

RESEARCH ARTICLE | JULY 14 2025

The singlet excited states of fulvene and of its 6,6-dimethyl derivative: A combined study of their energy levels by absorption spectroscopy, configuration interaction, and density functional calculations

Michael H. Palmer ; Søren Vrønning Hoffmann ; Nykola C. Jones  ; Marcello Coreno ; Monica de Simone ; Cesare Grazioli ; R. Alan Aitken ; Iain L. J. Patterson 



J. Chem. Phys. 163, 024323 (2025)
<https://doi.org/10.1063/5.0278573>



Articles You May Be Interested In

Theoretical analysis of vibronic structure of absorption spectrum of fulvene

J. Chem. Phys. (April 1995)

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

J. Chem. Phys. (October 2022)

The low-lying electronic states of 4H-pyran-4-thione; a photoionization and vacuum ultraviolet absorption study, with interpretation by configuration interaction and density functional calculations for the ionic and singlet states

J. Chem. Phys. (January 2025)

The singlet excited states of fulvene and of its 6,6-dimethyl derivative: A combined study of their energy levels by absorption spectroscopy, configuration interaction, and density functional calculations

Cite as: *J. Chem. Phys.* **163**, 024323 (2025); doi: [10.1063/5.0278573](https://doi.org/10.1063/5.0278573)

Submitted: 30 April 2025 • Accepted: 19 June 2025 •

Published Online: 14 July 2025



View Online



Export Citation



CrossMark

Michael H. Palmer,¹ Søren Vrønning Hoffmann,^{2,a)} Nykola C. Jones,^{2,b)} Marcello Coreno,^{3,c)}
Monica de Simone,^{4,d)} Cesare Grazioli,^{4,e)} R. Alan Aitken,^{5,f)} and Iain L. J. Patterson^{5,g)}

AFFILIATIONS

¹School of Chemistry, University of Edinburgh, Joseph Black Building, David Brewster Road, Edinburgh EH9 3FJ, Scotland, United Kingdom

²ISA, Department of Physics and Astronomy, Aarhus University, Ny Munkegade 120, DK-8000 Aarhus C, Denmark

³ISM-CNR, Istituto di Struttura della Materia, LD2 Unit, 34149 Trieste, Italy

⁴IOM-CNR, Istituto Officina dei Materiali, Basovizza SS-14, Km 163.5, 34149 Trieste, Italy

⁵School of Chemistry, University of St Andrews, North Haugh, St Andrews, Fife KY16 9ST, Scotland, United Kingdom

^{a)}Electronic mail: vronning@phys.au.dk

^{b)}Author to whom correspondence should be addressed: nykj@phys.au.dk

^{c)}Electronic mail: marcello.coreno@cnr.it

^{d)}Electronic mail: desimone@iom.cnr.it

^{e)}Electronic mail: grazioli@iom.cnr.it

^{f)}Electronic mail: raa@st-andrews.ac.uk

^{g)}Electronic mail: iljp@st-andrews.ac.uk

ABSTRACT

The ultraviolet and vacuum ultraviolet (VUV) photo absorption spectra of fulvene were reconsidered by a combination of configuration interaction and density functional methods and extended to the newly acquired VUV photo absorption spectrum of the 6,6-dimethylfulvene derivative, where several Rydberg states have been identified. Singlet states of fulvene were studied using multi-root multi-reference configuration interaction with the H₂C unit either coplanar with, or perpendicular to the ring. In contrast to ethylene, the lowest states are coplanar. The vibrational structure of the lowest (¹B₂) excited states of fulvene is well reproduced by calculated values. The second singlet state of fulvene, previously assigned as ¹A₁ on the basis of intensity, is incompatible with the calculated planar ¹A₁ state, which itself is a saddle point. This state shows significant quartic character on bending, and the best interpretation of the observed UV band of fulvene is of a bent form. The UV spectral state with low onset intensity is probably a ¹B₁ state of C_s symmetry. Theoretical Rydberg states were determined for fulvene; the closest fit to the two known Rydberg states is to the 3p and 4p states (¹B₁). Comparison of the separation of the ²A₂ and ²B₁ states in the photoelectron spectra of the two compounds, with the threshold photoelectron spectrum of fulvene, shows that the ²B₁ state vibrational structure is largely lost for both molecules. A reconsideration of the interaction between the X²A₂ and A²B₁ ionic states has led to the identification of the ⁴A₂ quartic state of fulvene.

© 2025 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution-NonCommercial-NoDerivs 4.0 International (CC BY-NC-ND) license (<https://creativecommons.org/licenses/by-nc-nd/4.0/>). <https://doi.org/10.1063/5.0278573>

I. INTRODUCTION

Recently we reported¹ a new synchrotron-based photoelectron spectrum (PES) of 6,6-dimethylfulvene (II) and performed high level theoretical analyses of it and that of its parent compound fulvene (I), as shown in Fig. 1. These compounds are alternatively known as pentafulvenes² and are among the first known colored hydrocarbons;^{2,3} an absorption maximum at 360 nm gives rise to the yellow color of II.⁴ The PES study of II established the sequence of the most intense ionic states¹ and analyzed the observed vibrational structure on the two lowest ionization energies (IEs). These were found to be 8.050 (X^2A_2) and 8.738 eV (A^2B_1) and contrast with the previous PES for I,⁵ which gave the lowest IE at 8.55 eV, with shoulders at 8.36 and 8.71 eV. For both compounds, the second IE showed only four broad vibrational peaks over a total width close to 0.6 eV, whereas the X^2A_2 state showed many more vibrations over the same energy range; the contrast is demonstrated by Figs. 3 and 4 of Ref. 1. Our vibrational calculations did not indicate differences in vibrational structure. The A^2B_1 state is degraded by the presence of the lower energy ionic state; this is a subject that we have discussed numerous times previously and will be expanded on below. In this paper, we use electron volts (eV) and convert wavelength and other units in the literature, but for convenience in comparisons, literature units are duplicated in the Introduction.

Heilbronner *et al.*⁵ regarded fulvene as a *cis*-butadiene, weakly perturbed by the exocyclic C=CH₂ group. Their perturbation approach for the interaction used the known IE for ethylene (10.51 eV); values for *cis*-butadiene were based on those for *trans*-butadiene (9.06 and 11.47 eV). These were then correlated with similar calculations on benzene and 3,4-dimethylenecyclobutene.⁶ The predicted IEs for fulvene were 8.8 ($1a_2^{-1}$), 9.5 ($2b_1^{-1}$), and 12.4 eV ($1b_1^{-1}$), close to their observed IEs at 8.55, 9.54, and 12.8 eV, respectively. An intervening σ -IE, not included in the calculations, occurs at 11.5 eV ($7b_2^{-1}$). This sequence, by symmetry, remains correct to the present day.^{1,7}

A. The absorption spectra of fulvene and 6,6-dimethylfulvene

Fulvene is also isomeric with benzvalene and Dewar benzene, and comparisons between the electronic states of all these benzene

isomers have long been made.^{8–11} Furthermore, these isomers interconvert at specific irradiation frequencies;^{12–19} since our primary interest lies in the excited state sequence of energy levels and static properties for the isolated molecules of I and II, these interconversions lie outside the scope of this study; a summary is given in SM1 of the supplementary material.

The fulvene UV onset lies at 2.441 eV (19 685 cm⁻¹) in the gas phase with a very weak vibrational structure;⁸ in contrast, the intense UV maximum at 5.276 eV (235 nm),⁸ after a weak onset, shows considerable fine structure with two vibrational progressions; the stronger one has 20 members, and a weaker one has 6 members, but both have the same spacing of 495 cm⁻¹. The high intensity of the second band led to assignment as a 1A_1 excited state.⁴ A further band at 6.199 eV (200 nm) with a sharp maximum at 6.147 eV (201.7 nm) is of comparable intensity to the 235 nm band, while a further band lies close to 6.965 eV (178 nm).⁴ Both the 200 and 170 nm bands disappear under high pressures of helium, a characteristic of Rydberg states. Assignments as 3s (6.146 eV, 200 nm) and 4s states (6.965 eV, 178 nm) were based on an IE of 8.55 eV.⁵ However, the two lowest IEs for fulvene are 8.398 eV (X^2A_2),²⁰ followed by 9.541 eV (A^2B_1).²⁰ Thus, the assignment^{4,9} of these 3s and 4s Rydberg assignments should be to the 2A_2 ionic state, which is optically forbidden.⁴ Later, these states were re-assigned to 3p and 4p, based on X^2A_2 , by Robin,³ while a further suggestion of 3d (2A_2) has been suggested.¹¹

The Rydberg equation, expressed as $IE - E = R/(n - \delta)^2$, where E is the Rydberg state energy, n is the principal quantum number, and δ is the quantum defect, has well-established values for $\delta = 0.7–1.0$ for ns , $0.3–0.6$ for np , and $0.1–0.0$ for both nd and nf . The spectral data only evaluates $(n - \delta)$, necessitating the choice of appropriate n and δ values. The 6.965 eV band leads to $(n - \delta) = 3.082$; using $n = 4$ gives $\delta = 0.928$, which suggests assignment to the optically forbidden 4s-Rydberg state¹¹ or a 5d-state or 5f-state. If the reference IE is chosen as A^2B_1 , then $(n - \delta) = 2.299$ would be acceptable for a 3s state based on IE_2 . These assignments are discussed further below. We will use our present calculations to analyze the experimental ultraviolet (UV) spectra.

The threshold photoelectron spectrum (TPES) of fulvene was recently reported from a photoelectron photo-ion coincidence (PEPICO) study of the isomerization of 1,5-hexadiyne.²⁰ The authors have kindly provided us with this TPES for the energy range 8.3–10.2 eV. Our vibrational structures for the two lowest IE of both I and II are remarkably like this TPES, showing that both are X^2A_2 states.¹ This will assist us in the identification of Rydberg states in fulvene itself.²⁰

There is no wide scan vacuum ultraviolet (VUV) absorption study of fulvene, but we report the spectrum for its 6,6-dimethyl-derivative below. The most comprehensive study of the VUV region for fulvene is an electron energy loss (EEL) electron impact study; two residual energies of 20 and 3.5 eV enhance the singlet (including Rydberg states) relative to triplet states, respectively.²¹ The two lowest singlets were at 3.444 and 5.276 eV, while triplets were at 2.46 and 3.10 eV; these states were assigned to 1,3B_2 and 1,3A_1 states. In addition, these spectra show the Rydberg states near 6.61 and 7.15 eV, evident in the optical spectra, but at significantly lower resolution. These studies were supported by multi-configurational

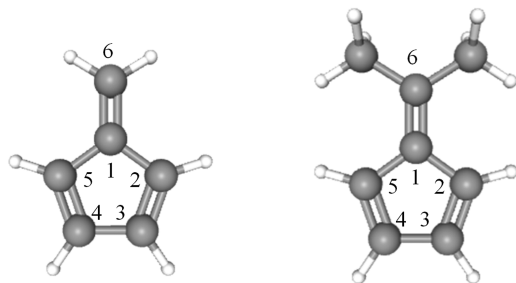


FIG. 1. Structure and labeling of fulvene (I, left) and 6,6-dimethylfulvene (II, right) structures.

second order perturbation calculations (CASSCF/CASPT2) on the singlet and triplet valence states above.

Many of the ground state orbitals of fulvene have been reported.¹⁷ The highest occupied molecular orbital (HOMO) is predominantly localized in the *cis*-butadiene moiety, which is similar to the HOMO of cyclopentadiene,⁵ where the first ionic state is at 8.58 eV (²B₁).²⁴ EEL spectra of cyclopentadiene²² show a feature at 6.3 eV, reminiscent of the 6.52 eV feature in fulvene; this was previously assigned to two 3p-Rydberg type transitions.²³

Among the seminal theoretical approaches to the energy levels of fulvene, one of the earliest is the variable electronegativity self-consistent field (VESCF) method,²⁵ which gave a realistic account of the two lowest excited state energies. Other semi-empirical and *ab initio* multi-configuration self-consistent-field (MCSCF) calculations using a 4-31G basis set lead to the conclusion²⁶ that the observed ³B₂ triplet state is planar. The stabilization with respect to a structure twisted by 90° around the exocyclic C=C bond amounted to 0.62 eV. As expected, there was a minor change in excitation energy between the lowest singlet and triplet states for the unsubstituted and 6,6-dimethyl compounds.²⁶

B. Molecular structures of fulvene and 6,6-dimethylfulvene

This section is necessary since we will be determining equilibrium structures. Microwave spectroscopy (MW) of seven isotopomers of fulvene^{27–29} has given the substitution structure and the conclusion that the molecule has an extremely low dipole moment [0.4236(13) D]. The final structure that emerges for fulvene is essentially three weakly coupled ethylenic entities with bond lengths C₁–C₂ = 1.470 Å, C₂=C₃ = 1.355 Å, C₃–C₄ = 1.476 Å, and C₁=C₆ = 1.3485 Å; the C–H bond distances and ring angles are close to expected values.

An early electron diffraction (ED) study of 6,6-dimethylfulvene also showed the classical alternating double bonded planar structure;⁷ a slightly distorted but eclipsed conformation gave a best fit to the radial distribution curve.³⁰ An x-ray crystal structure³¹ for the 6,6-dimethylfulvene at –50 °C also suggests that the methyl substitution has no significant effect on the skeletal dimensions³⁰ and that all these results are internally consistent. Unusually for that time, the x-ray structure gave clear indications of the methyl group H-atom positions, which implicitly denies free rotation.

The instability of fulvene makes it essential for the synthesis and spectra to be obtained in the same laboratory, a facility not available to us. In this paper, we will utilize earlier spectroscopic results for fulvene^{4,8,9} and combine them with new theoretical studies that offer a more rigorous interpretation of the singlet states, with a concentration on their vibrational structure. The much more stable 6,6-dimethyl derivative enables us to report an experimental and theoretical study of its singlet and triplet states in the VUV region up to ~11 eV. The methyl group substitution is not expected to have a major effect on the spectroscopic sequence of low-lying valence or Rydberg states. In addition, these calculations will address the problems of over interpretation of the valence vs Rydberg state assignments by previous groups.^{3,4,8,9}

II. METHODS

A. Synthesis

The 6,6-dimethylfulvene sample, CAS registry number 2175-91-9, was prepared by standard methods,³² and the purity was checked by ¹H and ¹³C nuclear magnetic resonance.

B. Theoretical methods

We have sought both vertical and adiabatic singlet and triplet state energies. The vertical studies used both the symmetry-adapted coupled-cluster configuration interaction (SAC-CI), part of the Gaussian-16 suite (G-16),³³ and the multi-reference multi-root singles and doubles CI (MRD-CI), part of GAMESS-UK.³⁴ The adiabatic studies used the time-dependent density functional method (TDDFT), a single excitation procedure, which is also part of G-16. The density functional used was the Becke 3-parameter hybrid functional (B3LYP),³⁵ modified by a long-range correction term, using the Coulomb-attenuating method (CAM-B3LYP).³⁶ The non-Coulomb part of exchange functionals typically dies off too rapidly, making them unsuitable for studying electron excitations to higher excited states.

Most recent basis sets have important levels of polarization functions (PFs) to offer universal applicability for valence, Rydberg, and charge-transfer states. These PFs, often including f- and g-functions on C-atoms, for example, contribute little to the bonding. Several basis sets were used, all being triple-zeta with polarization (TZVP) and strictly valence basis sets. These included the Pople style 6-311(d,p)³⁷ for the SAC-CI study, TZVP³⁸ for the MRD-CI study, and the Ahlrichs type Def2-TZVP^{39,40} for the TDDFT study. Rydberg states were studied by adding very diffuse Gaussian functions, with exponents 0.021, 0.0080, and 0.0026, to the ring C₆-atom (Fig. 1), using the Def2-TZVP basis set. We use the 5d and 7f options for the *ns* and *nf* polarization functions, respectively, to remove the implicit s-functions, which would arise from the 6d and 10f cases. When using G-16, Rydberg functions must be mounted on atomic centers, and their site is listed first in the geometric specification; the standard structural numbering in Fig. 1 was rearranged in the Rydberg state calculations with C₆ relabeled as C₁.

The X¹A₁ state of fulvene has doubly occupied molecular orbitals (DOMOs) filled up to 7a₁², 2b₁², 5b₂², and 1a₂²; the highest occupied orbitals are 1a₂ (HOMO) and 2b₁ (HOMO-1), while 1b₁ is HOMO-3. Even when Rydberg functions are present, the lowest unoccupied orbitals (LUMOs) are 3b₁^{*} and 8a₁^{*}. The 3s, 3p, and 3d lowest Rydberg orbitals follow next in the ascending sequence, with 4s and 5s, etc., lying higher in the virtual orbital manifold. When fulvene is in its twisted form, where the H₂C group is perpendicular to the ring structure, the conformation is still C_{2v} symmetry, but the occupied orbitals are up to 7a₁², 3b₁², 4b₂², and 1a₂². The orbital occupancy differs since the antisymmetric combination of H₂C MOs leads to the exchange of a b₂ for a b₁ orbital relative to the all-planar ground state. Thus, the orbital occupancy of the perpendicular form is a doubly excited state of the coplanar form.

C. Vacuum ultraviolet absorption spectroscopy of 6,6-dimethylfulvene

The VUV photo absorption spectrum of 6,6-dimethylfulvene was measured on the AU-UV beamline of the ASTRID2 synchrotron

(Aarhus, Denmark), using methods described previously.⁴¹ Spectra were measured in the gaseous phase at 25 °C. The full energy range, 3.647 eV (340 nm) to 10.735 eV (115.5 nm), was covered by 2088 data points. The photon resolution of 0.08 nm over the operational range of the grating corresponds to 7, 3, and 1 meV at the high, mid, and low energy ranges, respectively. The full spectrum, shown in Fig. 2, has been corrected for ~12% water contamination by subtraction of features due to the presence of water and scaling of the spectral cross section to compensate for a lower real pressure of the sample. There is no comparable VUV absorption spectrum for fulvene, but bands 1–4 reported by Brown *et al.*⁴ are reproduced (in blue) in Fig. 2 for comparison. It is immediately apparent that the vibrational structure shown by the dimethyl-derivative is markedly less than that for fulvene itself; this is attributed to the presence of several conformers that occur for the dimethyl groups.

D. Near ultraviolet spectroscopy of 6,6-dimethylfulvene

A Thermo Scientific Evolution 300 benchtop spectrometer was used for the 6,6-dimethylfulvene study, with the following scanning parameters: a quartz cell path length of 100 mm, a bandwidth of 0.5 nm, a step size of 0.5 nm, and a scan speed of 60 nm/min; the data shown, inset in Fig. 2, were obtained at 25 °C and are the mean of several scans. The onset (S_1) of absorption is 2.455 eV, which lies at a longer wavelength (lower energy) than fulvene, with a peak maximum of 3.507 eV (353.5 nm). In this UV absorption study, the common energy regions between the synchrotron and the benchtop spectrometer are the same. Domaille *et al.*⁸ have found that fulvene itself shows considerable vibrational fine structure up to 500 nm; we did not observe this for 6,6-dimethylfulvene under our measurement

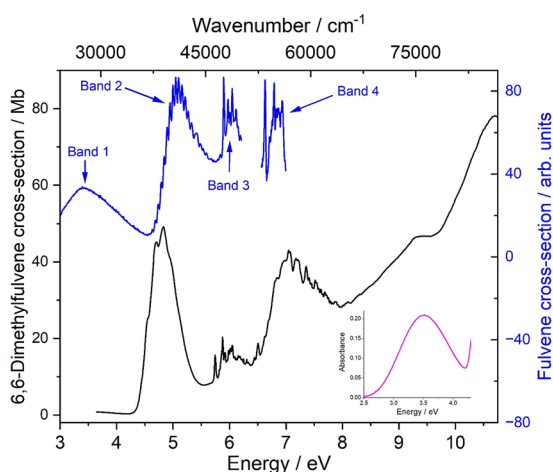


FIG. 2. Synchrotron-based VUV spectrum of 6,6-dimethylfulvene (in black) together with the UV spectrum taken using a benchtop spectrometer inset in magenta; the labeled bands observed by Brown *et al.*⁴ for fulvene are superimposed in blue.

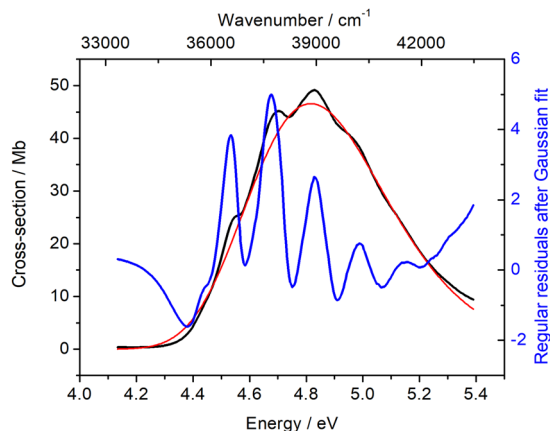


FIG. 3. Residual spectrum after subtraction of a broad Gaussian function exposes the underlying major vibrations.

conditions, which gave peak maxima and intensities of 4.509 eV ($37\,174\text{ cm}^{-1}$, 269 nm, $\epsilon = 15\,948$) and 3.942 eV ($28\,169\text{ cm}^{-1}$, 355 nm, $\epsilon = 256$), both in acetonitrile as solvent.

Unresolved structure is present between 4.5 and 5.5 eV for 6,6-dimethylfulvene; we deconvoluted this band by fitting the data points to a Gaussian function, followed by plotting the regular residuals, as shown in Fig. 3. The original curve (in black) has the best Gaussian fit (red line), while the regular residuals are in blue. The separation of the three main peaks in Fig. 3 is $1202 \pm 24\text{ cm}^{-1}$. A similar procedure was performed for the whole synchrotron-based VUV spectrum, as shown in SM2 of the [supplementary material](#).

III. RESULTS AND DISCUSSION

A. The fulvene X^1A_1 and excited state equilibrium structures

Brown *et al.*^{27–29} performed Fourier-transform microwave spectral (FTMW) analysis for several isotopomers of the X^1A_1 state of fulvene. The derived rotational constants (A, B, C) for the abundant C/H isotopes gave A: 8189.505, B: 3802.781, and C: 2596.44 MHz.²⁸ Our results at the CAM-B3LYP level with the aug-cc-pVTZ basis set, to the same level of accuracy, are A: 8281.426, B: 3860.476, and C: 2630.012 MHz; the differences (calc – expt.) are 92, 58, and 34 Hz, and very acceptable. Substitution and equilibrium structures are expected to be similar but non-identical owing to the lack of vibrational averaging for the latter. The FTMW study led to the identification of several ^{13}C isotopic species and the derivation of the complete molecular structure. The molecule has a small, but accurately determined, dipole moment of 0.4236(13) D.²⁸ Our structures for several singlet and triplet valence states are not central to the main investigation, but some are relegated to SM3 of the [supplementary material](#).

B. Valence states in the UV and VUV spectra for fulvene

1. The theoretical valence states

Our molecular framework is either planar or perpendicular for the H_2C unit relative to the ring plane; both are C_{2v} symmetry. The SAC-CI and MRD-CI methods are restricted to vertical excitation at the X^1A_1 ground state structure. The MRD-CI results for the low-lying states are shown in Table I for the singlet states under C_{2v} symmetry and discussed below. Tables of the SAC-CI singlet and triplet state results are given in SM4 of the supplementary material. Higher singlet states obtained using the MRD-CI method are given in SM5 of the supplementary material. The energy levels shown in Fig. 4 were obtained using the MRD-CI suite together with a cc-pVTZ basis set. In each geometry, the reference configurations include all configuration state functions (CSF) printed by the suite for each state; thus, all CSF with a density of ≥ 0.002 electrons are included in the reference configurations. No energy scaling has been included in our theoretical excitation energies. Two singlet valence states, S_1 and S_2 , have been detected in previous EEL studies, at 3.35(1) and 4.9(5) eV.^{21,26} The UV and VUV bands 3 and 4, designated by Brown *et al.*,⁴ have been combined with the MRD-CI results in Fig. 4. The coplanar excited states show two $\pi\pi^*$ states initially, with leading terms $1a_23b_1^*$ (1B_2) and the 1A_1 symmetric combination ($2b_13b_1^* + 1a_22a_2^*$); the antisymmetric third $\pi\pi^*$ state, also of 1A_1 symmetry, ($1a_22a_2^* - 2b_13b_1^*$), lies substantially higher in energy, with several $\sigma\pi^*$ and $\pi\sigma^*$ states in between.

The lowest state in the situation where the CH_2 unit is perpendicular to the ring shows a low energy, optically inactive 1A_2 state close to 4 eV in Fig. 4. The correlation favors the entirely coplanar structure. We note that the nuclear–nuclear repulsion energy taken alone favors the perpendicular form since the H_6/H_6 vs H_2/H_5 distance is increased over that for the coplanar form. However, the electron–nuclear attraction and electron–electron repulsion overall lead to the total energies favoring the planar situation. This is the reverse of that observed for ethylene in its lowest excited valence state.

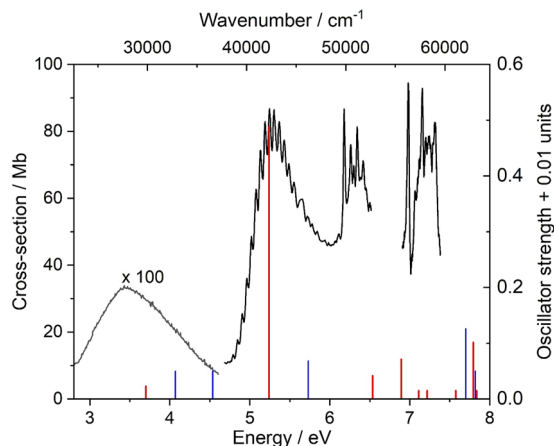


FIG. 4. Combined UV and VUV bands 1–4 of Brown *et al.* (shown in black),⁴ with the MRD-CI results. Those assuming co-planarity of the system in C_{2v} are in red; those assuming the H_2C unit is perpendicular are shown in blue. The computed oscillator strengths (dipole length operator) have been increased by 0.01 units to allow very weak excited states to appear.

2. Theoretical studies of the singlet and triplet valence states in the planar configurations

The TDDFT method, a single-excitation configuration interaction (CIS) procedure in G-16, gives results compatible with our vibrational analysis, as shown below.

We have determined the equilibrium structures of the singlet states of fulvene by TDDFT calculations, using the cc-pVTZ basis set, with the CAM-B3LYP functional; initially, we assume the states are planar under C_{2v} symmetry. In the second stage, we allow the 6- CH_2 unit to rotate out-of-plane. In this method, the two lowest C_{2v} valence states have energy minima at 2.692 and 5.107 eV and are the $\pi\pi^*$ states above, while the third at 5.437 eV is a 1B_1 ($\sigma\pi^*$) state ($8a_13b_1^* - 7a_13b_1^*$). Both the 1A_1 states have high oscillator

TABLE I. Fulvene singly excited state extrapolated energies, with Davidson corrections, in C_{2v} symmetry, when all atoms are coplanar (columns 1–3) and the CH_2 group is perpendicular (columns 4–6). Doubly excited states have been excluded on the basis that they will not contribute significantly to the absorption spectra.

Coplanar system in C_{2v}			CH_2 unit perpendicular but also in C_{2v}		
Energy (eV)	Symmetry	Leading config.	Energy (eV)	Symmetry	Leading config.
3.701	1B_2	$1a_23b_1^*$	3.053	1A_2	$3b_15b_2^*$
5.239	1A_1	$2b_13b_1^* + 1a_22a_2^*$	4.067	1B_1	$1a_25b_2^*$
7.111	1A_2	$5b_23b_1^*$	7.069	1A_2	$2b_15b_2^*$
7.216	1B_1	$7a_13b_1^*$	7.701	1B_1	$3b_110a_1^*$
7.574	1A_2	$1a_28,9a_1^*$	8.507	1B_2	$7a_15b_2^*$
8.130	1B_1	$1a_26b_2^*$	9.378	1B_2	$6a_15b_2^*$
8.222	1B_1	$6a_13b_1^*$	9.613	1A_1	$3b_14b_1^*$
8.413	1A_2	$4b_23b_1^*$	9.737	1A_1	$3b_25b_2^*$
8.634	1A_1	$1a_22a_2^* - 2b_13b_1^*$	9.763	1B_1	$3b_19a_1^*$

strengths [$f(r)$ 0.4384 and 0.2267, respectively], but the 1B_2 and 1B_1 states are very weak.

The lowest state, 1B_2 , is clearly planar, with a sinusoidal energy surface when bending occurs, as shown in SM6 of the [supplementary material](#). The lowest calculated 1A_1 state shows a negative vibration frequency under C_{2v} symmetry, indicating a saddle point. A plot of the energy surface, when the 6-CH₂ unit undergoes symmetric out-of-plane bending, reduces the overall molecular symmetry to C_s , while anti-symmetric out-of-plane bending generates C_2 symmetry. The 1A_1 (C_{2v}) state shows that the oscillator strength is retained when the ring partially folds along the C_6C_1 axis. The smooth curve shows an apparent single minimum at the planar state, as in SM7 of the [supplementary material](#). However, the data points with energy $E(n)$ in wavenumbers (cm^{-1}) from the ground state give a close fit of the potential using $E(n) = A \cdot x^2 + B \cdot x^4$, where x is the angle of folding; this gives $A = -4.51$ and $B = 0.42$. While the local maximum predicted by the quartic term is not apparent, owing to its shallow value, there is a substantial level of quartic character. A further feature that denies the earlier 1A_1 symmetry assignment⁴ to the second excited state of fulvene is that the calculated C_{2v} electronic state has a high 0–0 band, in contrast to the observed spectrum; both are shown in SM8 of the [supplementary material](#).

3. Singlet states of fulvene with non-planar upper states

The Heilbronner *et al.*⁵ analysis of the fulvene PES considered it to be a weakly coupled linear combination of the semi-localized π -orbitals of *cis*-butadiene with an ethylene moiety. This allowed the use of the known IE from the PES of this pair of molecules. The $C_1=C_6$ π -bond of fulvene can perform in the same way, leading to perpendicular excited states while retaining C_{2v} symmetry. In addition, there is the possibility of bending along the C_6-C_1 axis. These bent states have low symmetry, and it is most convenient to describe the potential energy when at the planar C_{2v} state. The higher occupied MOs of the 1B_1 state ($3b_18a_1^*$), shown in Fig. 5, are analogous to the twisting of ethylene, discussed in detail previously.^{42–45} The three lowest states where the 6-CH₂ is perpendicular have symmetries 1A_2 , 1B_1 , and 1A_2 .

A feature for fulvene that contrasts with that for ethylene is that the high oscillator strength [$f(r)$] of the 1A_1 state decreases when the 6-CH₂ group twists from the coplanar with the ring, perpendicular.

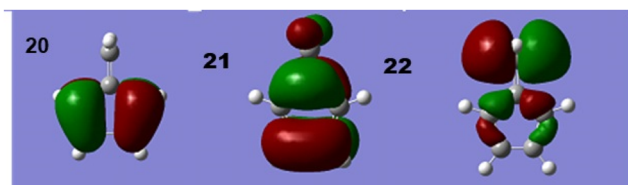


FIG. 5. Higher occupied orbitals of the perpendicular states, exemplified by the 1B_1 ($3b_18a_1^*$, 7.510 eV) state; see the text.

C. Comparison of the theoretical Rydberg state manifold with the experimental VUV spectrum of fulvene

As mentioned in Sec. II, the Rydberg state virtual molecular orbitals (VMOs) have energies immediately above two valence state orbitals in the unoccupied orbital sequence, irrespective of being ns , np , nd , or nf in nature. We have calculated the positions of the lowest three Rydberg state equilibrium structures for each of these types. We note that all three Rydberg states, for example, 3s, 4s, and 5s, having the same symmetry, are simultaneously optimized, since each is expected to have the same structure. These calculations were performed with the TDDFT module within the G-16 suite. The basis set used was Def2-TZVP with the CAM-B3LYP density functional. However, this module defines the adiabatic ionization of the ionic state relative to the X^1A_1 state at the excited state structure; this contrasts with spectroscopy, where both the upper and lower states are at their respective minima. We present corrected values in Table II while noting that there is a close correlation between the uncorrected and corrected AIE, with the corrected values being on average 3.1% higher; the correlation goes through the origin since the intercept is smaller than its standard error.

The lowest Rydberg states for the ns , np , nd , and nf states are 5.48 (1A_2), 5.95 (1B_1), 6.72 (1B_2), and 7.06 (1A_2), respectively. The lowest Rydberg state of 1B_1 symmetry is higher by 0.47 eV than that of the lowest 1A_2 state. Brown *et al.*⁴ give the lowest peak of their band 3 of fulvene at 6.15 eV, with band 4 being 0.82 eV higher at 6.97 eV.

The closest fit for these bands with our results has 3p (1B_1 calculated at 5.95 eV) and 4p (1B_1 calculated at 6.80 eV) respectively; the next closest fit for band 4 is with the 3d state (1B_2 , calculated at 6.72 eV). Harman *et al.*⁹ suggested 3s and 4s Rydberg states of 1B_1 symmetry, which they denoted as ($\pi_2, 3s$) and ($\pi_2, 4s$). Robin³ proposed the assignment ($\pi_3, 3p$) and ($\pi_3, 4p$); this assignment resulted in a quantum defect of 0.51, consistent with a 3p assignment. It also agrees with the calculated energies of Galasso (6.43 eV for 3px and 6.59 eV for 3py, both having similar oscillator strengths).¹¹ The first Rydberg band is now relatively undisputed.

In Fig. 6, we have plotted the TPES²⁰ vs bands 3 and 4 by Brown *et al.*,⁴ with shifts to lower energy by 2.2386 eV for the TPES and

TABLE II. Calculated Rydberg state vertical excitation energies of fulvene. An MRD-Cl study, using a triple-zeta valence basis set Def2-TZVP, augmented by Rydberg diffuse functions placed on the C_1 carbon atom using Fig. 1. Our previously calculated ionization energies¹ used the 6-311G(d,p) basis set with the CAM-B3LYP density functional.

State symmetry	Rydberg state type	Principal quantum number (n)		
		3	4	5
1A_2	ns	5.4848	6.6310	7.0597
1B_1	np	5.9529	6.7985	7.4073
1B_2	nd	6.7152	7.0793	7.6684
1A_1	nf	7.0556	7.2517	7.4649
1B_1	ns	6.5142	7.6868	8.0333

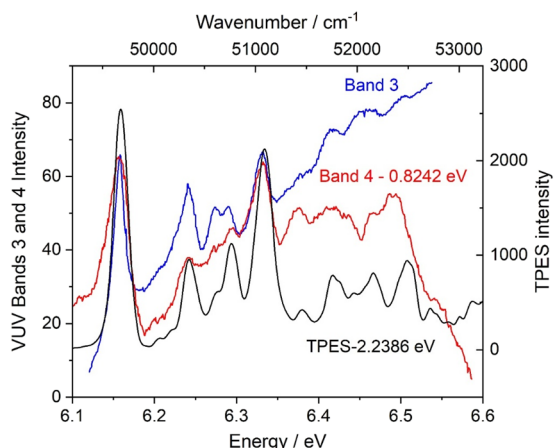


FIG. 6. Super-position of the Brown *et al.*⁴ optical spectra bands 3 and 4 with the TPES of the X^2A_2 state, with shifts of the energy scale by the amounts shown to bring coincidence. Every peak in the TPES spectrum is present in the two VUV bands 3 and 4. This confirms that those bands are Rydberg in nature, rather than the 1B_2 and 1A_1 valence transitions, according to Brown *et al.*⁴

0.8242 eV for band 4, which allows super-position of these two spectra with the onset of band 3. It is immediately apparent that the vibrational peak profiles of the three spectra shown are in almost exact energy agreement. This confirms that bands 3 and 4 of Brown *et al.*⁴ are Rydberg in nature. Whether the vibrational patterns for these bands conform to those for either of the two lowest IE, X^2A_2 or the A^2B_1 state, is discussed below. Neither the MRD-CI nor SAC-CI calculations predict a valence state near 6.3 eV, and this is consistent with its assignment above as a Rydberg state. On the other hand, these calculations do suggest that a valence state lies under the Rydberg state envelope of Band 4, close to 7 eV. Some strong bands are predicted between 8 and 9 eV for fulvene, but the spectral data are not yet available. The VUV spectrum of the 6,6-dimethylfulvene molecule will contribute to this subject below.

D. The vibrational structure of the excited states of fulvene

The symmetric vibrational frequencies determined for the X^1A_1 , X^1B_2 , and A^1A_1 excited states are shown in Table III; the full sets of fundamentals are shown in SM9 of the supplementary material. All were calculated at the CAM-B3LYP level with the Def2-TZVP basis set. The normal modes are 1–11 (a_1), 12–15 (a_2), 16–20 (b_1), and 21–30 (b_2).

1. The 1B_2 state

The lowest excited state in the fulvene UV absorption is very weak and ranges from 19 685 to 36 000 cm^{-1} , with oscillator strength $f(r) = 0.008$.^{4,8} The principal structure consists of a 653 cm^{-1} mode, with other modes superimposed. An expanded trace of this visible spectrum, with our 1B_2 state onset, is shown in Fig. 7. The theoretical spectrum has been linearly shifted to lower energy by 1975 cm^{-1} , and all frequencies shown are unscaled. The match between theory and experiment shows that the experimental frequencies are slightly smaller than those in the calculated spectrum. We present

TABLE III. Ground and excited state vibration frequencies for fulvene, limited to the a_1 vibrations. The full set is shown in SM9 of the supplementary material.

Mode	Ascending sequence	Symmetry	Frequency (cm^{-1})		
			X^1A_1	1A_1	1B_2
1	30	a_1	3253	3257	3265
2	27	a_1	3230	3237	3231
3	25	a_1	3160	3158	3196
4	24	a_1	1748	1541	1624
5	22	a_1	1573	1454	1524
6	21	a_1	1469	1402	1454
7	20	a_1	1390	1237	1313
8	16	a_1	1114	1096	1141
9	15	a_1	1011	1028	1057
10	10	a_1	921	911	988
11	5	a_1	687	659	686

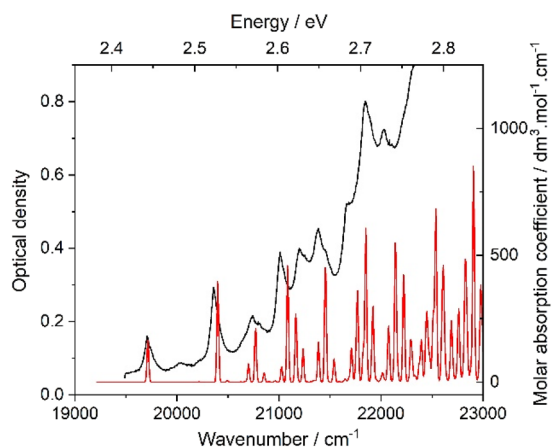


FIG. 7. Onset of the visible spectrum of fulvene with the (unscaled) calculated vibrational envelope for the 1B_2 state. This was determined with the CAM-B3LYP functional and the cc-pVTZ basis set by use of the TDDFT suite.

the full set of theoretical vibrations for the spectral onset in Table IV; this shows the pattern of the fundamentals and even-quanta of non-symmetric modes that occur. As noted by Domaille *et al.*,⁸ congestion of the spectrum sets in rapidly at wavelengths shorter than the range shown and is evidenced in SM10 of the supplementary material. The principal fundamentals of a_1 symmetry determined in the calculations are the modes with harmonic frequencies 686, 988, 1057, 1141, 1312, 1524, and 1623 cm^{-1} ; the lowest at 686 cm^{-1} is correlated with the experimental 653 cm^{-1} mode, with the harmonic frequency higher than the experiment, as expected. In addition, several non-symmetric modes occur with even quanta, especially the a_2 symmetry vibration frequency of 390 cm^{-1} . Full onsets calculated for the 1A_1 and 1B_1 singlet states are shown in SM11 of the supplementary material.

TABLE IV. 1B_2 state principal vibrations of fulvene. Theoretical energy of the 0–0 transition: 21 713 cm^{-1} (2.692 eV). Intensities are molar absorption coefficients in $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$.

Frequency (cm^{-1})	Intensity	Assignment	Frequency (cm^{-1})	Intensity	Assignment
0	164	0–0	1373	459	11^2
686	397	11^1	1454	266	6^1
782	6	14^2	1468	9	$11^1; 15^2$
955	2	19^2	1524	132	5^1
988	72	10^1	1602	2	$11^1; 14^1; 15^1$
1057	187	9^1	1624	4	4^1
1141	38	8^1	1641	5	$11^1; 19^2$
1193	2	$11^1; 20^2$	1675	116	$10^1; 11^1$
1250	4	18^2	1743	450	$9^1; 11^1$
1313	53	7^1			

2. The previously assigned UV band of fulvene

The very weak onset at 4.79 eV leads to a strong peak maximum at 5.25 eV ($42\,363 \text{ cm}^{-1}$).⁸ There are two vibrational series; the stronger has at least 20 vibrational maxima, of which some 16 members were assigned. Many fewer members are apparent in the second series,⁸ and it was unclear whether this is a second fundamental or a hot band progression. Both the strong and the weak series⁸ appear to have the same vibration frequency of 495 cm^{-1} . These vibrations were correlated with the closest ground state vibration of 614 cm^{-1} (ν_{19}, b_1), with the implication⁸ that the state has lower symmetry, being either C_s or C_1 ; the lowest a_1 fundamental is ν_{11} , at 894 cm^{-1} .⁴ This contrasts with the previous assignment as a 1A_1 state in C_{2v} based on the high oscillator strength.⁸ In our experience, most high intensity 1A_1 states have high 0–0 bands, with declining intensity thereafter. A more probable solution is that the UV band is a distorted 1B_1 or 1B_2 state; these are often characterized by low onset intensity and peak maxima to significantly higher energy. The characteristics observed in the UV band of fulvene are shown in Fig. 8.

Our CAM-B3LYP calculations with the cc-pVTZ basis set under coplanar conditions, as above, lead to the second root of TDDFT calculations as a 1A_1 excited state, with two leading configurations, $0.69(2b_13b_1^*) + 0.15(1a_2, 2a_2^*)$, and high oscillator strength [$f(r)$]. However, it is a saddle point and, hence, has a double minimum, with the exocyclic H-atoms rotating out-of-plane in a symmetric manner; this is discussed below. A 1B_1 ($8a_1, 3b_1^*$) excited state, with an equilibrium structure only 0.189 eV higher in energy, shares the same upper state and has the lowest a_1 symmetry harmonic vibration of 573 cm^{-1} , rather higher than the observed 495 cm^{-1} , offering another interpretation, but its $f(r)$ is almost zero.

The overall second root of the TDDFT sequence of singly excited states in C_s symmetry is ${}^1A'$; it retains the high $f(r)$, with a' harmonic frequencies of 454 and 624 cm^{-1} . The former is too low since harmonic frequencies are expected to be too large when compared with the experiment. The appearance of the ${}^1A'$ spectrum is of a number of fairly evenly spaced lines, as in Fig. 8. However, no variations in linewidth generate the individual peaks close to the overall maximum and down the high energy side.

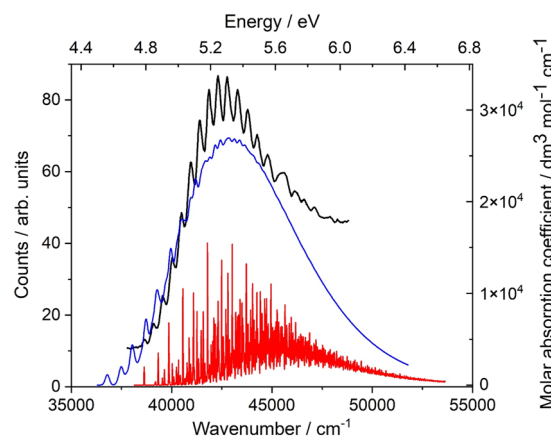


FIG. 8. UV band of fulvene after Brown *et al.*,⁴ with the 1B_1 state superimposed. The frequencies of the theoretical band are unscaled. Although the general oscillations are reproduced for the leading edge, we are unable to reproduce the peak maximum and trailing edge, owing to the density of states of higher vibrational levels.

The perpendicular form of fulvene shows the TDDFT second root of 1B_1 symmetry has two very close frequencies, 529 (a_2) and 552 cm^{-1} (b_1), but the oscillator strengths of all the low-lying perpendicular states are effectively zero, and this does not offer a solution to the experimental spectrum shown in Fig. 8. This contrasts with the situation in ethylene, as mentioned above.

E. The UV and VUV absorption of 6,6-dimethylfulvene

The spectrum of 6,6-dimethylfulvene in Fig. 2 shows similar fine structure to fulvene in the energy range 5.5–8.0 eV; this is best visualized through the subtraction of the underlying broad featureless cross section. Subtraction of a series of simple Gaussian functions from the VUV spectrum leads to the “residual spectrum” in Fig. 9. Further details are shown in SM2 of the [supplementary material](#).

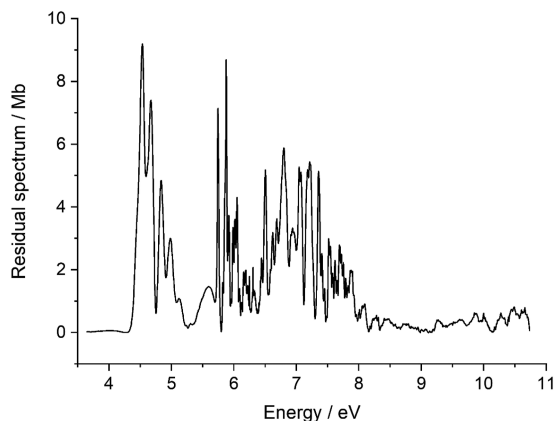


FIG. 9. VUV spectrum of 6,6-dimethylfulvene after subtraction of broad structures using Gaussian functions.

F. Analysis of the UV and VUV absorption of 6,6-dimethylfulvene

All modes are positive under planar C_{2v} symmetry for the X^1A_1 electronic state. Modes are labeled in decreasing sequences $a_1 < a_2 < b_1 < b_2$ and are $16a_1 + 8a_2 + 9b_1 + 15b_2$; their frequencies, rounded to integers, are shown in Table V. That symmetry cannot be assumed for the singlet excited states, so all related studies were performed starting with a C_1 symmetry z-matrix, in which all variables were optimized using the cc-pVTZ basis set at the CAM-B3LYP density functional level. The X^1A_1 state has three low frequencies associated with methyl group vibrations; the lowest excited states of C_2 symmetry, shown in Tables VI and VII, also have very low frequencies.

The section of the subtracted VUV spectral profile shows a broad peak from 5.37 to 5.70 eV, followed by a series of sharp peaks up to 6.37 eV. The sharp peaks are clearly reminiscent of the PES

TABLE V. Vibrational frequencies (cm^{-1}) of 6,6-dimethylfulvene in C_{2v} symmetry.

a_1	3259	3230	3170	3047	1743	1558	1497	1428	1415
...	1182	1111	1026	947	884	582	373		
a_2	3086	1477	979	961	724	581	130	103	
b_1	3091	1499	1109	948	796	645	453	197	127
b_2	3254	3218	3170	3041	1649	1487	1424	1362	1287
...	1187	1123	966	834	481	246			

spectrum; the two spectra are superimposed in Fig. 10 after a linear shift of the latter by 2.147 eV to lower energy. Other than the marked increase in VUV intensity at 5.877 and 6.051 eV and the three peaks marked as X, Y, and Z in Fig. 10, there is a 1:1 correspondence between the two spectra. Thus, the set of peaks starting at 5.746 eV are a p -Rydberg state with $PQN = 3$ and $\delta = 0.483$. Further states are identified in Fig. 11, with analyses in Sec. III G.

G. Interpretation of the Rydberg states for 6,6-dimethylfulvene

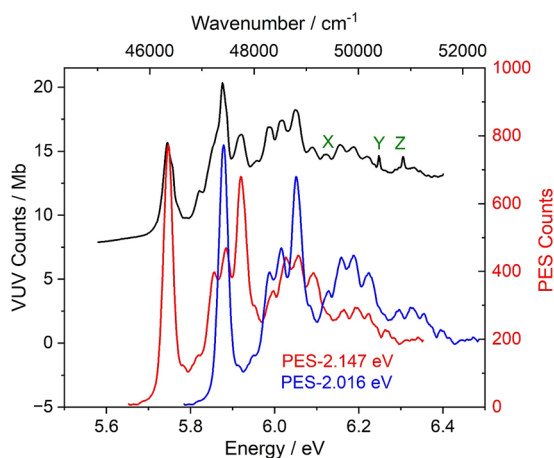
In Figs. 10 and 11, the observed Rydberg states for this geminal-dimethyl are shown, with the corresponding ionic state superimposed, while the necessary shift of the ionic state is indicated. Using the standard equation for the relationship between ionization energy (IE) and Rydberg state energy (E_0), we have $IE - E_0 = R/(n - \delta)^2$, where R is the Rydberg constant, with a value of 13.6057 eV. We find five Rydberg states, all based upon the lowest IE of 8.050 eV, corresponding to the 2A_2 state; these states have energy lowering (ΔE) of the PES spectrum to lead to the coincidences of the superimposed Rydberg state and PES of 2.147, 2.016, 1.389, 1.096, and 0.849 eV, respectively. Evaluation for the $n - \delta$ term leads to the solutions $n = 3$ with $\delta = 0.483$, a 3p-state; $n = 3$ and $\delta = 0.402$ (a different 3p-state); $n = 3$ with $\delta = -0.130$, a 3d-state; $n = 4$ with $\delta = 0.139$, a 4d-state; and finally, $n = 4$ with $\delta = -0.003$ for a 4f-state. The δ -values here are as expected, with ns high (but here symmetry is forbidden for a 1A_2 optical state), np medium δ , and nd and

TABLE VI. Vibrational frequencies (cm^{-1}) of the lowest excited state of 6,6-dimethylfulvene in C_2 symmetry.

Frequency (cm^{-1})	Symmetry	Frequency (cm^{-1})	Symmetry	Frequency (cm^{-1})	Symmetry	Frequency (cm^{-1})	Symmetry
3260	A	1504	A	1126	A	706	B
3243	B	1489	B	1050	A	597	A
3233	A	1482	B	1050	B	531	A
3227	B	1478	A	1018	B	490	B
3125	A	1473	A	1001	B	447	B
3116	B	1428	A	978	A	366	B
2995	A	1408	B	972	A	353	A
2992	B	1385	B	934	A	195	B
2979	A	1375	A	873	A	163	B
2970	B	1308	B	867	B	114	A
1624	A	1253	B	866	B	85	A
1569	B	1171	A	858	A	21	B

TABLE VII. Vibrational frequencies (cm^{-1}) of the second lowest excited state of 6,6-dimethylfulvene in C_2 symmetry, which is close to the 1A_1 high intensity state.

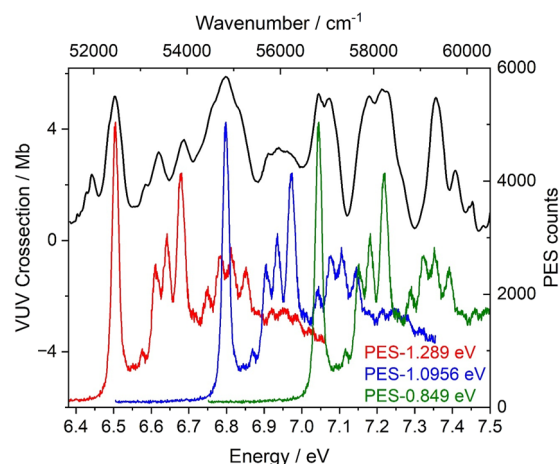
Frequency (cm^{-1})	Symmetry	Frequency (cm^{-1})	Symmetry	Frequency (cm^{-1})	Symmetry	Frequency (cm^{-1})	Symmetry
3240	A	1498	B	1099	B	632	A
3231	B	1453	A	1091	A	620	B
3214	A	1444	B	1074	B	577	A
3204	B	1437	A	1029	B	465	B
3117	A	1430	A	1015	A	464	A
3110	B	1417	B	902	A	347	A
2866	A	1395	A	900	A	334	B
2842	B	1358	B	865	A	240	A
2830	A	1326	A	843	B	204	B
2818	B	1312	B	834	A	198	B
1546	B	1206	B	753	B	144	B
1508	A	1160	A	671	B	-96	A

**FIG. 10.** 5.6–6.5 eV region of the 6,6-dimethylfulvene VUV spectrum (in black) together with the photoelectron spectrum (PES) lowered in energy by 2.016 (blue) and 2.147 eV (red) to expose two 3p-Rydberg states. Unidentified peaks X, Y, and Z are marked in olive green.

nf close to zero δ . We note that Asmis *et al.*²¹ claim to observe a shoulder in the EEL spectrum of fulvene at 6.75 eV, which they attribute to the ${}^1\pi_33S$ state, 1B_1 ; there is no evidence with this in the VUV absorption spectrum depicted in Fig. 9. Their spectrum for the 6,6-dimethyl compound shows a small peak between two Rydberg states at 6.51 eV. These are poorly resolved, as is their PES comparison, but they were assigned to ${}^1\pi_33p$ and ${}^1\pi_34p$.

H. The absence of Rydberg states based on the second IE, A^2B_1 at 8.738 eV

The TPES for fulvene, kindly supplied to us by Savee *et al.*²⁰ and exhibited in SM12 of the [supplementary material](#), shows that IE_1 (X^2A_2) is well resolved, whereas IE_2 (A^2B_1) shows only two prominent peaks, with a poorly resolved intervening structure. The

**FIG. 11.** Further Rydberg states identified in the 6.4–7.5 eV region of the spectrum.

spectral baseline is close to re-establishment between the two states in the TPES, where the energy separation for the two states is 1.139 eV. The same two states are less separated, 0.843 eV,¹ for 6,6-dimethylfulvene, which shows that the 2B_1 state vibrational structure is largely lost for both molecules. We have had experience of this broadening effect generated by a low IE on the vibrational structure of the next higher IE; several examples were present in the PES spectra of mono-halogenobenzenes (PhX, X = I, Br, Cl, and F).^{41,46} A simple but useful concept is that there is destructive interference between the vibrational levels of the lowest ionic state and that of the following state in the overlapping region, but we will return to this aspect below.

I. The 4A_2 state of fulvene

We have endeavored to quantify the degree of interaction between the two lowest ionic states for fulvene. The necessary software for this study, by Barone *et al.*,⁴⁷ was available in Gaussian-09

(G-09) and described in detail elsewhere;⁴⁷ it is not available in our version of G-16.³³ Vibrationally resolved electronic spectra are normally studied by Franck–Condon overlaps (FCO) between the X^1A_1 state and any singlet or doublet state of interest.⁴⁷ The software in G-09 allows the X^1A_1 state to be replaced by any lower state while generating the FCO with any higher state and multiplicity.

We have applied this procedure to the X^2A_2 and A^2B_1 states of fulvene, as shown in Fig. 12, with two different linewidths, expressed as half-width at half-maximum (HWHM) for the vibrational states. The top energy baseline refers to the energy above the X^2A_2 state. As the peak width is increased, the maximum reduces, so Fig. 12 shows the intensity scaled by 7:1 to separate the two spectra. An isolated vibrational peak has a width close to 70 cm^{-1} , exemplified by the blue curve.

The maxima of the peaks lie close to 1.5 eV above the 0–0 band onset of the 2B_1 state at 9.541 eV²⁰ and, hence, lie beyond the tail of the 2B_1 state; this cannot provide an explanation of the broadening observed on the 2B_1 state but discloses a further electronic state. The analysis shown in Fig. 12 yields vibration frequencies with apparent fundamentals at 671, 904, 963, 1128, 1341, 1457, 1527, and 1642 cm^{-1} ; none of these correspond to vibrations in any of our ionic doublet state calculations. A novel explanation for these vibrations is in terms of quartet states based on the interaction of the 2A_2 and 2B_1 states. The lowest quartet state is 4A_2 , with a_1 fundamentals at 652, 942, 1075, 1124, 1249, 1458, 1476, and 1573 cm^{-1} at the CAM-B3LYP functional with a cc-pVTZ basis set level. These two sets of data give a linear correlation (adjacent $R^2 = 0.959$) of the form $\text{Freq}_{\text{Spectrum}} = 1.086(77) * \text{Freq}_{\text{Quartet}} - 92(95)$, with standard errors in parentheses; this correlation line passes through the origin, since the standard error on the intercept is greater than its value, while the slope is close to unity. These quartet calculations offer an alternative explanation for the “interference pattern” suggested above, since the software was able to classify the vibrations into fundamentals, overtones, and combination bands. We are unaware of any quartet states being observed spectroscopically for fulvene. Further details of the quartet state of fulvene are shown in SM13 of the

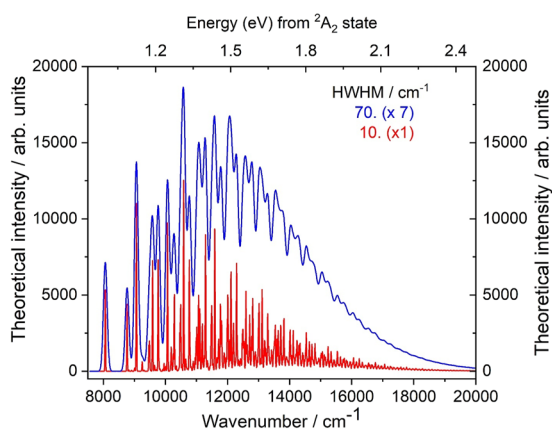


FIG. 12. Interference pattern for IE_2 overlapping the tail of IE_1 . The red and blue vibrational states have full-width at half-height of 10 and 70 cm^{-1} , and intensities are increased by the factors shown to separate the spectra.

supplementary material. The three open shell orbitals differ significantly from the corresponding π -orbitals of the fulvene ground state, which are shown in SM14 of the supplementary material.

IV. CONCLUSIONS

The instability of fulvene has led to the observation that all previous spectroscopic analyses of fulvene have been performed in places where the synthesis and spectroscopy are adjacent, a luxury that does not apply to our work. Thus, we have adopted spectroscopic data for fulvene from Brown *et al.*,⁴ especially, to correlate with our theoretical studies; in addition, we have studied the more stable 6,6-dimethyl derivative. As expected, the ultraviolet (UV) and vacuum UV absorption spectrum of the dimethyl derivative are similar to fulvene itself.

We have reconsidered both fulvenes by a combination of configuration interaction and density functional methods. The ground state of 6,6-dimethylfulvene shows genuine minimum energy at the C_{2V} structure, but that is not true for either of the two lowest singly excited states, owing to the internal rotation of the methyl groups to C_1 symmetry. The detailed conformations of the gem-dimethyl groups lead to additional complications since not all electronic states will have the same conformation in that unit. For both molecules, the absorption onset consists of a very weak band followed by a strong one. For fulvene, these two singlet states were previously assigned as X^1B_2 and A^1A_1 in C_{2V} symmetry. However, the shape of the A-state observed is incompatible with this symmetry, since it shows a slow onset, only leading to the intense maximum after many vibrational states. This is incompatible with the calculated planar A^1A_1 state, which has an intense 0–0 band. However, that state is a saddle point, arising from a negative vibration frequency. We believe that the A-state for both molecules is a folded structure of C_2 or even C_1 symmetry.

Rydberg states were evaluated by super-position of the photoelectron on the absorption spectrum, where the evaluation of the necessary energy shifts, the $n - \delta$ term, leads to the solutions $n = 3$ with $\delta = 0.483$, a 3p-state; $n = 3$ with $\delta = 0.402$ (a different 3p-state); $n = 3$ with $\delta = -0.130$, a 3d-state; $n = 4$ with $\delta = 0.139$, a 4d-state; and finally, $n = 4$ with $\delta = -0.003$ for a 4f-state. A detailed theoretical study of the Rydberg states for fulvene has led to alternative solutions for the higher of its two Rydberg states previously observed.

The situation is complex owing to the lack of vibrational structure in the A^2B_1 ionic state. The count rate doesn't return to the baseline between the two states, so the higher energy state lies in the tail of the lower energy state. This is now attributed to the interaction between the lower energy X^2A_2 and A^2B_1 ionic states, leading to the partial collapse of the higher energy state vibrational structure, as depicted in Fig. 12. We have studied this phenomenon in detail for several examples of the halogenobenzenes previously,^{41,46} but here a novel explanation arose from the Franck–Condon overlap. Rather than an interference pattern, this showed a set of apparent fundamentals, overtones, and combination bands, indicating another electronic state. This has been identified as a quartet state of fulvene, where the lowest energy one is 4A_2 , and does not appear to have been identified spectroscopically. This computational procedure is general and could lead to many related predictions of novel states.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for additional information on each of the following: 1. Some observations on the interconversion of fulvene with its isomers. 2. Separation of fine structure from underlying broad, featureless peaks. 3. Examples of the equilibrium structures for conformers of 6,6-dimethylfulvene. 4. SACCI singlet and triplet valence state vertical excitation energies. 5. Full MRD-CI results for fulvene. 6. The potential energy curve for the X^1B_2 state. 7. The folding of the 1A_1 state. 8. The fulvene UV band with the 1A_1 state. 9. The full sets of vibrational frequencies for the three lowest states of fulvene. 10. The calculated 1B_2 singlet state vibrational structure. 11. The full onsets of the 1A_1 and 1B_1 singlet states. 12. Comparison of the vibrational structure between the present synchrotron-based PES for 6,6-dimethylfulvene and the threshold (TPES). 13. The doubly occupied and virtual p and p^* orbitals for fulvene. 14. The doubly occupied π -orbitals (17, 1b₁; 20, 2b₁; 21, 1a₂) and virtual π^* (22, 26, 30) for fulvene.

DEDICATION

This paper is dedicated to the memory of Dr. Ian Gosney (1941–2024), formerly of the University of Edinburgh, who was a valued colleague and friend to two of us (M.H.P. and R.A.A.) over many years.

Dr. Michael H. Palmer passed away before the completion of the final revisions of this manuscript. This work stands as a tribute to his unwavering dedication to molecular spectroscopy. His scientific insight and commitment remained vivid until the very end in his 92nd year, and his contributions will continue to guide and influence our work.

ACKNOWLEDGMENTS

We thank (a) ISA, Department of Physics and Astronomy, Aarhus University, for the beam time on the AU-UV beamline on ASTRID2; (b) the University of Edinburgh (Eddie3) and Edinburgh Parallel Computing Center's (Cirrus) super-computing facilities for support; (c) numerical fitting was performed using GnuPlot-5.0.5;⁴⁸ (d) plotting used Origin 7.0;⁴⁹ and (e) MOs were drawn by GaussView.⁵⁰

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Michael H. Palmer: Conceptualization (equal); Investigation (equal); Writing – review & editing (equal). **Soren Vronning Hoffmann:** Data curation (equal); Methodology (equal); Resources (equal); Validation (equal). **Nykola C. Jones:** Data curation (equal); Investigation (equal); Methodology (equal); Resources (equal). **Marcello Coreno:** Investigation (equal); Project administration (equal); Supervision (equal); Validation (equal). **Monica de Simone:** Data curation (equal); Formal analysis (equal); Resources (equal); Supervision (equal); Validation (equal). **Cesare Grazioli:** Data curation (equal); Formal analysis (equal); Investigation (equal);

Resources (equal); Supervision (equal); Validation (equal). **R. Alan Aitken:** Investigation (equal); Methodology (equal); Resources (equal); Visualization (equal). **Iain L. J. Patterson:** Data curation (equal); Investigation (equal); Methodology (equal); Resources (equal); Supervision (equal); Visualization (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#) and are available from the corresponding author upon reasonable request.

REFERENCES

- 1 M. H. Palmer, M. Coreno, M. de Simone, C. Grazioli, N. C. Jones, S. Vronning Hoffmann, and R. A. Aitken, "The ionized states of 6,6-dimethylfulvene; the vibrational energy levels studied by photoionization, configuration interaction and density functional calculations," *Chem. Phys. Lett.* **796**, 139558 (2022).
- 2 P. Preethalayam, K. S. Krishnan, S. Thulasi, S. S. Chand, J. Joseph, V. Nair, F. Jaroschik, and K. V. Radhakrishnan, "Recent advances in the chemistry of pentafulvenes," *Chem. Rev.* **117**, 3930–3989 (2017).
- 3 M. B. Robin, *Higher Excited States of Polyatomic Molecules, Volume III* (Academic Press, New York, 1985), pp. 214–227.
- 4 R. D. Brown, P. J. Dommelle, and J. E. Kent, "The experimental electronic and vibrational spectra of fulvene," *Aust. J. Chem.* **23**, 1707–1720 (1970).
- 5 E. Heilbronner, R. Gleiter, H. Hopf, V. Hornung, and A. de Meijere, "Photoelectron-spectroscopic evidence for the orbital sequence in fulvene and 3,4-dimethylene-cyclobutene," *Helv. Chim. Acta* **54**, 783–794 (1971).
- 6 L. Praud, P. Millie, and G. Berthier, "Comparative calculations on electronic structure of conjugated isomers of benzene," *Theor. Chim. Acta* **11**, 169–173 (1968).
- 7 A. B. Trofimov, A. D. Skitnevskaya, A. M. Belogolova, E. K. Iakimova, and E. V. Gromov, "A study of the ionization spectrum of 6,6-dimethylfulvene using algebraic-diagrammatic construction and coupled cluster methods," *Russ. J. Phys. Chem. A* **98**, 878–885 (2024).
- 8 P. J. Dommelle, J. E. Kent, and M. F. O'Dwyer, "The visible spectrum of fulvene," *Chem. Phys.* **6**, 66–75 (1974).
- 9 P. J. Harman, J. E. Kent, M. F. O'Dwyer, and M. H. Smith, "Quartz ultraviolet Rydberg transitions in benzene isomers," *Aust. J. Chem.* **32**, 2579–2587 (1979).
- 10 P. Rancurel, B. Huron, L. Praud, J. P. Malrieu, and G. Berthier, "The electronic spectra of benzene and its conjugated isomers: A full perturbative CI approach," *J. Mol. Spectrosc.* **60**, 259–276 (1976).
- 11 V. Galasso, "Ab initio calculations on the one- and two-photon electronic transitions of the conjugated isomers of benzene," *Chem. Phys.* **171**, 171–178 (1993).
- 12 H. R. Ward, J. S. Wishnok, and P. D. Sherman, "The vacuum ultraviolet photolysis of benzene," *J. Am. Chem. Soc.* **89**, 162–163 (1967).
- 13 H. R. Ward and J. S. Wishnok, "Vacuum ultraviolet photolysis of benzene," *J. Am. Chem. Soc.* **90**, 5353–5357 (1968).
- 14 L. Kaplan and K. E. Wilzbach, "Photolysis of benzene vapor at 1849 Å," *J. Am. Chem. Soc.* **89**, 1030–1031 (1967).
- 15 J. E. Kent, P. J. Harman, and M. F. O'Dwyer, "Photochemistry of benzene isomers. I. Fulvene and 3,4-dimethylenecyclobutene," *J. Phys. Chem.* **85**, 2726–2730 (1981).
- 16 D. Bryce-Smith and H. C. Languet-Higgins, "Photochemical transformation of the benzene ring," *Chem. Commun.* **1966**, 593–594.
- 17 B. K. Carpenter, G. B. Ellison, M. R. Nimlos, and A. M. Scheer, "A conical intersection influences the ground state rearrangement of fulvene to benzene," *J. Phys. Chem. A* **126**, 1429–1447 (2022).
- 18 J. Dreyer and M. Kessinger, "The photochemical formation of fulvene from benzene via refugence—A theoretical study," *Chem. - Eur. J.* **2**, 335–341 (1996).
- 19 M. A. Robb, "In this molecule there must be a conical intersection," *Adv. Phys. Org. Chem.* **48**, 189–228 (2014).

- ²⁰J. D. Savee, B. Sztáray, P. Hemberger, J. Zádor, A. Bodi, and D. L. Osborn, "Unimolecular isomerisation of 1,5-hexadiyne observed by threshold photoelectron photo ion coincidence spectroscopy," *Faraday Discuss.* **238**, 645–664 (2022).
- ²¹K. R. Asmis, M. Allan, O. Schafer, and M. Fülcher, "Electron-energy-loss spectroscopy and theoretical study of triplet and singlet excited states of fulvene," *J. Phys. Chem. A* **101**, 2089–2095 (1997).
- ²²R. P. Frueholz, W. M. Flicker, O. A. Mosher, and A. Kuppermann, "Electronic spectroscopy of 1,3-cyclopentadiene, 1,3-cyclohexadiene and 1,3-cycloheptadiene by electron impact," *J. Chem. Phys.* **70**, 2003–2013 (1979).
- ²³L. Serrano-Andres, M. Merchán, I. Nebot-Gil, B. O. Roos, and M. Fülcher, "Theoretical study of the electronic spectra of cyclopentadiene, pyrrole, and furan," *J. Am. Chem. Soc.* **115**, 6184–6197 (1993).
- ²⁴P. J. Derrick, L. Åsbrink, O. Edqvist, B.-Ö. Jonsson, and E. Lindholm, "Rydberg series in small molecules: XIII. Photoelectron spectroscopy and electronic structure of cyclopentadiene," *Int. J. Mass Spectrom. Ion Phys.* **6**, 203–215 (1971).
- ²⁵R. D. Brown, F. R. Burden, and G. R. Williams, "Ultraviolet spectra of non-alternant hydrocarbons: The significance of non-neighbour resonance integrals and of configuration-interaction," *Aust. J. Chem.* **21**, 1939–1951 (1968).
- ²⁶P. Swiderek, M. Michaud, and L. Sanche, "Electron-energy-loss spectroscopy of 6,6'-dimethylfulvene: First detection of the triplet state," *J. Chem. Phys.* **103**, 8424–8432 (1995).
- ²⁷R. D. Brown, F. R. Burden, and J. E. Kent, "Dipole moment, microwave spectrum, and electronic structure of fulvene," *J. Chem. Phys.* **49**, 5542 (1968).
- ²⁸P. A. Baron, R. D. Brown, F. R. Burden, P. J. Domaille, and J. E. Kent, "The microwave spectrum and structure of fulvene," *J. Mol. Spectrosc.* **43**, 401–410 (1972).
- ²⁹R. D. Brown, F. R. Burden, and G. M. Mohay, "Polarities of hydrocarbons and non-neighbour resonance integrals," *Aust. J. Chem.* **21**, 1695–1702 (1968).
- ³⁰M. Rouault and Z. L. Waziutynska, "Structure de la molécule de fulvène par diffraction des électrons," *Acta Crystallogr.* **10**, 804–805 (1957).
- ³¹J. F. Chiang and S. H. Bauer, "Studies of conjugated ring hydrocarbons: The structure of dimethylfulvene," *J. Am. Chem. Soc.* **92**, 261–265 (1970).
- ³²K. J. Stone and R. D. Little, "An exceptionally simple and efficient method for the preparation of a wide variety of fulvenes," *J. Org. Chem.* **49**, 1849–1853 (1984).
- ³³M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. N. Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian 16 Revision A.03*, Gaussian, Inc., Wallingford, CT, 2016.
- ³⁴M. F. Guest, I. J. Bush, H. J. J. Van Dam, P. Sherwood, J. M. H. Thomas, J. H. Van Lenthe, R. W. A. Havenith, and J. Kendrick, *Mol. Phys.* **103**, 719–747 (2005).
- ³⁵A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange," *J. Chem. Phys.* **98**, 5648–5652 (1993).
- ³⁶T. Yanai, D. P. Tew, and N. C. Handy, "A new hybrid exchange–correlation functional using the Coulomb-attenuating method (CAM-B3LYP)," *Chem. Phys. Lett.* **393**, 51–57 (2004).
- ³⁷R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, "Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions," *J. Chem. Phys.* **72**, 650–654 (1980).
- ³⁸A. D. McLean and G. S. Chandler, "Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, $Z=11-18$," *J. Chem. Phys.* **72**, 5639–5648 (1980).
- ³⁹F. Weigend and R. Ahlrichs, "Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy," *Phys. Chem. Chem. Phys.* **7**, 3297–3305 (2005).
- ⁴⁰M. J. Frisch, J. A. Pople, and J. S. Binkley, "Self-consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets," *J. Chem. Phys.* **80**, 3265–3269 (1984).
- ⁴¹M. H. Palmer, T. Ridley, S. V. Hoffmann, N. C. Jones, M. Coreno, M. de Simone, C. Grazioli, M. Biczysko, A. Baiardi, and P. Limão-Vieira, "Interpretation of the vacuum ultraviolet photoabsorption spectrum of iodobenzene by ab initio computations," *J. Chem. Phys.* **142**, 134302 (2015).
- ⁴²P. G. Wilkinson and R. S. Mulliken, "Far ultraviolet absorption spectra of ethylene and ethylene-d₄," *J. Chem. Phys.* **23**, 1895–1907 (1955).
- ⁴³G. Herzberg, *Molecular Spectra and Molecular Structure. Vol. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules* (van Nostrand Reinhold Co., New York, 1966), Chap. V.4, pp. 533–536.
- ⁴⁴G. H. Kirby and K. Miller, "The CNDO geometry of ethylene in the first singlet excited state," *Chem. Phys. Lett.* **3**, 643–645 (1969).
- ⁴⁵C. Petrongolo, R. J. Buenker, and S. D. Peyerimhoff, "Nonadiabatic treatment of the intensity distribution in the V–N bands of ethylene," *J. Chem. Phys.* **76**, 3655–3667 (1982).
- ⁴⁶M. H. Palmer, T. Ridley, S. V. Hoffmann, N. C. Jones, M. Coreno, M. de Simone, C. Grazioli, M. Biczysko, and A. Baiardi, "The ionic states of iodobenzene studied by photoionization and ab initio configuration interaction and DFT Computations," *J. Chem. Phys.* **142**, 134301 (2015).
- ⁴⁷V. Barone, J. Bloino, and M. Biczysko, *Gaussian 09 Revision A.02*, June 24, 2010; see www.fc.up.pt/pessoas/mjramos/EMTCCM-2016/EMTCCM_MalgorzataBiczysko_3.pdf.
- ⁴⁸See <http://www.gnuplot.info/> for Gnuplot Release 5.0.7.
- ⁴⁹Origin Version 2019, OriginLab Corporation, Northampton, MA, USA, 2019.
- ⁵⁰R. Dennington, T. A. Keith, and J. M. Millam, *GaussView, Version 6.1*, Semichem, Inc., Shawnee Mission, KS, 2016.