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How to cite this publication:

J. Chem. Phys. **151**, 084304 (2019); <https://doi.org/10.1063/1.5115997>

Publication metadata

Title:	The electronically excited states of cyclooctatetraene—An analysis of the vacuum ultraviolet absorption spectrum by <i>ab initio</i> configuration interaction methods
Author(s):	Michael H. Palmer, Søren Vrønning Hoffmann, Nykola C. Jones, Marcello Coreno, Monica de Simone, and Cesare Grazioli
Journal:	The Journal of Chemical Physics
DOI/Link:	https://doi.org/10.1063/1.5115997
Document version:	Publisher's PDF (Version of Record)

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The electronically excited states of cyclooctatetraene—An analysis of the vacuum ultraviolet absorption spectrum by *ab initio* configuration interaction methods

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Submitted: 20 June 2019 . Accepted: 05 August 2019 . Published Online: 26 August 2019

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Submitted: 20 June 2019 • Accepted: 5 August 2019 •

Published Online: 26 August 2019

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ABSTRACT

A new synchrotron-based study of the vacuum ultraviolet (VUV) absorption spectrum for cyclooctatetraene (COT) shows a series of broad peaks. A significant sharp structure was extracted from the strongest band between 5.9 and 6.3 eV by fitting this range of the spectrum to a polynomial; the regular residuals show a set of sharp peaks. Comparison of this region of the VUV with the photoelectron spectrum demonstrates the presence of several Rydberg states, all based on the lowest observed ionization energy ionic state. The UV onset contains a broad band in the range 4.0 eV–5.3 eV. Theoretical vertical excitation energies, determined by configuration interaction (CI) studies at the multireference multiroot singles and doubles CI level, enabled interpretation of the principal absorption bands of the VUV spectrum. Adiabatic excitation energies (AEEs) for several singlet and triplet valence states (V) were evaluated by multiconfiguration self-consistent field methods. Theoretical Rydberg series AEEs were obtained by use of extremely diffuse Gaussian orbitals in highly correlated wave-functions. The second moments of the charge distribution identify which roots are valence or Rydberg states. A contrast was found between some density functional methods and Hartree-Fock (HF) wave-functions during single-excitation CI, when degenerate orbitals were involved in the leading configurations. The $7a_16e^*$ state contained the expected 8-membered ring in the density functional theory calculations. The HF wave-functions led to a 1,5-cross-ring interaction which converged on a singlet excited state of a bicyclo[3,3,0]octatriene; this is reminiscent of the photochemical conversion of COT to semibullvalene.

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I. INTRODUCTION

We have recently reported a reinvestigation of the photoelectron spectrum (PES) of cyclooctatetraene (C_8H_8 , abbreviated to COT).¹ We now report a parallel study of its previously

unknown vacuum ultraviolet (VUV) spectrum. The history of COT is worth repeating: its first synthesis by Willstätter and Waser² in 1911 was disbelieved, with confirmation and acceptance delayed until 1948 when Cope and Overberg³ repeated the experiments. All subsequent infrared + Raman studies,^{4,5} electron diffraction,⁶

FIG. 1. The $D_{2d} \rightleftharpoons D_{2d}$ interconversion of the all-cis (Z, Z, Z, Z)-conformation of COT.

crystallography,^{7,8} nematic phase nuclear magnetic resonance (NMR),^{9–12} and rotational coherence spectroscopy (RCS)¹³ have been interpreted in terms of a “tub” form with D_{2d} symmetry (Fig. 1). However, ^{13}C satellites in the ^1H NMR spectrum of COT showed a series of changes with temperature,^{8–10} which are now attributed to two main structural processes, (a) $\text{C}=\text{C} \rightleftharpoons \text{C}-\text{C}$ bond interchanges and (b) ring inversion $D_{2d} \rightleftharpoons D_{2d}$. These are assumed to involve a planar transition state.^{14–20} The equilibrium structure for the all-cis (Z) conformation, shown in Figs. 1(a) and 1(b), is used throughout this study. The principal aim of this paper is to present and interpret the VUV spectrum in contemporary terms and compare with electron impact (EI) spectra.^{21,22} It is a major upgrade to an early configuration interaction (CI) study of the excited and ionized states of COT²³ and will entail determination of the equilibrium structures for several electronic states in a rigid structural framework. A Rydberg state analysis links results from both this study and our reinvestigation of the photoelectron (PES) spectrum of COT.¹

II. EXPERIMENTAL AND COMPUTATIONAL PROCEDURES

A. Experimental spectra

The sample (from ABCR, assay 98%, product number AB132991, CAS No. 629-20-9) was measured as supplied with no further purification. The VUV spectrum was recorded at room temperature, using the AU-UV beam line on the synchrotron radiation source ASTRID2, using procedures similar to those recently described.²⁴ The full spectrum, shown in Fig. 2, is from 3.75 to 10.5 eV. The inset highlights the weak fine structure in the range 5.9–6.3 eV. Regular residuals (RR) after fitting of the local portion of the spectrum to a polynomial, in order to amplify the weak structure exposed by the process, will be presented in Sec. III C 1 below.

Although there is a very weak maximum between 3.8 and 5.25 eV, the principal absorption lies above 5.5 eV.

B. Theoretical methods

No single quantum chemistry package contains all the methods used; the principal theoretical suites used were GAUSSIAN-16 (G-16),²⁵ GAMESS-UK,²⁶ and MOLPRO.^{27–29} Selected singlet valence state adiabatic excitation energies (AEEs) were determined,

FIG. 2. The measured vacuum ultraviolet spectrum of cyclooctatetraene. The inset highlights the weak fine structure in the range 5.9–6.3 eV.

via their equilibrium structures, by multiconfiguration self-consistent field (MCSCF) calculations. These used a set of 16 active [$5a_1, 4b_1, 4b_2, 3a_2$] molecular orbitals (MOs) and generated approximately 250 000 configuration state functions (800 000 determinants) for each state. These structures are shown in the [supplementary material](#) as SM1. These cannot be directly linked into the Franck-Condon vibrational analysis codes in G-16.²⁵ However, single-excitation CI (CIS),^{25,30,31} also used to determine some low-lying AEEs, does allow direct input into these vibrational analysis codes in G-16.²⁵

In order to compare the theoretical calculated state energy and intensity manifold with the overall VUV spectral profile, a broad brush approach was performed using the multireference singles and doubles configuration interaction (MRD-CI) method³² within GAMESS-UK.²⁶ In this procedure, all valence shell electrons (24e) were permuted, as single or double excitations, into the lowest set of 116 virtual MOs (VMOs), using the X^1A_1 ground state equilibrium geometry.

Basis sets used were all triple zeta valence with polarization (TZVP)^{33,34} and include the Ahlrich Group default second series,^{35,36} which includes additional diffuse functions (Def2-TZVPPD). Rydberg state (s, p, d, or f) functions, with exponents in the range 0.021 to 0.0008, were incorporated to calculate the onset of Rydberg states (R) using GAMESS-UK.²⁶ These exponents are necessarily diffuse and were placed at the molecular center using the molecular structure of the 2A_1 state in D_{2d} symmetry. The vibrational structure (footprint) of Rydberg states is generally very similar to that exhibited by the ionic states in the PES. Therefore, this procedure will give a close approximation to the adiabatic excitation energies (AEEs), which contrasts with the broad-brush approach above.

In CIS methods,^{25,30,31} the AEE is evaluated from the energy difference between the ground and excited states, where both are determined at the excited state equilibrium geometry. When the structure changes significantly over the excitation process, this can lead to considerable error. The AEEs reported in Table III are redefined as the difference in energy between the ground state (X^1A_1) and the excited state, both at their respective equilibrium structures;

this is consistent with the standard definition in spectroscopy. The corrections necessary when compared with the use of a single structure for both states vary with the state under investigation but can be 1 eV or more in energy.

The TZVP basis set³³ was the choice of carrier for the Rydberg exponents (TZVPR) since all its exponents are clearly valence (V), and the derived electronic states are more likely to be R or V, rather than mixed (R + V). More recent bases^{35,36} generally contain relatively diffuse exponents, which can behave as R or V in nature. Our TZVPR basis includes very diffuse functions (of *s*, *p*, *d*, and *f* types) to represent the Rydberg orbitals. These are placed on a dummy atom at the center of the molecule and are processed by the MRD-CI method³² within GAMESS-UK.²⁶

The degenerate E symmetry MOs of COT occur in many electronically excited singlet and triplet states, with open shell occupancy, $E^2 = A_1 + A_2 + B_1 + B_2$. Many E^2 excited state structures, which have e^2 open shell occupation, lead to structural distortion through Jahn-Teller effects. Most of the present calculations beyond the Hartree-Fock (HF) level, although structurally D_{2d} in symmetry, are also treated as C_{2v} . In some of these states, the equilibrium structure becomes lowered to C_2 symmetry during the optimization process. In these cases, states of B symmetry have markedly higher oscillator strength [$f(r)$ 0.1–0.8] than those for A symmetry which generally have $f(r)$ below 0.02 and frequently zero. This does not appear to be a case of allowed vs forbidden selection rules but more likely to result from the fact that many COT 1A_1 states in C_{2v} have very low transition dipole moments, owing to the high symmetry.

III. RESULTS

A. Theoretical study of the COT electronic ground state

1. Molecular structure

Experimental structures, compared with the present D_{2d} symmetry equilibrium structures in Table I, show that the bond lengths and angles are almost invariant across a wide range of basis sets and irrespective of Hartree-Fock (HF) or density functional theory (DFT) single configuration procedures. The most precise experimental determination¹³ is from rotational coherence spectroscopy (FS-RCS), in combination with theoretical coupled-cluster single double selected triple CCSD(T) calculations. The stability of our

tub shape of COT indicates a deep minimum energy surface and is consistent with the view of COT as “essentially strain-free”.³⁷ This has been attributed to “two-way hyperconjugation” between $\sigma(C-C/C-H)$ and $\pi(C=C)$.^{38,39}

2. Electronic structure

The self-consistent field (SCF) X^1A_1 ground state, using valence shell numbering only, has doubly occupied molecular orbitals (DOMOs): 1-7a₁, 1-5e (b₁+ b₂), and 1-3a₂. The highest occupied (HOMO, 7a₁) and lowest unoccupied molecular orbital (LUMO, 4a₂) are important to the nature of several low-lying electronically excited states. These two MOs are shown in Fig. 3; several other important MOs for COT from both the occupied and virtual sets are shown in the supplementary material as SM2. Most of the UV + VUV absorption intensities involves excitations between the occupied MOs 4e or 5e and the virtual orbitals 6e* or 7e*. The high symmetry of COT is probably responsible for the generally low intensity of the 1A_1 manifold below 10 eV, although several higher intensity 1A_1 states occur above that energy.

3. Harmonic and anharmonic vibrational modes of COT

The 42 modes [11a₁, 11a₂, 10e (10b₁+10b₂)], shown in Table II, were determined at the D_{2d} equilibrium structure using the Def2-TZVPPD basis set. Vibrational frequencies for the electronically excited states described here were determined using the TZVP basis sets and are described in the supplementary material as SM3.

B. The electronically excited states

1. The theoretical sequence of major excited states

The lowest group of electronically excited states determined by MCSCF procedures, shown in Table III, gives AEE for the lowest-lying states; our version of MOLPRO does not generate oscillator strengths. Pairs of 1E states arise from interchange of b₁ and b₂ MOs in the leading terms. The importance of the HOMO (7a₁) and LUMO (4a₂*) and doubly excited states in Table III is clear; similar low-lying double excitations also occur in the MRD-CI study.

The considerable number of low-lying doubly excited states is unexpected. The basket-type structure of COT, with dihedral angle C=C–C=C close to 55.4°, makes the level of π -electron conjugation between the C=C groups very much lower than in

TABLE I. Comparison of structural data for the ground state of COT and the bond shift transition state (TS).

State	Method	Basis set	C=C	C–C	C–H	C=C–C	C=C–H	C–C–H
X^1A_1	Electron diffraction ⁵	Observed r_g	1.334(1)	1.462(1)	1.090(5)	126.5(2)	118.3(60)	
X^1A_1	X-ray ⁷	Observed	1.333	1.469		122.8		
X^1A_1	FS-RCS ¹² + CCSD(T) ¹³	Observed + <i>ab initio</i>	1.3371(10)	1.4702(5)	1.0794(10)	126.55(1)	117.698(4)	115.613(5)
		CCSD(T) ¹³						
		aug-cc-pVTZ	1.3535	1.4828	1.079	126.55	117.74	115.57
X^1A_1	B3LYP	Def2-TZVPPD	1.3358	1.4688	1.0861	127.6	117.4	114.9
X^1A_1	B3LYP	aug-cc-pVTZ	1.3357	1.4687		127.6	117.3	114.9
X^1A_1	HF	TZVP	1.3216	1.4771	1.0776	127.4	117.7	114.8

FIG. 3. The highest occupied and lowest unoccupied molecular orbitals of COT.

planar systems but certainly far from zero. This residual interaction together with the claimed “two-way hyperconjugation”^{44,45} will lead to a considerable overlap of the constituent atomic orbitals (AOs). It seems possible that the high level of configurational mixing of HOMO and LUMO may be an indicator of the non-aromatic characteristics of COT. Further studies are necessary to see whether high levels of HOMO/LUMO interaction might be developed into a more general feature of fully conjugated but nonaromatic molecules. If true, there would be a contrast to aromatics, where such HOMO/LUMO interactions would be expected to be less.

Several vertically excited states (VEE) determined by the MRD-CI method, including those with the highest intensity $f(r)$, are shown in Table IV. These are used below to interpret the principal absorption of COT. Differences in sequence between the MCSCF and MRD-CI study for states arise from different forms of correlation between the two methods. Both methods include single and double substitutions in the active MO occupancy, leading to a wide range of excited configurations. However, the MCSCF method varies the 16 active orbital compositions during the optimization. MRD-CI uses a much larger sequence of active MOs, but all the MOs have the original Hartree-Fock composition.

TABLE II. Harmonic and anharmonic frequencies calculated by the DEF2-TZVPPD basis set with the B3LYP functional.

Mode(n)/Sym.	Harmonic/ cm^{-1}	Anharmonic/ cm^{-1}	Mode(n)/ Sym.	Harmonic/ cm^{-1}	Anharmonic/ cm^{-1}
1a ₁	3132	3000	22a ₂	239	237
2a ₁	3118	2984	23b ₁	3126	2995
3a ₁	1707	1655	24b ₁	3102	2936
4a ₁	1694	1657	25b ₁	1686	1640
5a ₁	1245	1227	26b ₁	1437	1410
6a ₁	1242	1222	27b ₁	1260	1241
7a ₁	889	875	28b ₁	1015	991
8a ₁	777	770	29b ₁	958	941
9a ₁	690	682	30b ₁	816	806
10a ₁	293	290	31b ₁	656	642
11a ₁	182	182	32b ₁	369	364
12a ₂	3108	2942	33b ₂	3126	2992
13a ₂	3099	2937	34b ₂	3102	2940
14a ₂	1473	1439	35b ₂	1686	1640
15a ₂	1396	1368	36b ₂	1437	1404
16a ₂	1051	1034	37b ₂	1260	1243
17a ₂	1024	1001	38b ₂	1015	991
18a ₂	988	971	39b ₂	958	943
19a ₂	947	924	40b ₂	816	806
20a ₂	677	666	41b ₂	656	642
21a ₂	267	260	42b ₂	369	363

TABLE III. The adiabatic excitation energies of the lower singlet states determined by MCSCF methods.

Energy/eV	Symmetry	Excitation type	Leading configurations
0.0	X^1A_1	Ground state	$1-7a_1^2 1-5b_1^2 1-5b_2^2 1-3a_2^2$
1.8380	2^1A_1	Double	$-7a_1^{2*} + 4a_2^{2*}$
2.9835	1^1A_2	Single	$7a_14a_2^*$
5.8045	$1^1B_2(E)$	Double	$7a_15b_24a_2^{2*} + 4b_14a_2^* + 7a_16b_2^*$
5.8047	$1^1B_1(E)$	Double	$7a_15b_14a_2^{2*} + 4b_24a_2^* + 7a_16b_1^*$
7.0181	2^1A_2	Double	$7a_1^0 + 8a_1^*4a_2^*$
7.0227	3^1A_1	Single	$7a_18a_1^*$
7.4132	2^1B_1	Single	$4b_24a_2^*$
8.3672	3^1B_1	Double	$7a_15b_14a_2^{2*} + 5b_24a_2^*$
8.3888	2^1B_2	Single	$7a_16b_2^* + 5b_14a_2^*$
8.8953	3^1A_2	Single	$5b_16b_2^* + 6a_14a_2^*$
8.9228	3^1B_2	Single	$7a_16b_2^* - 4b_14a_2^*$

2. The wide scan UV + VUV absorption spectrum

Comparison with the electron impact (EI) profile, in Fig. 4 for the energy range up to 11 eV,^{21,22} shows considerable similarities; this is to be expected for EI using a high beam energy with a low scattering angle. The clear peak at 4.43 eV in the EI profile²¹ confirms the very weak UV absorption observed there.

3. The wide scan VUV spectral assignment

Electronic state onsets are not apparent in the experimental spectrum. This is probably a result of both the high density of states and low 0-0 band intensities. We concentrate on band maxima and assign the principal VUV bands in terms of singlet states with high oscillator strength, using the MRD-CI calculated VEE. A comparison of theory with the experimental VUV spectrum, shown in Fig. 5, gives a generally good comparison between the observed spectral and theoretical profiles. Several theoretical VEE assignments, chosen through high oscillator strength [$f(r)$], are listed in Table IV and can be correlated with the observed band maxima. A full list of excited valence state energies, oscillator strengths, and second moments

(SecMoms) of the charge distribution ($\langle x^2 \rangle$, $\langle y^2 \rangle$, and $\langle z^2 \rangle$) in the coordinate axes (x, y, z) are shown in the [supplementary material](#) in SM4. If a state has SecMoms relatively close to comparable terms in the X^1A_1 state, then it is identified as a valence state; these are expected from the TZVP basis set, in particular. We will find very much larger magnitudes for the SecMom of some Rydberg states below.

4. Individual spectral regions

The overall spectrum shows a series of broad bands, and we assign several states to each. The most important calculated VEE, shown in Table IV and SM4, should be compared with the spectrum in Fig. 5. Our VEE are absolute values since no scaling has been performed. The dipole transition probabilities and their lifetime (τ) reciprocals vary over a range of 10^{10} s, in an apparently random manner; these are appended to SM4 but do not appear to offer any guidance on the linewidth of the electronic states or the lifetimes in the bond-switching phenomenon.

TABLE IV. The most intense valence state VEE calculated by the MRD-CI method. These states are expected to account for much of the absorption shown in the VUV spectrum. An extended set of 100 VEE calculated by this method is shown in the [supplementary material](#) as SM4.

Energy/eV	Oscillator strength	State symmetry	Leading configurations	Energy/eV	Oscillator strength	State symmetry	Leading configurations
6.051	0.184	1B_2	$5b_17a_2^*; 6a_16b_2^*$	8.566	0.161	1B_1	$5b_18a_1^*; 7a_18b_1^*$
6.114	0.351	1B_2	$5b_14a_2^*; 7a_16b_2^*$	9.264	0.168	1B_2	$5b_28a_1^*; 7a_19b_2^*$
6.377	0.099	1B_2	$4b_14a_2^*$	9.329	0.135	1B_2	$3a_27b_1^*; 5b_210a_1^*; 4b_210a_1^*$
6.388	0.097	1A_1	$7a_19,11,8a_1^*$	9.474	0.051	1A_1	$7a_110a_1^*$
6.554	0.390	1B_1	$7a_16b_1^*; 5b_24a_2^*$	9.999	0.038	1B_1	$3a_26b_2^*$
6.965	0.036	1B_1	$4b_24a_2^*$	10.203	0.043	1A_1	$5b_16b_1^*; 5b_26b_2^*$
7.507	0.071	1B_2	$7a_16,5b_2^*; 5b_14a_2^*$	10.428	0.097	1B_2	$5b_210a_1^*; 3a_27b_1^*$
7.607	0.127	1B_1	$6a_16,7b_1^*$	10.743	0.059	1A_1	$4b_16b_1^*; 4b_26b_2^*$
7.880	0.119	1B_1	$3b_24a_2^*$	10.922	0.083	1B_1	$4b_18a_1^*; 5b_110a_1^*$
8.427	0.063	1B_1	$5b_24a_2^*; 7a_17b_1^*$	11.562	0.086	1B_1	$3a_27b_2^*; 4b_18a_1^*$

FIG. 4. Comparison of the overall profiles of the VUV (black) and electron impact (red) spectra. Ten times expansions demonstrate that our extremely weak absorption near 4.43 eV also occurs in the EI spectrum of Frueholz and Kuppermann.²¹ This was labeled S1 and was detected from 50 eV electron impact energy and a low scattering angle of 10°.

- (i). **The spectrum between 5.5 and 6.9 eV.** This is the strongest band in the spectrum with a weak fine structure on both leading (low energy side) and trailing edges. The fine structure, discussed in detail below, is clearly not responsible for the high intensity.

The high molecular symmetry leads to many 1A_1 states having zero intensity. Consequently, the spectrum is dominated by composites of 1B_1 and 1B_2 states. Two states calculated at 6.114 (1B_2) and 6.554 eV (1B_1) have the highest oscillator strength [$f(r)$]; these correlate well with the observed 5.5–6.9 eV band. Both these 1B_2 and 1B_1 state wave-functions show two leading configurations

FIG. 5. VUV spectrum with unscaled VEE valence states calculated by the MRD-CI method, shown in blue. The summation of these states, shown as a series of Gaussian peaks in red, uses a full-width at half maximum (FWHM) of 0.35 eV. Doubly excited and 1A_2 states are not shown.

($5b_14a_2^* - 7a_16b_2$) and ($7a_16b_1^* + 5b_24a_2^*$), respectively. Other high intensity contributors in this energy range are 6.051 eV (1B_2 , $5b_27a_2^* + 6a_16b_2^*$) and 6.377 eV (1B_2 , $4b_14a_2^*$). The 1A_1 state at 6.388 eV (1A_1 , $7a_19a_1^* + 11a_1^*$) is the most intense in the spectrum for that symmetry.

- (ii). **The VUV spectrum above 7.0 eV.** The most intense bands at higher energy have maxima at 7.092, 8.400, 9.137, 10.218, and 10.587 eV. The density of calculated excited states becomes considerable, and this may offer an interpretation of the broad bands observed. The 7.092 eV band maximum is assigned to the 1B_1 state calculated at 7.607 eV ($6a_16b_1^*$ and $7b_1^*$) together with 7.880 eV ($3b_24a_2^*$); these have the largest theoretical $f(r)$ in this part of the spectrum. The largest calculated intensity for the 8.4 eV region is the 1B_1 state at 8.566 eV [$f(r)$ 0.161]. Finally, the theoretical interpretation of the 10.218 eV band suggests that there are two main components of 1B_2 symmetry, calculated at 9.264 eV ($5b_28a_1^*$) and 9.329 eV ($3a_27b_1^*$).

- (iii). **The spectral region below 5.5 eV.** The existence of a very weak band in the UV near 4.43 eV, shown in Fig. 4, is confirmed by EI studies.^{21,22} The present MRD-CI calculations show that a closely spaced pair of 1B_1 and 1B_2 states with similar $f(r)$ occurs in this energy range. We combine these as 1E , given the similar MOs involved, which leads to a more probable assignment than a 1A_2 state,^{21,22} which can only appear via vibronic coupling.

Several other very low-lying electronic states, identified by EI, lie below the onset of our VUV spectrum; these vary with both impact energy and scattering angle. Three triplet states near 3.05, 4.05, and 4.84 eV, observed by Frueholz and Kuppermann,²¹ have an apparent vibrational structure. In contrast, the spectrum of Knoop *et al.*²² apparently shows a weak structure on a single broad peak covering the range 3.4–4.1 eV. There is no apparent identification of a COT triplet state, showing an absorption maximum at 3.542 eV (350 nm), which was observed using a linear electron accelerator.⁴⁰ Overall only one band, near 4 eV, is common to these EI studies.^{21,22} The present calculations in SM1 and SM4 show several vertical states occur below 5.5 eV; several of these have zero $f(r)$ although not optically forbidden by symmetry.

C. Rydberg states observed in the VUV spectrum and their theoretical study

1. The experimental identification of the Rydberg states

After our curve fitting process (subtraction), the regular residuals (RR) disclose very weak fine structure between about 5.9 and 6.3 eV as was shown in Fig. 2. Above 6.67 eV, the RR are apparently devoid of fine structure, but higher resolution in the future might well disclose further clusters of states.

In order to extract fine structure in the 6 eV region more precisely, the data points were fitted to an 8th order polynomial function. This was the lowest polynomial which gave a close fit to the undulating contour. The RR after removal of the polynomial show 4 main groups of peaks, as seen in Fig. 6. The lowest energy group, with the center close to $48\,000\text{ cm}^{-1}$, appears different from the wider group centered on $49\,182\text{ cm}^{-1}$.

FIG. 6. Details of the VUV spectrum between 5.9 and 6.45 eV exposed by an 8th order polynomial fit to the underlying broad band. The relative peak separations are thought to be unchanged by the subtraction, but peak intensities differ from direct measurement.

Other local bands centered near 50 550 and 51 720 cm^{-1} show increasing complexity.

The simplest group of lines shown in Fig. 6 are a well resolved series of 10 or more peaks close to 6.1 eV. Their mean separation is 157 cm^{-1} , but the individual separations decrease from 175 to 133 cm^{-1} with increasing energy; the bands appear narrower at the higher energy end. The considerable broadening in the central region close to 49 490 and 49 666 cm^{-1} suggests that merging of two sequences occurs there. The assignment of these sharp bands to the Rydberg state structure superimposed on the main valence state peaks is discussed below.

The lowest ionic state (2A_1) in the COT PES has peak maximum (IE_V) at 8.392 eV, with a full width at half height (FWHH) of 0.508 eV.¹ Its onset is poorly defined, but significant intensity is still apparent at 7.787 eV.¹ This IE band shape makes it necessary to define the observed COT Rydberg state energies relative to the vertical IE_V .

2. Analysis of the regular residuals from the photoelectron spectrum of COT

Experimentally, the vibrational profiles of Rydberg states have similar footprints to their limiting ionic state in the PES. In order to identify Rydberg states in the VUV spectrum by conventional methods, we need to extract the vibrational structure from the PES. Subtraction of an asymmetric Gaussian function from the main peak in the PES (IE_1)¹ led to two sets of RR, corresponding to the leading (low energy) and trailing edges of the PES band. However, although these two sets of RR differ somewhat in appearance, the line separations are found to be very similar. This implies that these differences arise from the density of states under the PES peak and that there is a single set of vibrations, as expected.

A double overlay of the RR of the VUV spectrum across both halves of the PES RR, shown in Fig. 7, shows that there is

FIG. 7. Identification of Rydberg state positions occurs via the energy shifts of the PES or VUV spectra to obtain spectral superposition. Here, we show the VUV spectral RR, in red and blue, superimposed onto the leading and trailing edge PES RR, in black. There is a close correspondence between the PES and VUV bands. The similarity between both the leading and trailing edge PES RR, and the VUV RR shows that the two sets of PES RR are the same vibrational state. The close correspondence of the VUV bands with the peaks of the PES is a clear indication of the presence of a Rydberg state.

reasonable agreement between the two spectra for both halves of the PES RR. Most peaks in the VUV match in the PES spectrum, although the resultants of this process are noisy. This is to be expected given the two sets of very weak RR. Both in the VUV absorption and the PES, the subtraction has removed a high proportion of the total intensity, and a close agreement between the two sets of RRs is not realistic. Also, not all the peaks in the VUV spectrum need to be accounted for by the PES set; there is underlying valence absorption in the VUV spectrum expected to be present. Overall, we believe that the presence of a Rydberg state in Fig. 7 is confirmed.

Here, we have overlaid the VUV on the PES profile, a reversal of the conventional overlay to identify Rydberg states. It is more usual to superimpose the PES on the VUV spectrum.

After adjusting the energy scale of the VUV band by various amounts, we arrive at the series of Rydberg states shown in Table V. The relationship between the Rydberg state energy (E), the ionization energy (IE_V or IE_A), the principal quantum number (n), the quantum defect (δ), and R 13.605 eV is

$$IE - E = R/(n - \delta)^2. \quad (1)$$

TABLE V. Rydberg states identified in the VUV spectrum of COT.

Energy E/eV	$(n - \delta)$	PQN (n)	Quantum defect (δ)	State
6.023	2.513	3	0.487	3p
7.101	3.549	4	0.451	4p
7.334	4.003	5	0.997	5s
7.540	4.621	5	0.376	5p

3. Theoretical adiabatic ionization energies (AIE) from extrapolated energies of Rydberg series

Our theoretical approach, which has general application, provides a reliable procedure to obtain Rydberg series. Extrapolation of the series results yields the AIE; this resembles the standard method for determining experimental AIE. Clearly, the overlay of valence states can disturb the position of the individual members of the Rydberg series, both experimentally and theoretically. We concentrate on Rydberg series leading to the $2A_1$ ionic state. The TZVPR basis, described in Sec. II B, describes a set of very diffuse functions representing the Rydberg orbitals, which are placed on a dummy atom at the center of the molecule. Crucially for this purpose, the MRD-CI procedure³² is performed at the equilibrium structure of the $2A_1$ state rather than the normal procedure using the X^1A_1 state equilibrium structure. The Rydberg state energies (*s*, *p*, *d*, or *f* types) in Table V vs the principal quantum number (*n*) in Eq. (1) are subjected to least squares numerical fitting, with extrapolation to infinite *n*. The asymptotic energy values yield the Rydberg series AIE. Extrapolation of each Rydberg state series energy from Table V into Eq. (1) all enable the AIE to be estimated. The *s*, *p*, *d*, and *f* Rydberg series values obtained are 7.078 (*s*), 7.148 (*p*), 7.074 (*d*), and 6.975 eV (*f*). The extrapolation fit errors are lower than 1% in each case, with the corresponding values for the quantum defect $\delta = 0.909$ (*s*-series), $\delta = 0.256$ (*p*-series), $\delta = -0.107$ (*d*-series), and $\delta = -0.264$ (*f*-series). The estimates of the AIE are clearly not in exact agreement, varying by about 2.4%; these values are reasonable since experimental values are also subject to uncertainty if valence states perturb individual members as applies here. Similarly, the range of δ values is wider than expected; generally, in our experience, experimental *d*- and *f*- δ values are positive and close to zero respectively. If the four series are combined and fitted, the result is AIE 7.075 (± 0.058) eV. As noted above, there is still significant intensity in the PES of COT at 7.787 eV;¹ the AIE must be lower than that value; our MCSCF studies show that the onset is often significantly lower than can be measured precisely.

However, the calculated values are all subject to another uncertainty. The apparent Rydberg state energies are all evaluated as a difference from the X^1A_1 state at the same equilibrium structure. The electron correlation for the neutral and ionic states differs considerably, in part because of the diffuse nature of the excited electron. Thus, it is impossible to obtain a complete balance between the ground and Rydberg states in each determination. A low calculated AIE is a feature of that difficulty.

The MRD-CI method in GAMESS-UK²⁶ itself uses an energy evaluation by extrapolation from chosen configuration selection thresholds to a zero threshold. The present results are based upon these extrapolated energies in the configuration selection process.

Since the TZVPR basis set generates valence and Rydberg states, differentiation between these is imperative to assign the nature of the states. One simple procedure involves pairs of calculations, using either the TZVP (which yield V-states only) or the TZVPR bases (which yield both V and Rydberg states), at the same equilibrium structure. Comparison allows the state nature to be identified since the valence state energies are only slightly affected by the presence of Rydberg functions. A more reliable method for differentiation between valence and Rydberg states

is to determine the 6 components of the second moments (SecMoms) of the electronic charge distribution. These are the operators (r^2) in the term $\langle \psi | e r^2 | \psi \rangle$, where ψ is the electronic state wavefunction, with e as the electronic charge [-1 in atomic units (a.u.)]. In GAMESS-UK,²⁶ all SecMoms are negative because of inclusion of the electronic charge in the operator; some other computational chemistry suites do not include this term and yield only positive values.

Valence states have compact values, numerically close to the electronic ground state, for the six terms (x^2 , y^2 , z^2 , xy , xz , yz); typical absolute values are in the range 20–30 atomic units (a.u.). Rydberg state SecMoms have absolute values one or more orders of magnitude larger. The diagonal terms for each of the operators xx , yy , and zz in the overall r^2 operator are numerically similar for *s*-R states. For *p*-states, one of xx , yy , or zz is much larger in magnitude. For *d*- and *f*-Rydberg states, individual combinations of the off-diagonal terms xy , xz , and yz , or xyx , yyz , etc., are the most important. Thus, a d_{xz} Rydberg state has the xz term largest. Mixing of the calculated Rydberg and valence states, although potentially problematic, is readily solved. An example is the 7.193 eV state shown in Table VI. This is a V state from the second moment values and clearly very different from the Rydberg states shown; it is deliberately omitted from the Rydberg extrapolation to generate the IE_A. This procedure for estimation of theoretical IE_A via the Rydberg series extrapolation appears novel and has promise for other molecular systems.

These calculated Rydberg state equilibrium structures show only positive vibrational frequencies and are true minima on their respective energy surfaces. For example, the *s*-states show a single vibrational progression, frequency 131 cm⁻¹, and maximum intensity at the 6th member, together with a very low 0-0 band.

4. Theoretical AEE by the CI singles (CIS) method

Several low-lying valence states, shown in Table VII, exhibit slight structural distortion to C₂ symmetry; these AEE correlate with the principal MRD-CI states above but are (unexpectedly) at higher excitation energy than the VEE. This arises since the MRD-CI results are much more highly correlated. These CIS states also show only positive vibration frequencies, indicating true minima. The *a*₁ modes shown in Table VII will dominate the Franck-Condon envelopes.

5. Comparison of the present results with a previous study of both valence and Rydberg state AEE for singlet excited states of COT by Frutos et al.

This employed both complete active space SCF (CASSCF) and second-order perturbation theory (CASPT2);⁴¹ the active space comprised eight active electrons distributed among eight valence MOs (two each of *a*₁, *b*₁, *b*₂, and *a*₂). For many states,⁴¹ these two methods give AEE differing by substantial amounts, even close to 4 eV in some circumstances; the lowest allowed state, the 1E valence state, was obtained at 7.88 (CASSCF) and 5.56 eV (CASPT2).⁴¹ The value from our MCSCF study, in Table III, is 5.805 eV. There is no comparable CASPT2 energy for our doubly excited 2^1A_1 state. Two higher 1A_1 CASPT2 states are given with energies 6.14 and 7.41 eV.⁴¹ Our 3^1A_1 valence state lies between these, and this may be a result of mutual repulsion of states of the same symmetry in our MCSCF study.

TABLE VI. Rydberg states determined by the MRD-CI method, calculated with the TZVP + Rydberg basis set (TZVPR).

AEE	Symmetry	Leading configuration	State type	Second moments of the charge distribution		
				$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$
0.0	1A_1	X^1A_1	V	−32	−32	−40
4.357 ^a	1A_1	$7a_13s$	R	−61	−60	−68
5.275 ^a	1A_1	$7a_14s$	R	−334	−334	−347
7.035 ^a	1A_1	$7a_15s$	R	−439	−439	−453
7.193	1A_1	$7a_18a_1^b$	V	−64	−62	−81
5.180 ^c	1B_1	$7a_13px$	R	−551	−201	−214
6.165 ^c	1B_1	$7a_14px$	R	−1120	−391	−403
6.827 ^c	1B_1	$7a_15px$	R	−230	−96	−108
6.137	1A_1	$7a_14pz$	R	−51	−51	−117
7.026	1A_1	$7a_15pz$	R	−225	−225	−638
5.764 ^d	1B_1	$7a_13dxz$	R	−85	−43	−97
6.480 ^d	1B_1	$7a_14dxz$	R	−397	−147	−410
6.634 ^d	1B_1	$7a_15dxz$	R	−537	−194	−551
6.234 ^e	1B_1	$7a_14fxyz$	R	−1184	−1192	−328
6.460 ^e	1B_1	$7a_15fxyz$	R	−956	−329	−1122
6.645 ^e	1B_1	$7a_16fxyz$	R	−768	−268	−904

^aRydberg s-states used in extrapolation.^bValence state omitted from extrapolation.^cRydberg p-states used in extrapolation.^dRydberg d-states used in extrapolation.^eRydberg f-states used in extrapolation.

The Rydberg state CASPT2 study⁴¹ is unusual in ascribing considerable oscillator strength to several states; one is given with $f(r) = 0.1346$ ($4b_23d_{xz}$, $3d_{yz}$); several others have $f(r) > 0.01$. The state with $f(r) = 0.1346$ is certainly not a Rydberg state. Considerable valence-Rydberg state mixing appears to have occurred in the CASPT2 study and much more than occurs in the present work.

Our (lowest) Rydberg 3s- and 4s-states have calculated energies at 4.357 and 5.275 eV; the higher of these is close to a CASPT2 value (5.58 eV) for a 3s-state.⁴¹ Conversely, we observe an experimental 3p-state at 6.023 eV which is close to a CASPT2 value of 5.93 eV ($5a_13p_{xy}$).

6. Vibrational analysis of low-lying states

Singlet states which involve excitations from e-MOs generate lower symmetry, specifically C_2 excited states; these generally have two or more imaginary frequencies. Vibrational analyses of these currently cannot be processed by the Pisa Group Franck-Condon analysis software^{42–44} within G-16.²⁵ Only 1A_2 (the lowest excited state) and many 1A_1 states lead to all positive frequencies under D_{2d} symmetry. These have zero oscillator strength in the VUV and are of low importance to the current study. We give details of the 1A_2 state in the [supplementary material](#) as SM5, as an example.

TABLE VII. Selected COT AEE for low-lying singlet valence states. These were calculated using the CIS method, with the TZVP basis set. Minor distortions to C_2 symmetry occur in some cases; the leading C_{2v} configuration is given with the corresponding C_2 configuration in parentheses.

AEE/eV	$f(r)$	State symmetry	Type	a_1 (C_{2v}) or a, b (C_2) modes/cm ^{−1}
2.151	0.0	1A_2 (A)	$7a_14a_2^*$	153, 157, 532, 811, 1022
4.231	0.2056	1B	$10b11a^*$	82, 253, 594, 627, 751, 796, 850
5.696	0.0070	1B_1	$7a_18b_1^* - 7a_110b_1^* + 7a_16b_1^*$	134, 332, 726, 831, 1050, 1348, 1426, 1758, 1831, 3309, 3351,
6.599	0.0	1A_1 (A)	$7a_18a_1^*$	85, 226, 338, 363, 518, 632, 801, 918, 1041, 1095, 1136, 1202
6.759	0.0385	1B_1	$7a_16b_1^* + 5b_24a_2^*$	180, 291, 616, 840, 935, 1258, 1308, 1541, 1793, 3185, 3315
7.217	0.8554	1B_1	$7a_16b_1^* + 5b_24a_2^*$	217, 314, 713, 839, 947, 1287, 1343, 1761, 1850, 3205, 3306
8.011	0.2862	1B_2	$7a_17b_2^* - 5b_28a_1^*$	181, 315, 708, 843, 993, 1323, 1352, 1765, 1825, 3231, 3297

FIG. 8. [(a) and (b)] The 1,5-interaction leading to a singlet pentalene diradical; this is analogous to the corresponding triplet state implicated in the photochemical transformation of COT to semibullvalene. The dotted line between C_2 and C_8 is a new bond, and those between C_3C_4 and C_6C_7 are conversion of the allyl group into a single and a double bond as semibullvalene is formed.

D. Structural changes to the COT framework under CIS excited state studies

Very late in this investigation, some CIS excitation states were found which did not lead to the expected 8-membered ring excited states. These include an equilibrium structure search for the $7a_16e^*$ process, which proceeded by a very different route. Sufficient distortion of the input 8-membered ring occurred that a 1,5-crossing interaction resulted; the CIS converged on an excited state of bicyclo[3,3,0]octatriene, as shown in Figs. 8(a) and 8(b). The C_2 symmetry ring is a singlet diradical. The corresponding triplet state was previously postulated⁴⁵ as an intermediate in the photochemical cyclization of COT to semibullvalene and is shown in Fig. 8(a). The ring system is alternatively named as a dihydropentalene by IUPAC. Clearly, the nonequivalent treatment of the upper e-MO, owing to its single occupancy in the CIS calculation, leads to a Jahn-Teller distortion. Preliminary studies showed that neither the B3LYP⁴⁶ or M11⁴⁷ density functional theory methods led to this 1,5-interaction, and the 8-membered ring was retained.

IV. CONCLUSIONS

Our synchrotron-based VUV spectrum, and theoretical study in parallel, has led to considerable new information concerning the COT electronically excited states. The high signal to noise ratio in the spectrum has enabled weak vibrational structure to be extracted. Using best fit mathematical functions over short ranges of the VUV spectrum enabled investigation of the regular residuals after subtraction. Similar treatment of our recent photoelectron spectrum²⁶ has previously led to the discovery of weak vibrational structure on the lowest ionization energy through the corresponding set of its RR.

Superposition of the RR from ionization and absorption spectra has led to identification of several Rydberg state vertical excitation energies via the energy shift necessary for coincidence of the spectra.

Our calculations indicate that COT has very low vibrational modes in several of its electronically excited states. Furthermore, these states seem to have low intensity onsets, which make identification of the adiabatic excitation energies problematic. Thus, we have used comparisons of vertical values during overlay of the envelopes in comparisons of PES and VUV spectral data. These allow reasonable estimates of adiabatic values from comparisons of vertical excitation profiles.

A broad-brush interpretation of the VUV spectrum, by use of highly correlated vertical excitation calculations, appears to interpret the positions of the main VUV peaks. All double and single excitations from a large set of reference functions are included in the MRD-CI regime. MCSCF calculations of the lowest adiabatic excitation energies demonstrate the importance of both the HOMO and the LUMO since several low-lying doubly excited states were determined; these MOs are of critical importance to those states. An interesting speculation is that this HOMO/LUMO double occupancy switching may be a feature of non-aromatic fully conjugated all-*cis* hydrocarbons; further work is needed to determine whether this is absent in regular aromatic hydrocarbons.

Very diffuse Gaussian functions at the center of the COT molecule have been used to generate the lower members of (theoretical) Rydberg series; members of each of *s*-, *p*-, *d*-, and *f*-series functions were successfully used. Use of the theoretical equilibrium structure of the first ionic state (2A_1) in the MRD-CI code generates adiabatic ionization energies for these Rydberg states. This procedure, which appears to be of general usage, has an apparent limitation, namely, interference of valence states in the excitation sequence. However, this is readily solved by use of the second moments of the charge distribution. The variation in the terms $\langle x^2 \rangle$, $\langle y^2 \rangle$, $\langle z^2 \rangle$ and higher terms in the excited states gives an immediate measure of V and/or R characteristics. Valence states have values for these operators which are like those of the X^1A_1 ground state.

An unexpected feature of one CIS calculation using the Hartree-Fock method gave a different ring system, via a 1,5-crossing interaction. The singlet species found is a more detailed version of the triplet bicyclo[3,3,0]octatriene, previously proposed as an intermediate in the photochemical conversion of COT to semibullvalene.

Vibrational analysis of low-lying states failed owing to a combination of two main issues. Considerable distortion of the ring structure from D_{2d} to C_2 led to very poor overlap of the ground and excited state vibrational wave-functions. Only CIS wave-functions were suitable for insertion into the Pisa Group software in G-16, and many of the singly excited states are clearly saddle points, often with two or more negative eigenvalues; these cannot be processed in G-16 at present. Several of the excited states generated several low frequencies, leading to a high density of states. This may be a reason why the VUV spectrum shows so little vibrational structure;

alternatively, the bond-switching process, which lies outside our expertise, may be responsible. The (lowest excited) 1A_2 state and many 1A_1 states lead to all positive frequencies under D_{2d} symmetry; these have zero oscillator strength and are of low importance to the current VUV spectrum.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for SM1–SM5.

ACKNOWLEDGMENTS

We thank The University of Edinburgh EPCC supercomputing facility (Cirrus) for support; the ASTRID2 facility for grants to carry out the VUV absorption study; the Elettra Synchrotron facility for a Grant of beam time for the parallel photoelectron study; and the Italian MIUR Project No. PON01-01078/8.

This Paper is dedicated to Dr. Isobel C. Walker who was a regular coauthor with M.H.P. for many years. We are saddened by her death on 1st March 2019.

REFERENCES

- 1 M. H. Palmer, M. Coreno, M. de Simone, C. Grazioli, S. Vronning Hoffmann, and N. C. Jones, “The ionic states of cyclooctatetraene. Analysis of a new experimental photoelectron spectrum by *ab initio* and density functional method,” *J. Chem. Phys.* **150**, 194305 (2019).
- 2 R. Willstätter and E. Waser, *Ber. Dtsch. Chem. Ges.* **44**, 3423–3445 (1911).
- 3 A. C. Cope and C. G. Overberg, *J. Am. Chem. Soc.* **70**, 1433 (1948).
- 4 E. R. Lippincott, R. C. Lord, and R. S. McDonald, *J. Am. Chem. Soc.* **73**, 3370 (1951).
- 5 S. N. Tkachev, M. Pravica, E. Kim, E. Romano, and P. F. Week, *J. Phys. Chem. A* **112**, 11501 (2008).
- 6 M. Traetteberg, *Acta Chem. Scand.* **20**, 1724 (1966).
- 7 K. H. Claus and K. Krueger, “COT crystal structure,” *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **44**, 1632 (1988).
- 8 Z. Luz and S. Meiboom, *J. Chem. Phys.* **59**, 1077 (1973).
- 9 R. Naor and Z. Luz, *J. Chem. Phys.* **76**, 5662 (1982).
- 10 J. F. M. Oth, *Pure Appl. Chem.* **25**, 573 (1971).
- 11 F. A. L. Anet, *J. Am. Chem. Soc.* **84**, 671 (1962).
- 12 L. A. Paquette, *Pure Appl. Chem.* **54**, 987 (1982).
- 13 D. S. Kumli, S. Lobsiger, H.-M. Frey, S. Leutwyler, and J. F. Stanton, *J. Phys. Chem. A* **112**, 9134 (2008).
- 14 D. P. Craig, in *Non-Benzenoid Aromatic Compounds*, edited by D. Ginsburg (Interscience Publishers, New York, 1959), pp. 1–42.
- 15 L. Salem, in *The Molecular Orbital Theory of Conjugated Systems* (W. A. Benjamin, Inc., New York, Amsterdam, 1966), 576 p.
- 16 M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry* (McGraw-Hill Series in Advanced Chemistry, 1969).
- 17 P. Politzer, J. S. Murray, and J. M. Seminario, “Antiaromaticity in relation to 1,3,5,7-cyclooctatetraene structures,” *Int. J. Quantum Chem.* **50**, 273 (1994).
- 18 J. L. Andrés, O. Castaño, A. Morreale, R. Palmeiro, and R. Gomperts, “Potential energy surface of cyclooctatetraene,” *J. Chem. Phys.* **108**, 203 (1998).
- 19 M. K. Cyranski, “Energetic aspects of cyclic π -electron delocalization: evaluation of the methods of estimating aromatic stabilization energies,” *Chem. Rev.* **105**, 3773 (2005).
- 20 A. Y. Sokolov, D. B. Magers, J. I. Wu, W. D. Allen, P. v. R. Schleyer, and H. F. Schaefer, “Free cyclooctatetraene dianion: Planarity, aromaticity, and theoretical challenges,” *J. Chem. Theory Comput.* **9**, 4436 (2013).
- 21 R. P. Fruholz and A. Kuppermann, “Electronic spectroscopy of 1,3,5,7-cyclooctatetraene by low-energy, variable-angle electron impact,” *J. Chem. Phys.* **69**, 3614 (1978).
- 22 F. W. E. Knoop, J. Kistemakerm, and L. J. Oosterhoff, “Low energy electron impact excitation spectra of 1,3,5-cycloheptatriene and 1,3,5,7-cyclooctatetraene,” *Chem. Phys. Lett.* **3**, 73 (1969).
- 23 M. H. Palmer, “Assignment of the UV-photoelectron and low-energy electronic spectrum of cycloocta-1,3,5,7-tetraene,” *J. Mol. Struct.* **178**, 79–87 (1988).
- 24 M. H. Palmer, S. Vronning Hoffmann, N. C. Jones, M. Coreno, M. de Simone, and C. Grazioli, “The valence and Rydberg states of difluoromethane: A combined experimental vacuum ultraviolet spectrum absorption and theoretical study by *ab initio* configuration interaction and density functional computations,” *J. Chem. Phys.* **148**, 214304 (2018).
- 25 M. 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. Nakajima, 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.
- 26 M. 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, “The GAMESS-UK electronic structure package: Algorithms, developments and applications,” *Mol. Phys.* **103**, 719 (2007).
- 27 H.-J. Werner, P. J. Knowles, F. R. Manby, M. Schütz, P. Celani, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklaß, D. P. O’Neill, P. Palmieri, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang, and A. Wolf, *MOLPRO*, Version 2012.1 a package of *ab initio* programs, 2012, see <http://www.molpro.net/>.
- 28 H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **82**, 5053 (1985).
- 29 P. J. Knowles and H.-J. Werner, *Chem. Phys. Lett.* **115**, 259 (1985).
- 30 J. B. Foresman, M. Head-Gordon, J. A. Pople, and M. J. Frisch, “Toward a systematic molecular orbital theory for excited states,” *J. Phys. Chem.* **96**, 135–149 (1992).
- 31 M. Head-Gordon, D. Maurice, and M. Oumi, “A perturbative correction to restricted open-shell configuration-interaction with single substitutions for excited-states of radicals,” *Chem. Phys. Lett.* **246**, 114–121 (1995).
- 32 R. J. Buenker and S. Krebs, “The configuration-driven approach for multireference configuration interaction calculations,” in *Recent Advances in Computational Chemistry*, Recent Advances in Multireference Methods, edited by K. Hirao (World Scientific, Singapore, 1999), Vol. 4, pp. 1–29.
- 33 T. H. Dunning, “Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen,” *J. Chem. Phys.* **90**, 1007 (1989).
- 34 R. A. Kendall, T. H. Dunning, and R. J. Harrison, “Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions,” *J. Chem. Phys.* **96**, 6796 (1992).
- 35 F. 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).
- 36 F. Weigend, “Accurate Coulomb-fitting basis sets for H to Rn,” *Phys. Chem. Chem. Phys.* **8**, 1057–1065 (2006).
- 37 W. B. Person, G. C. Pimental, and K. S. Pitzer, *J. Am. Chem. Soc.* **74**, 3437 (1952).
- 38 J. I. Wu, I. Fernandez, Y. Mo, and P. V. R. Schleyer, “Why cyclooctatetraene is highly stabilized: The importance of ‘two-way’ (double) hyperconjugation,” *J. Chem. Theory Comput.* **8**, 1280 (2012).

- ³⁹J. I. Wu, J. I-Chia, and P. V. R. Schleyer, "Hyperconjugation in hydrocarbons: Not just a 'mild sort of conjugation'," *Pure and Appl. Chemistry* **85**, 921 (2013).
- ⁴⁰T. N. Das and K. I. Priyaarsini, "Triplet of cyclooctatetraene: Reactivity and properties," *J. Chem. Soc., Faraday Trans.* **90**, 963 (1994).
- ⁴¹L.-M. Frutos, O. Castano, and M. Merchán, "Theoretical determination of the singlet f singlet and singlet f triplet electronic spectra, lowest ionization potentials, and electron affinity of cyclooctatetraene," *J. Phys. Chem. A* **107**, 5472 (2003).
- ⁴²J. Bloino, M. Biczysko, O. Crescenzi, and V. Barone, "Integrated computational approach to vibrationally resolved electronic spectra: Anisole as a test case," *J. Chem. Phys.* **128**, 244105 (2008).
- ⁴³V. Barone, J. Bloino, M. Biczysko, and F. Santoro, "Fully integrated approach to compute vibrationally resolved optical spectra: From small molecules to macrosystems," *J. Chem. Theory Comput.* **5**, 540 (2009).
- ⁴⁴J. Bloino, M. Biczysko, F. Santoro, and V. Barone, "General approach to compute vibrationally resolved one-photon electronic spectra," *J. Chem. Theory Comput.* **6**, 1256 (2010).
- ⁴⁵H. E. Zimmerman and H. Iwamura, *J. Am. Chem. Soc.* **90**, 4763 (1968).
- ⁴⁶A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange," *J. Chem. Phys.* **98**, 5648 (1993).
- ⁴⁷R. Peverati and D. G. Truhlar, "Improving the accuracy of hybrid meta-GGA density functionals by range separation," *J. Phys. Chem. Lett.* **2**, 2810–2817 (2011).