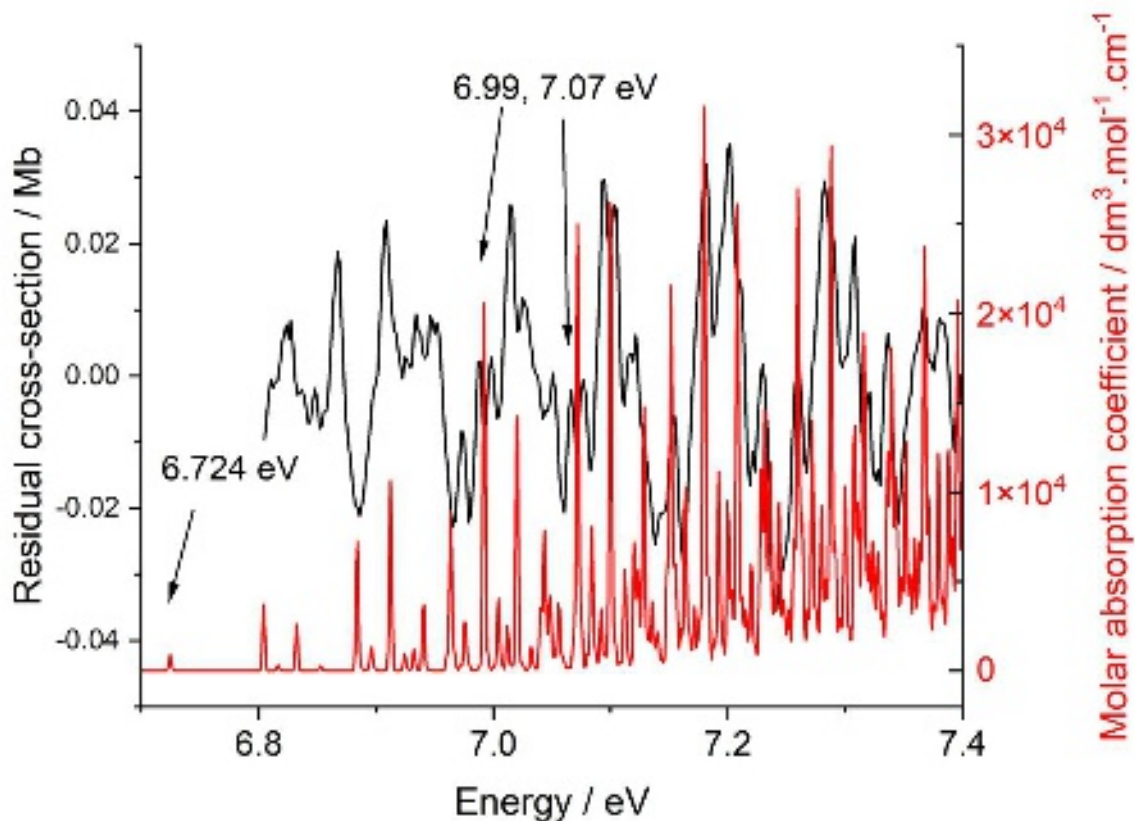
Figure 6. The 5.7 to 6.8 eV range of the QC VUV spectrum, with the Franck-Condon profile based of the $^1\text{B}_2$ state 3p-state superimposed. The band origin is shown.



The next selected region of the VUV spectrum, from 6.8 to 7.4 eV, shown in Figures 2 and 3, contains weak features on either side of a shallow minimum. Again, a polynomial fit to the raw data for this region exposed fine structure on both sides of the minimum, as shown in Figure 8. Many of the observed peaks are matched, but in some cases, peaks are doubled, as shown at 6.99 and 7.07 eV. The super-position of the FC envelope leads to the position of the 0-0 band being at 6.724 eV; this energy corresponds to a 3d Rydberg state, with $n = 3$ with $\delta = 0.136$.

Figure 7. The 6.7 to 7.4 eV range of the QC VUV spectrum, with the Franck-Condon profile superimposed; the onset is 6.724 eV and corresponds to a 3d Rydberg state.

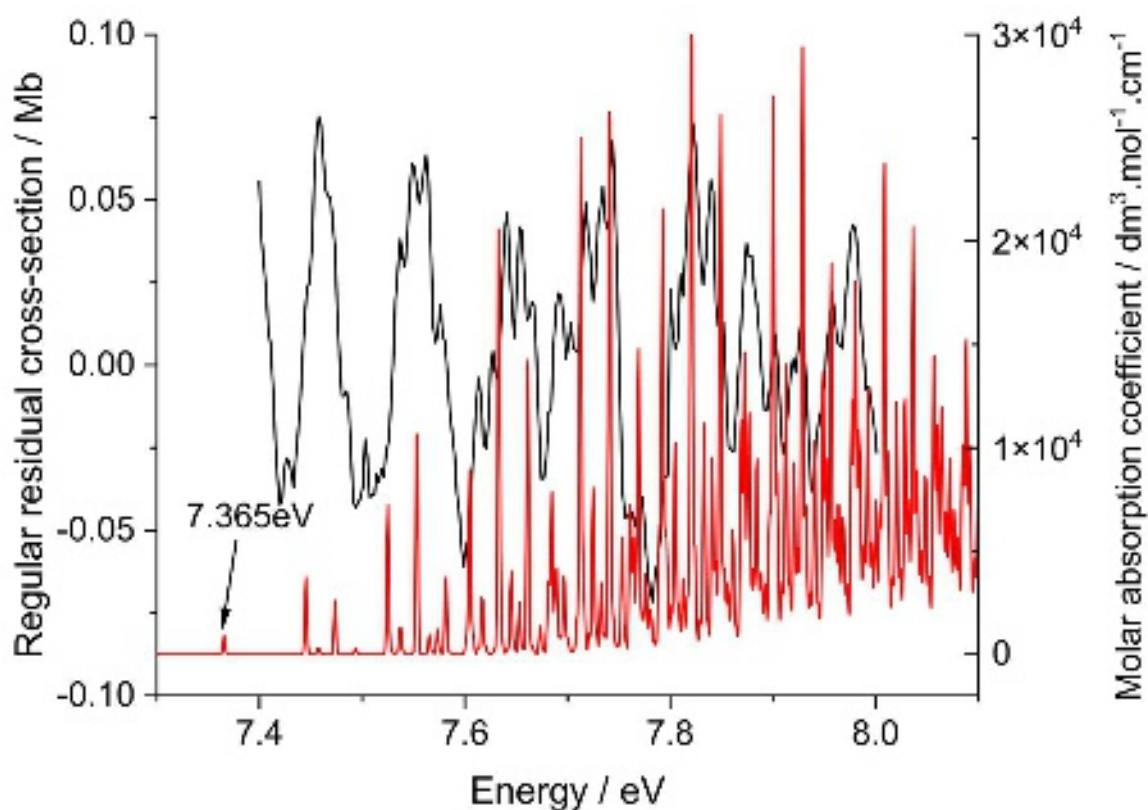
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Similar treatment, of the next higher energy range from 7.3 to 8.0 eV leads to Figure 9. This range includes energy of the X^2B_2 ionic state of QC, previously reported at 7.6706 eV.¹ Thus the onset in Figure 9 lies below the ionization energy, while the tail lies in the super-excited state region above the IE.

Figure 8. The 7.3 to 8.0 eV range of the QC VUV spectrum, with the Franck-Condon profile based on the $4s$ determination superimposed. The 0-0 band and onset region of the spectrum starts well below the X^2B_2 ionization energy, but the lengthy tail of the spectrum extends into the super-excited state region.

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(f) Herzberg-Teller (HT) analyses of the Rydberg states of QC and the impact for ionic states. Vibrational analyses for singlet and triplet states can readily be performed, using software such as that from the Pisa group in G-16. Both Franck-Condon and Herzberg-Teller processes are routine. However, ionic states cannot be analysed by HT processes using these packages owing to incompatibility between the Pisa (vibrational) and Gaussian (equilibrium geometry) codes in G-16 and its predecessors. This arises from the absence of the dipole derivatives being stored on the G-16 checkpoint file, and hence non-availability to the Pisa software. Currently, HT analyses of ionic states are limited to specialist packages, often not available in the public domain. This was the situation when we undertook the vibrational

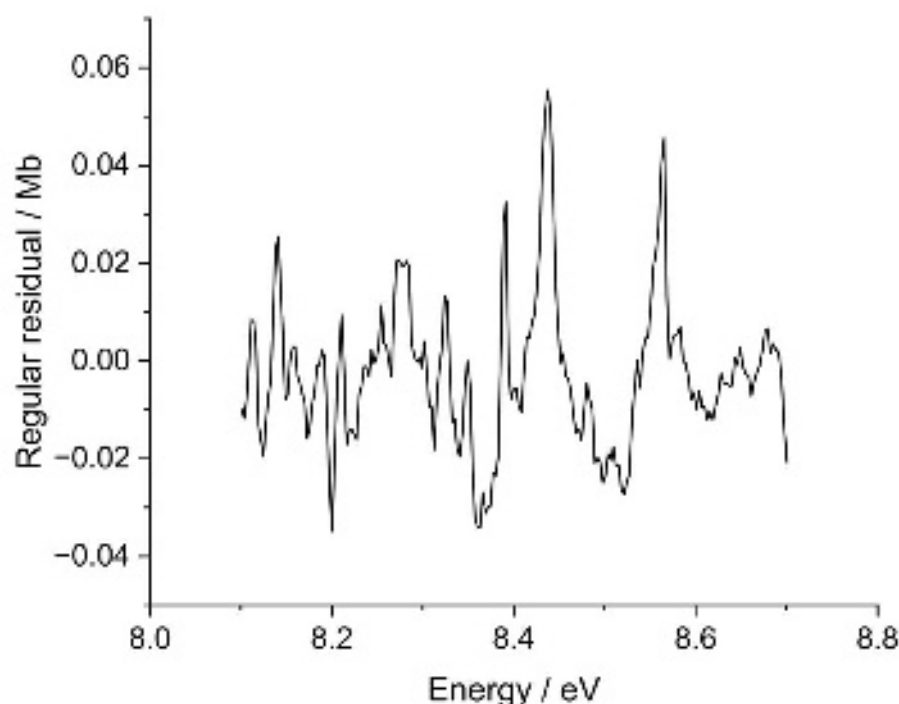
analysis of the photoelectron spectrum of quadricyclane.¹ We believe we have a remedy to this issue.

Rydberg states exhibit the same vibrational profile as their limiting ionic state, at least to first order. Hence, we can determine the HT component of vibrations for the ionic state by calculation of that for the Rydberg state. We have performed that here, with significant added information. This results in the contribution of HT vibrations to ionic states via Rydberg states being readily available within G-16 and other suite usage and does not require special techniques.

The HT results, in Table VI for the 3s Rydberg state, are more intense by a factor of 4 than those under FC conditions. However, only one nonsymmetric mode (368 cm^{-1} , b_2) appears. Many of the HT vibrations shown in Table VI are combination bands of 368 cm^{-1} with symmetric a_1 vibrations rather than nonsymmetric modes per se.

(g) Fine structure attributable to valence states. An example from this range of absorption is shown in Figure 10. Here, all excitation processes lie above the lowest ionization energy, but we have been unable to assign the vibrational structure to a particular state. Using the TDDFT method, but this time with the TZVP basis set, the lowest AEE valence state has the same symmetry (1^1B_2) as the lowest Rydberg state and is predicted to lie between the 3s and 4s Rydberg states, close to 5.803 eV. It shows many similar fundamentals to those for the Rydberg 3s state, but the frequencies are considerably different. A small selection of these valence state frequencies is shown in the supplementary material as SM8 and SM9. The differences from the Rydberg state in Figure 6, close to the onset are apparent.

Figure 9. The range from 8.0 to 8.7 eV which includes the lowest ionization energy of the QC VUV spectrum and above. These cannot relate to the Rydberg states evident at lower energy.



IV. CONCLUSIONS

We have presented and analysed the combined UV + VUV absorption spectrum of quadricyclane for the energy range up to 10.8 eV. The profile does not present any vibrational features but poorly-defined broad maxima. The completely σ -bonded structure of the molecule, leading to the absence of a chromophore, is responsible for this appearance. However, by polynomial fitting of local energy ranges, subtracting from the observed spectral intensity, and plotting the difference spectrum, otherwise known as the regular residuals, we have exposed extensive vibrational structure. Almost every vibration identified by the polynomial subtraction above, can be interpreted at the Franck-Condon level, for the onset.

The high energy of the σ^* -MOs leads to the onset of the UV spectrum being populated by Rydberg states. Hence, the onset of the UV + VUV spectrum cannot be interpreted by valence state calculations, even when using coupled cluster (SAC-CI) theoretical levels. However, these methods are successful when the Gaussian atomic orbitals (AOs) contain sufficiently

diffuse atomic functions to generate Rydberg states; this enables the spectral onset to be interpreted in detail.

Unexpectedly, there is a close correlation between the SAC-CI valence state energies and those determined by the CAM-B3LYP functional. The latter is a much less demanding procedure in computational terms but achieves remarkably similar numerical results.

The Franck-Condon analysis of the spectrum is complex, and shows a wide range of intensities, with very weak onsets. This leads to the conclusion that except for the lowest AEE, there is little chance in identification of experimental AEE for most Rydberg states unless jet-cooling can be utilised. The FC components of the onset singlet Rydberg state, successfully analysed above, are overwhelmed at higher energies by Herzberg-Teller states, leading to a loss of spectral definition.

Our study, arguably the largest to date for quadricyclane, shows that the inherent strain energy within the double cyclopropane system, can be released, without activation energy, during attempts at determination of the equilibrium structure for the lowest singlet and triplet states, $^{1,3}A_2$. The result is an excited state of norbornadiene some 6 eV above the ground state. However, several other singlet and triplet states of QC behave normally and generate global minima for equilibrium QC structures.

The Rydberg states, generate a profile almost identical to that of the limiting ionic state. Many quantum chemistry suites cannot calculate HT components directly for ionic states. The use of the vibrational profiles for the corresponding Rydberg states provides a simple method of achieving this aim, since no special coding is required. This avoids access to dedicated software, often not in the public domain.

We have shown that determination of Rydberg state energies with spherical harmonics through s, p, d, and f are easily performed. These provide theoretical 0-0 bands, which were used to

locate the spectral onsets in the experimental spectrum, which were not apparent in the QC spectrum.

ADDENDUM

A Reviewer has noted that we use three scales of intensity in this study, each for comparability with other work in the field of study. The numerical relationships between these and related units have been previously reported by Cohen and Taylor,³⁵ in Photoabsorption, Photoionization, and Photoelectron Spectroscopy.³⁶

SUPPLEMENTARY MATERIAL

Contents. The supplementary material contains additional information on each of the following: 1. SM1 The quadricyclane molecule re-labelled for Rydberg state calculations. 2. SM2. The lowest group of singlet valence states, determined by the B3LYP method using the Def2-TZVPPD basis set. 3. SM3. The wide scan VUV spectrum with the Def2-TZVPPD basis set using the B3LYP method. SM4. The lowest group of singlet valence states for quadricyclane, using the SAC-CI method. SM5. Comparison of the SAC-CI singlet state results with the B3LYP DFT procedure at the 6-311G(d, p) basis set level. SM6. The full range of regular residuals. SM7. The onset polynomial fit to the raw data. Below 5 eV, the two curves are indistinguishable at this scale. SM8. Table SM8 The 1^1B_2 valence state. Calculated onset 0-0 band at 5.8032 eV. Table SM9. The 1^1A_1 valence state. Calculated onset 0-0 band at 6.707 eV.

AUTHOR DECLARATIONS

The authors have no conflicts to disclose.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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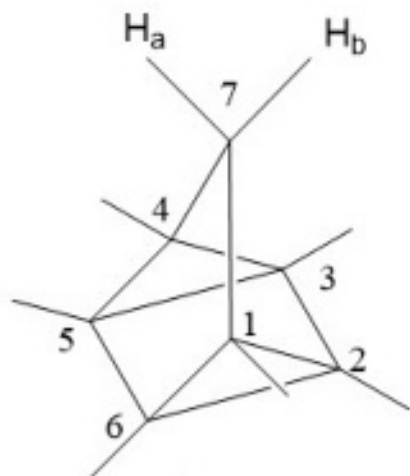
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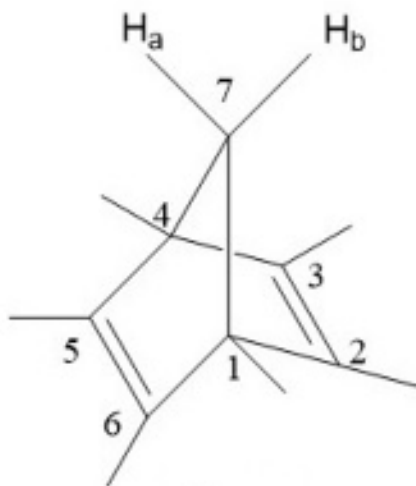
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Palmer et al Figure 1

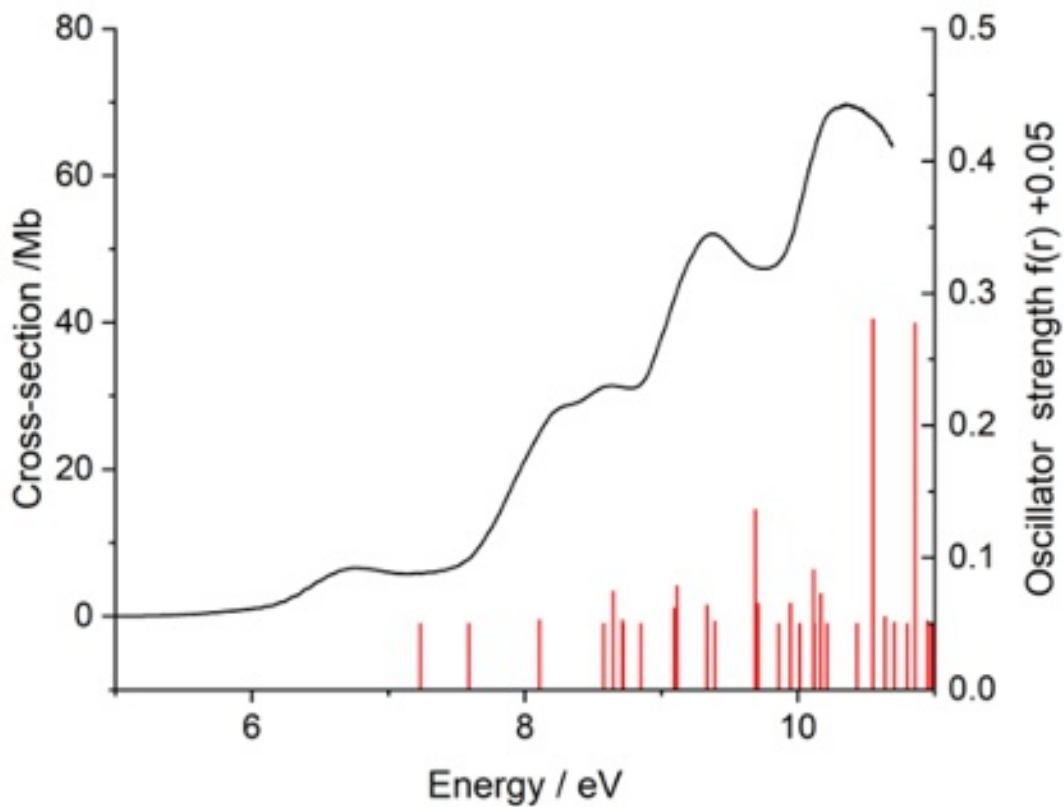


1, Quadricyclane

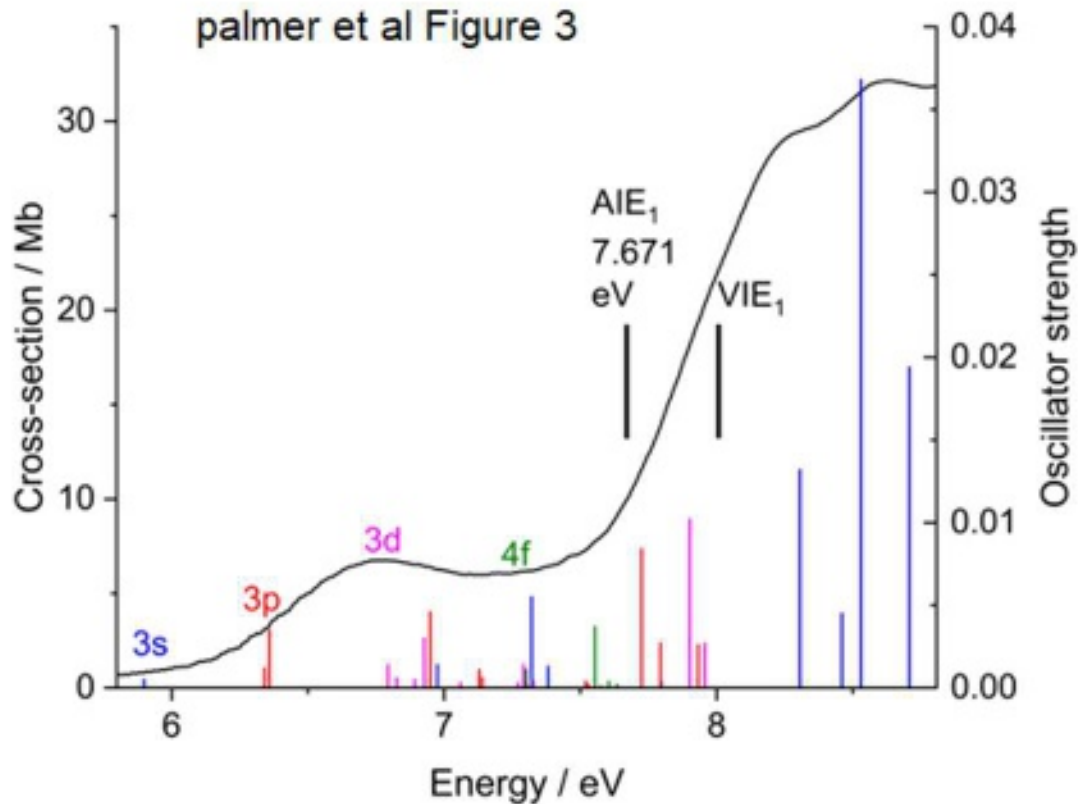


2, Norbornadiene

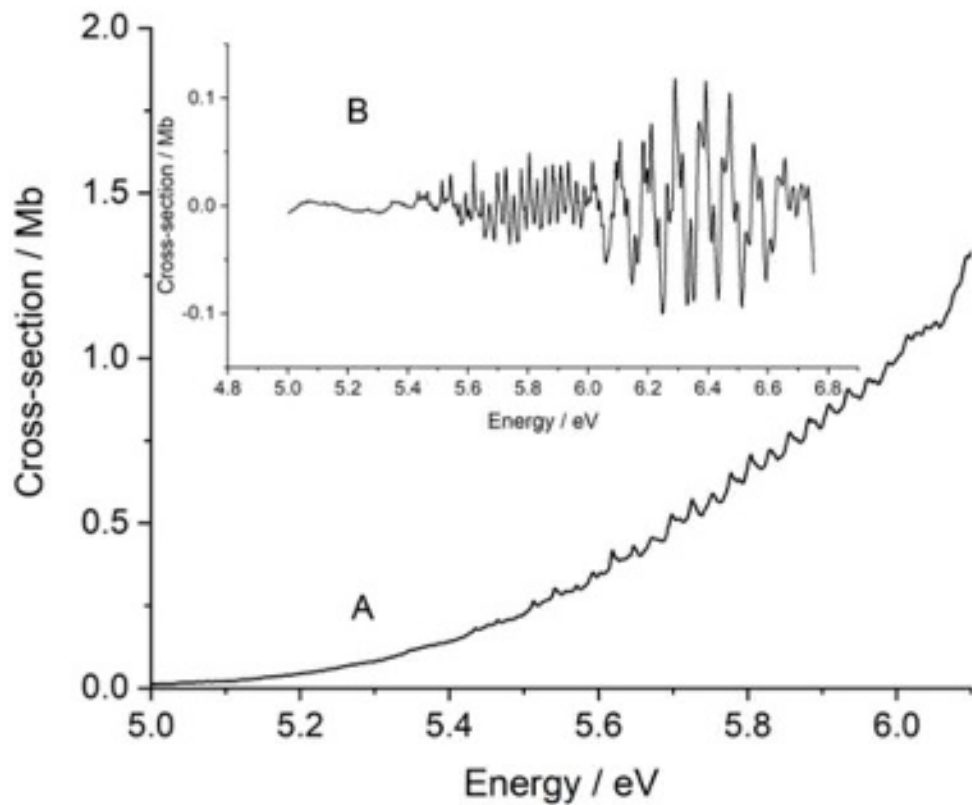
Palmer et al Figure 2



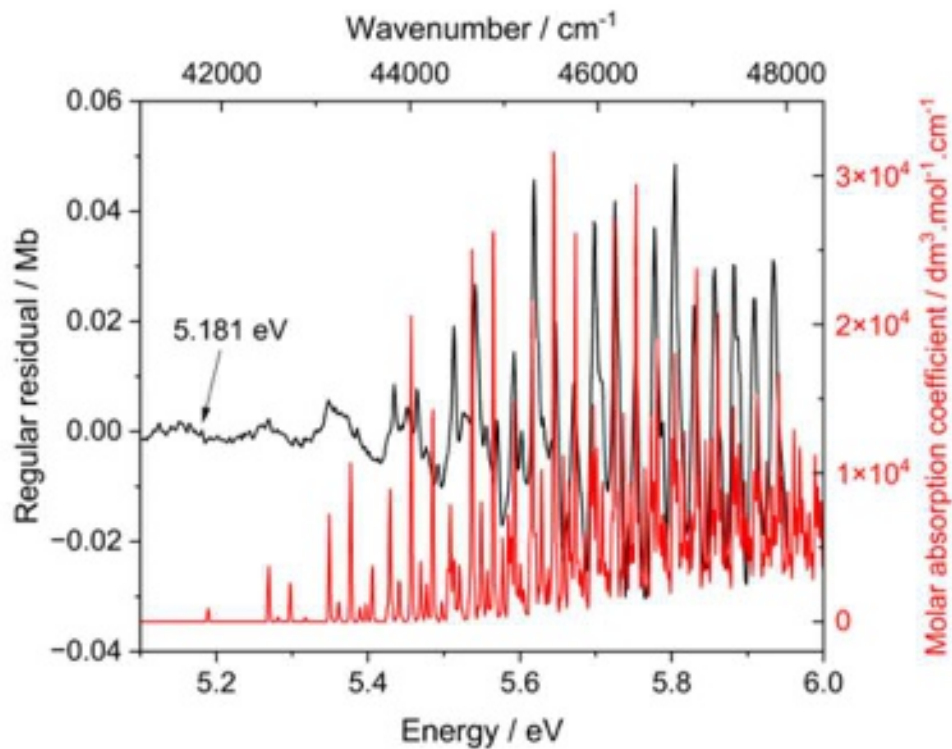
palmer et al Figure 3



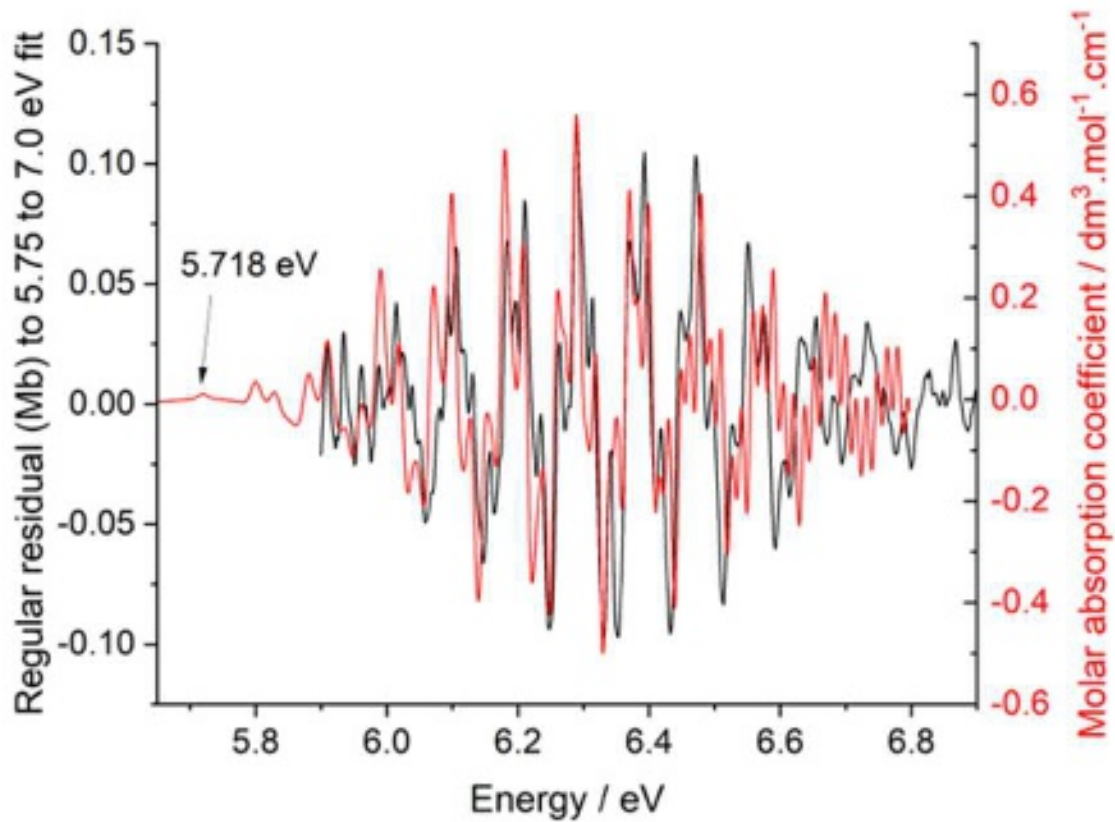
Palmer et al Figure 4



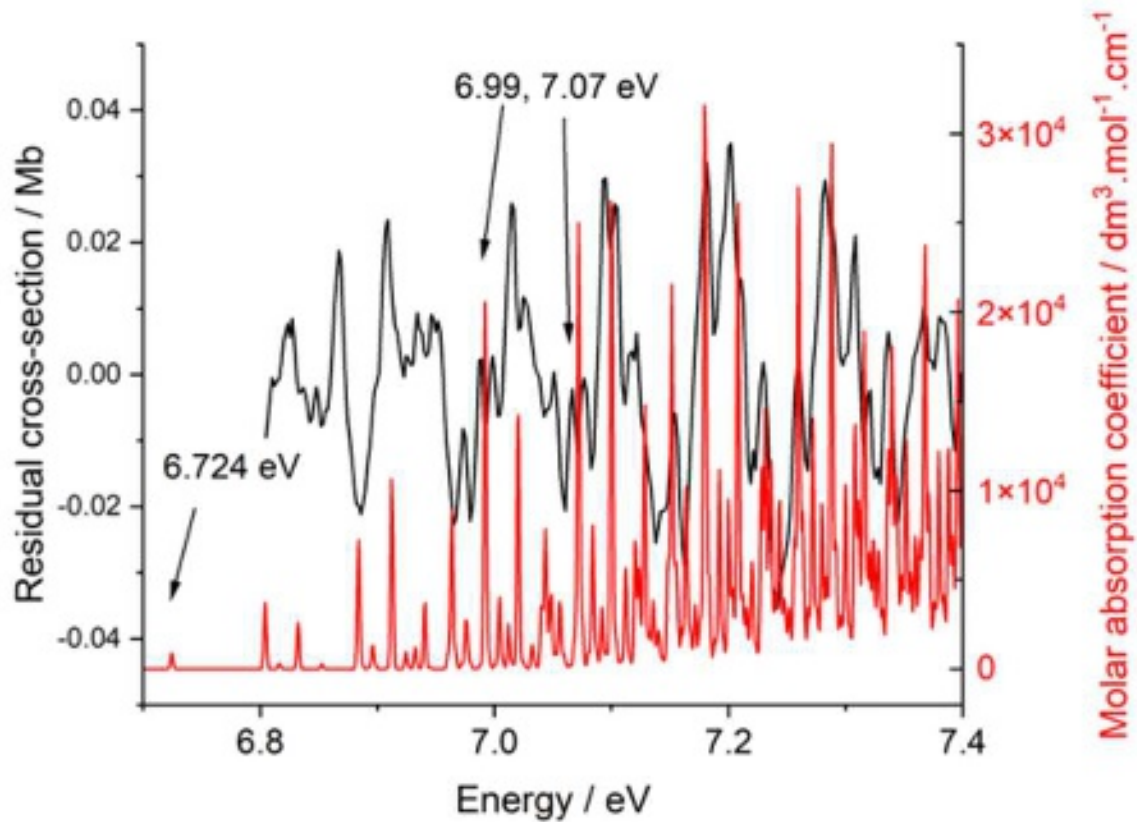
Palmer et al Figure 5



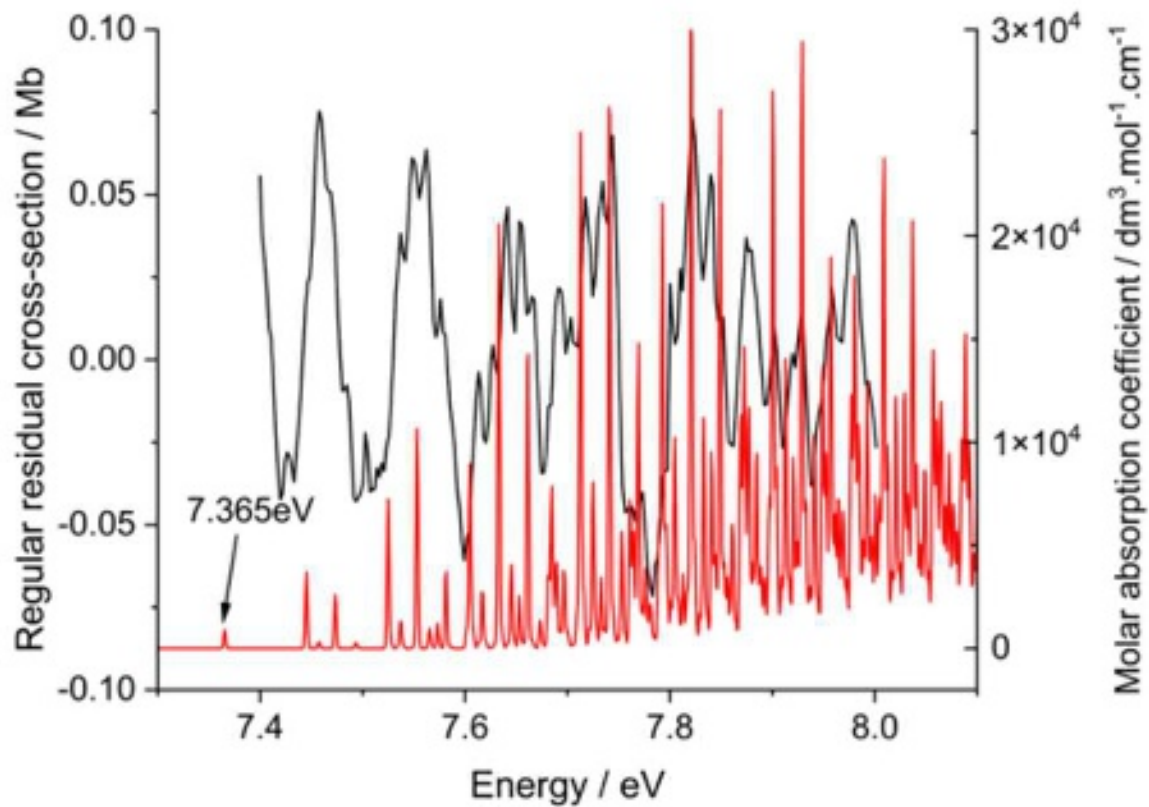
Palmer et al Figure 6



Palmer et al Figure 7



Palmer et al Figure 8



Palmer et al Figure 9

