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The ionic states of cyclooctatetraene: Analysis of a new experimental photoelectron spectrum by *ab initio* and density functional methods

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Michael H. Palmer,^{1,a)} Marcello Coreno,^{2,b)} Monica de Simone,^{3,b)} Cesare Grazioli,^{3,b)} Søren Vrønning Hoffmann,^{4,b)} and Nykola C. Jones^{4,b)}

AFFILIATIONS

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

²ISM-CNR, Istituto di Struttura della Materia, LD2 Unit, 34149 Trieste, Italy

³IOM-CNR Laboratorio TASC, Trieste, Italy

⁴ISA, Department of Physics and Astronomy, Aarhus University, Ny Munkegade 120, DK-8000 Aarhus C, Denmark

^{a)} Email: m.h.palmer@ed.ac.uk. Telephone: +44 (0) 131 650 4765.

^{b)} Electronic addresses: marcello.coreno@elettra.eu; desimone@iom.cnr.it; grazioli@ism.cnr.it; vronning@phys.au.dk; and nykj@phys.au.dk.

ABSTRACT

A synchrotron-based study of the photoelectron spectrum (PES) for cyclooctatetraene (COT) is reported, and this has been subjected to theoretical analysis in unprecedented detail. Weak vibrational structure was observed on the lowest ionization energy (IE₁), but the peaks generally show very broad features. Multiconfiguration self-consistent field study confirms that the adiabatic IE (AIE) sequence is $1^2A_1 < 1^2B_1 < 2^2A_1 < 1^2A_2 < 2^2B_1 < 3^2A_1$. The Tamm-Dancoff approximation gives an acceptable interpretation of the PES below 20 eV. Vibrational analysis of the PES bands by Franck-Condon methods predicts well-defined vibrational structure for these ionic states. The principal contributors to the PES envelopes are the a_1 modes, and only a few are responsible for the overall shape of most bands. The high density of vibrational states, together with the known $D_{2d} \rightleftharpoons D_{2d}$ interconversion process, where the C=C and C—C bonds interchange, is attributed to the lack of the observed structure. The transition state (TS) structures for the interconversion above of several ionic states of COT have been elucidated. The intrinsic reaction coordinate procedure gave a planar TS for the $X^1A_1 (D_{2d}) \rightleftharpoons ^1A_{1g} (D_{4h}) \rightleftharpoons X^1A_1 (D_{2d})$ process; this shows alternating C—C (1.4791 Å), C=C (1.3261 Å), and C—H (1.0780 Å) bond lengths. The planar TS is a very shallow maximum, with energy varying with the method used, Hartree-Fock 0.575 eV and second order Møller-Plesset 0.653 eV. A polynomial containing quadratic, quartic, and sextic terms gives an effectively exact fit to the surface. The lowest ionic state of COT (X^2A_1) shows a similar TS for the process $X^2A_1 (D_{2d}) \rightleftharpoons ^2B_{2u} (D_{4h})$. This structure has alternating C—C (1.4366 Å), C=C (1.3572 Å), and C—H (1.0756 Å) bonds.

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I. INTRODUCTION

The original synthesis of cyclooctatetraene (C₈H₈, here abbreviated to COT) by Willstätter and Waser in 1911¹ was disbelieved until confirmation by Cope and Overberg² in 1948. Infrared and Raman,³ electron diffraction,^{4,5} crystallography,⁶ and nuclear magnetic resonance (NMR)^{7–11} studies all interpreted the COT

structure in terms of a “tub” form of D_{2d} symmetry. However, the dynamic nature of the structure was demonstrated from ¹³C satellites in the ¹H NMR spectrum, which showed a complex series of changes with temperature.^{7–9} Two main structural processes occur simultaneously, namely, (a) C=C $\rightleftharpoons$ C—C bond interchanges and (b) ring inversion $D_{2d} \rightleftharpoons D_{2d}$; both are assumed to involve a planar transition state (TS),^{12–19} which is discussed

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

below. The equilibrium for the all-*cis* (*Z*) conformation, alternatively denoted as the *Z,Z,Z,Z*-conformer, is shown in Figs. 1(a) and 1(b).

The principal aim here is to present a new photoelectron spectrum (PES) and interpret this in contemporary terms. This is a major upgrade of an early configuration interaction (CI) study of COT in its electronically excited and ionized states.²⁰ To assist these aims, we will investigate the effects of the equilibrium in Fig. 1 on both the X^1A_1 ground state in D_{2d} symmetry and some ionized states. This will also entail determination of the equilibrium structures for several ionic states.

II. EXPERIMENTAL AND COMPUTATIONAL PROCEDURES

A. Experimental photon electron spectra

The cyclooctatetraene (98%, C_8H_8) sample (Sigma-Aldrich-Merck product number 138924, CAS No. 629-20-9), kindly supplied by Professor Polly Arnold, is liquid at room temperature. It was further purified through freeze-pump-thaw cycles until no bubbles were seen upon melting. The sample was introduced into the interaction region through a hypodermic needle. The PES was obtained at the gas phase photoemission beamline of the Elettra synchrotron in Trieste, Italy, as described previously.²¹ The original SES-200 electron analyzer²² is mounted at the magic angle (54.7°) with respect to the electric vector of the linearly polarized incident light. This angle allows angle-integrated electron spectra to be recorded, both at 30 eV, with an overall experimental resolution better than 10 meV, and at 55 eV.

B. Theoretical methods

Many aspects of this study, especially those at the CI level, are treated in C_{2v} symmetry, although the structure used is of D_{2d} symmetry. As is usual for GAUSSIAN (G-16),²² GAMESS-UK,²³ and many other computational chemistry packages, only the lowest adiabatic ionization energy (AIE) for each symmetry can be determined. Here, we used second order Møller-Plesset (MP2) perturbation theory. MOLPRO differs from these since the root within each symmetry can be nominated for energy optimization. Thus, higher AIE were obtained using the multiconfiguration self-consistent field (MCSCF) module in MOLPRO.^{25–27}

A broad-brush theoretical approach to generate an overall picture of the PES ionic state energies and intensities was performed by two methods. The Tamm-Dancoff approximation (TDA)

method,²⁴ a single excitation configuration interaction (SCI) procedure, generated vertical ionization energies (VIE) and used a set of 65 active MOs including the complete valence shell (28 MOs) in C_{2v} symmetry. The multireference singles and doubles configuration interaction (MRD-CI) method²⁸ also within GAMESS-UK²⁴ generated VIE for 80 states in total. Because the nature and level of electron correlation varies so widely between methods such as TDA and MRD-CI, it is normally only safe to compare energy separations rather than absolute values between such diverse methods.

Both G-16 and MOLPRO contain a variety of TS transition state (TS) recipes.^{29–32} The quadratic synchronous transit (QST) method with options QST2 and QST3 in G-16²⁹ were widely used; other methods used included that by Sun and Ruedenberg³² in the MOLPRO suite.

Vibrational analyses of the ionic state harmonic frequencies under Franck-Condon (FC) conditions were processed by the Pisa software^{33–35} within the G-16 suite.

All basis sets used were triple zeta valence with polarization (TZVP),³⁶ including the augmented-correlation consistent (aug-cc-pVTZ),³⁷ and the Ahlrich's Group default second series which includes additional diffuse functions (Def2-TZVPPD).^{38,39} These and the B3LYP density functional^{40,41} in G-16 enabled the FC analyses to be performed directly.

The main CI study of the ionic states by the MRD-CI procedure consisted of 39 electrons permuted, via single and double substitutions, into the lowest set of 110 virtual MOs (VMOs) generated by the TZVP basis set. The multireference set of configurations includes a variety of 1 and 3 open-shell MO reference configurations, which generate a limit of approximately 80 000 configurations, with up to 10 roots selected for ionic states of each symmetry.

The MCSCF method used an active occupied space of 16 MOs denoted as $[5a_1, 4b_1, 4b_2, 3a_2]$ in C_{2v} , permuted into 32 MOs $[10, 8, 8, 6]$. These generate 828 394 determinants for the X^1A_1 state with rather larger numbers for the ionic states; for example, the 2A_1 state generates 1 987 734 determinants. Using valence shell numbering throughout this study, the occupied orbitals are up to $7a_1$, $5b_1$, $5b_2$, and $3a_2$, where b_1 and b_2 are the $5e$ -orbitals.

III. RESULTS

A. Previous studies of the PES for COT

As expected, there have been several previous experimental studies.^{42–46} Generally, the earlier methods used are less rigorous than the present study. The present spectral range is similar to that of Bieri *et al.*⁴⁴ who used He(π), but our signal to noise ratio is markedly better. Our high signal to noise ratio in the spectrum has enabled weak vibrational structure on the spectrum to be extracted by the use of sigmoid or Gaussian best fit functions to the main spectral peaks and investigation of the regular residuals (RR) after subtraction. The experimentally determined asymmetry parameter (β) from angular distribution studies⁴⁶ shows that β is close to 1.0 for IE_1 – IE_3 , indicating vacated π -MOs, but around 0.5 for IE_4 , and hence ionization from a σ -MO. Ohno *et al.*⁴⁵ made substantial comparison with our earlier study²⁰ and used several single excitation methods of theoretical assignment. However, several of their

FIG. 2. The photoelectron spectrum (PES) of cyclooctatetraene (COT), shown in black, where the peaks are labeled A–L, and discussed in the text. The MCSCF calculations of adiabatic IE are shown above the spectrum. The pole strengths calculated for the vertical ionic states by the Tamm-Dancoff approximation (TDA) are shown in red, together with their summation (231 individual states) by a set of Gaussian functions in blue.

figures⁴⁵ show labeling of the PES spectra as cyanocyclopropane, **not** COT. Furthermore, the MO labeling is neither an all-electron or full valence shell, leading to inconsistent numbers of MOs in the discussion.

B. The wide scan COT PES spectrum up to 30 eV and its assignment

The principal peaks in the spectrum using 55 eV irradiation energy, shown in Fig. 2, are labeled A–L. Vertical ionization energy (VIE) analyses, based on the Tamm-Dancoff approximation (TDA)^{47–49} and Green's function (GF)^{50,51} theoretical assignments, a further single excitation CI procedure, are also shown in Fig. 2. The principal electronic states in the PES shown in Table I are based on the TDA results for the experimental PES bands A–L, and in Fig. 2, the pole strengths are shown as vertical bars. Further TDA results are shown in the [supplementary material](#) as Table SM1. The TDA profile compares well with the ionization energy (IE) range up to band H (18 eV). A summation of all the 231 TDA ionic states using a single Gaussian peak function for each state is shown in the blue curve. The Gaussian line width (3200 cm^{-1} , 0.397 eV) was used for the total energy range and was chosen to reproduce the splitting between bands C and D; widths matching the single ionization under band A (4900 cm^{-1}) were found to merge these two bands. In principle, the differences in cross section for specific orbitals for 55 eV irradiation are known, with H1s: 0.1586, C2s: 0.1748, and C2p: 1.1590, respectively.⁵² Whilst they could have been applied to interpret the TDA intensities in the one-electron processes ($1e$, Koopmans' states), application to the higher energy shake-up states where C_{2s} participation occurs was impracticable since insufficient data are available from the TDA code for that region.

The calculated pole strengths for the lower states are close to their limiting value of 1.0 and show a similar spacing to the spectral peaks up to band H (18 eV). At higher energies, the TDA ionic states occur as numerous combined ionization and electronically

TABLE I. Principal state symmetry assignments for the PES of cyclooctatetraene compared with previous studies. Experimental uncertainties in the measured IE are shown in parentheses. The TDA and Green's function (GF) results have been scaled by 0.855 and 0.909, respectively, to generate the results shown.

Experimental PES		Present work			
PES band	IE	Electronic state	Orbitals vacated	Scaled TDA (eV)	Scaled GF (eV)
A	8.318(6), 8.538(40)	2A_1	$7a_1^{-1}$	8.402	8.407
B	9.703(2), 10.014(3)	2E	$5e^{-1}$	9.954	10.014
C	11.042(2)	2A_1	$6a_1^{-1}$	11.157	11.218
D	11.558(3)	2A_2	$3a_2^{-1}$	11.588	11.439
E	12.266(0.4), 12.551(3)	2E	4×10^{-1}	12.434	12.319
F	13.805(4), 14.519(0.4), 15.044(3)	$^2A_1, ^2A_1,$	$5a_1^{-1}, 4a_1^{-1},$	13.985, 14.613,	14.151, 14.565,
		$^2E, ^2A_2$	$3 \times 10^{-1}, 2a_2^{-1}$	15.176, 15.221	14.976, 15.152
G	16.390(2), 16.504(3)	2A_1	$3a_1^{-1}$	16.296	16.356
H	17.886(1), 18.122(2)	2E	3×10^{-1}	17.931	17.952
I	20.328(2)	2A_2	$1a_2^{-1}$	20.327	
J	21.467(103), 21.446(3)	2A_1	$2a_1^{-1}$	22.059	
K	23.363(16)	$^2E, ^2E$	2×10^{-1}	23.794, 23.890	
L	24.762(121)		1×10^{-1}	24.277, 24.370, 24.407, 25.724	

excited states (shake-up states). The principal assignments by symmetry are shown in Table I. The $1e$ approximation breaks down close to 20.3 eV, and the poles at higher energies contain numerous contributions from electronically excited states.

The MCSCF energies for the adiabatic ionization energies (AIE) are shown above the PES in Fig. 2. The calculated AIE are 1^2A_1 6.844, 1^2B_1 8.587, 2^2A_1 10.350, 1^2A_2 10.983, 2^2B_1 11.924, and 3^2A_1 13.081 eV. In each case, the leading configuration was direct ionization from the designated orbital. Higher roots to the MCSCF led to shake-up states, where more than one electron was promoted in the state. The MCSCF led to approximately 2×10^6 determinants in each case. The AIE are all lower than the observed PES, but the onsets of each PES band are not well determined.

C. Curve fitting of broad bands to disclose fine structure in the PES by subtraction

Figure 3 shows the overall spectrum after fitting several Gaussian functions. The regular residuals (RR) shown have negligible count rates. Some shoulders in the unprocessed spectrum now appear as separate IE. The trailing edge of band A indicates a further broad peak at 8.962 eV higher than the maximum intensity at 8.403 eV. Band B, maximum 9.783 eV, is clearly complex with a shoulder on the trailing edge under normal resolution; the RR show two shoulders at 9.686 and 10.293 eV. The doublet for bands C and D, maxima at 11.062 and 11.538 eV, suggests that the observed band has at least three separate peaks, at 10.883, 11.556, and 11.883 eV.

The complex band E shows four sharp peaks, at 12.228, 12.459, 12.852, and 13.280 eV. A similar analysis can be performed on higher energy bands.

D. Theoretical vibrational contributions to the PES

The COT modes (high to low frequency) are labeled 1–11(a_1), 12–21(b_1), 22–31(b_2), and 32–42(a_2); degenerate pairs of modes “e” are ($b_1 + b_2$). The calculated harmonic frequencies for the principal contributors to the PES envelopes are the a_1 modes, which are summarized in Table II. Full sets of frequencies for the three lowest ionic states are shown in the supplementary material as Table SM2. There is a strong correlation between the MP2 and B3LYP calculated harmonic frequencies, with $\nu_{B3LYP} = 13.6(15.0) + 0.981(9)\nu_{MP2}$, with adjacent R^2 0.997 for the a_1 frequencies shown in Table II. This line goes through the origin since the intercept is smaller than its standard error.

1. Band A of the PES

This is the 1^2A_1 ionic state. The calculated Franck-Condon envelope for this state shows a simple structure, made up from overtones and combination bands where a_1 modes 11, 7, 3, and 1 dominate (Fig. 4). However, because of both low intensity of the 0^0 band and the low frequency of mode 11 (131.5 cm^{-1}), a high density of vibrational states occurs under the envelope. This high density of vibrational states in itself is sufficient to cause these to merge, leading to the largely smooth PES peak; this is further discussed below.

FIG. 3. A fit of the main bands of the 55 eV PES up to 25 eV, to 19 main peaks. A total of 4801 data points were used. The residual counts unaccounted for are shown in red.

TABLE II. The a_1 modes (1–11) for the lower ionic states. These were determined at each equilibrium geometry, determined using the TZVP basis set, with either the B3LYP method or the MP2 level of calculation. The 2B_1 and 2B_2 states are degenerate under D_{2h} symmetry. The structures and a full set of frequencies are shown in the [supplementary material](#) as Table SM2.

MP2	B3LYP	MP2	B3LYP	MP2	B3LYP
2A_1	2A_1	2A_2	2A_2	${}^2E ({}^2B_1 + {}^2B_2)$	${}^2E ({}^2B_1 + {}^2B_2)$
a_1	a_1	a_1	a_1	a_1	a_1
3220	3174	3183	3094	3252	3162
3210	3162	3138	3018	3249	3152
1691	1690	1678	1745	1663	1718
1623	1636	1667	1734	1568	1582
1305	1333	1139	1168	1227	1232
1255	1265	1133	1156	1161	1179
946	961	837	808	935	904
809	795	709	727	781	799
682	667	658	555	711	722
302	310	274	262	278	274
159	131	213	194	225	209

The observed PES profile declines more rapidly than the Franck-Condon one, and this indicates that the higher calculated harmonic frequencies may have less influence in the spectrum than occurs in the calculations.

2. Band B of the PES

This is the 2E ionic state. The principal contributors are modes 11, 10, 9, 7, and 4, which occur in various overtones and binary combination bands (Fig. 5). Mode 8 is evident in some weaker triple combination bands. Again, several a_1 modes have little importance in the overall calculated vibrational intensity. The shoulder on the high energy side may also indicate Jahn-Teller effects, which are not covered by the FC analysis.

FIG. 4. The 2A_1 state of COT with the Franck-Condon profile superimposed, where the FWHM vibronic contributions have line widths 10 cm^{-1} (blue) and 400 cm^{-1} (red).

FIG. 5. Band B of the PES with the calculated profile of the 2E state superimposed.

3. Bands C and D of the PES

These, shown in Fig. 6, are interpreted as the 2A_1 and 1A_2 ionic states, respectively. In each case, several fundamental harmonic frequencies are present, but not all the a_1 modes make a major intensity contribution. An unusual feature is that the 1A_2 ionic state shows several excitations involving b_1 and b_2 modes, as well as the regular a_1 set. The examples shown in Table III are the degenerate pair of combination band modes 31^132^1 and 41^142^1 . The 2A_1 ionic state shows a wider range of fundamental modes, but modes 2, 4, and 6 do not contribute to the main intensity.

E. Theoretical studies of D_{2d} structural interconversion for COT in its X^1A_1 and ionic states

Both ring buckling and interchange of C—C with C=C are necessary to explain the absence of isomers for disubstituted COT rings.^{8–12} The structures of the ionic states, compared with the

FIG. 6. Bands C and D of the PES with the calculated profile of the 2A_1 and 1A_2 states superimposed. The positions of the spectra have been arbitrarily chosen to offer a guess at the correct position.

TABLE III. The Franck-Condon vibrations for the ionic states.

Vibration (cm ⁻¹)	Energy (cm ⁻¹)	Intensity	Vibration (cm ⁻¹)	Energy (cm ⁻¹)	Intensity
1^2A_1 state					
0^0 (60 885 cm ⁻¹)	0	145	$7^1 11^5$	1618	4 807
11^3	394	2 268	$7^1 11^6$	1749	5 768
11^4	526	4 496	$7^1 11^7$	1881	5 532
11^5	657	6 738	$7^1 11^8$	2012	4 232
11^6	789	7 792	$7^1 11^9$	2144	2 595
11^7	920	7 114	$3^1 11^4$	2216	1 739
11^8	1051	5 253	$3^1 11^5$	2347	2 416
11^9	1183	3 070	$3^1 11^6$	2479	2 554
11^{10}	1314	1 436	$7^2 11^5$	2579	1 783
$7^1 11^3$	1355	1 509	$1^1 11^7$	4093	1 522
$7^1 11^4$	1487	3 093			
1^2A_2 state					
0^0 (88 153 cm ⁻¹)	0	109 100	$16^1 1^3$	1391	5 624
11^1	194	130 600	8^2	1455	4 357
11^2	389	75 490	$8^1 11^4$	1505	7 355
11^3	583	28 040	$7^1 8^1$	1536	4 426
8^1	727	27 680	$6^1 11^2$	1545	8 946
1^4	777	13 500	$7^1 11^4$	1586	2 999
7^1	808	17 260	$8^2 11^1$	1649	9 241
$31^1 32^1$	885	2 904	$7^1 8^1 11^1$	1730	9 765
$41^1 42^1$	885	2 902	4^1	1734	61 130
$8^1 11^1$	922	54 550	$8^2 11^2$	1843	6 913
11^5	972	3 596	$6^1 8^1$	1884	5 612
$7^1 11^1$	1003	22 530	$7^1 8^1 11^2$	1924	6 857
$31^1 32^1 11^1$	1080	2 938	$4^1 11^1$	1928	61 020
$41^1 42^1 11^1$	1080	2 935	$8^2 11^3$	2038	6 097
$8^1 11^2$	1116	35 590	$6^1 8^1 11^1$	2078	4 975
6^1	1156	18 130	$7^1 8^1 11^3$	2119	3 050
$7^1 11^2$	1197	14 090	$4^1 11^2$	2122	59 120
$41^2 11^1$	1285	2 599	$4^1 7^1 11^1$	2159	2 185
$8^2 11^1$	1285	2 598	$23^1 8^1 1^2$	2272	3 274
$8^1 11^3$	1310	14 820	$32^1 1^3$	2317	23 710
$6^1 11^1$	1351	14 120	$32^1 8^1$	2461	21 060
1^2E state					
0^0 (73 621 cm ⁻¹)	0	0	$10^2 11^{10}$	2620	3 190
11^4	829	3 706	$10^1 11^{11}$	2554	11 190
11^5	1037	7 478	$10^2 11^{11}$	2827	2 595
11^6	1244	12 050	$10^1 11^{12}$	2761	8 682
11^7	1451	17 810	$10^1 11^9$	2587	2 539
11^8	1659	22 080	$10^1 11^{10}$	2795	2 711
11^9	1866	24 190	$9^1 11^{11}$	3002	2 610
11^{10}	2073	23 720	$9^1 11^5$	1834	3 000
11^{11}	2281	21 020	$9^1 11^6$	2041	5 164
11^{12}	2488	10 920	$9^1 11^7$	2249	7 565

TABLE III. (Continued.)

Vibration (cm ⁻¹)	Energy (cm ⁻¹)	Intensity	Vibration (cm ⁻¹)	Energy (cm ⁻¹)	Intensity
1 ² E state					
11 ¹³	2695	8 720	9 ¹ 11 ⁸	2456	6 256
11 ¹⁴	2903	6 427	9 ¹ 11 ⁹	2663	7 568
11 ¹⁵	3110	4 396	9 ¹ 11 ¹⁰	2871	8 182
11 ¹⁶	3317	2 803	9 ¹ 11 ¹¹	3078	7 985
10 ¹ 11 ⁴	1103	2 535	7 ¹ 11 ⁶	2148	2 702
10 ¹ 11 ⁵	1310	4 952	7 ¹ 11 ⁷	2355	4 456
10 ¹ 11 ⁶	1517	8 005	7 ¹ 11 ⁸	2563	6 330
10 ² 11 ⁶	1790	2 302	7 ¹ 11 ⁹	2770	7 878
10 ¹ 11 ⁷	1725	11 020	7 ¹ 11 ¹⁰	2977	8 706
10 ² 11 ⁷	1998	3 044	7 ¹ 11 ¹¹	3185	8 637
10 ¹ 11 ⁸	1932	13 180	4 ¹ 11 ⁵	2618	3 297
10 ² 11 ⁸	2205	3 494	4 ¹ 11 ⁶	2826	5 309
10 ¹ 11 ⁹	2139	13 920	4 ¹ 11 ⁷	3033	7 286
10 ² 11 ⁹	2412	3 534	4 ¹ 11 ⁷	3240	8 697
10 ¹ 11 ¹⁰	2347	13 140	8 ¹ 4 ¹ 11 ⁹	2936	5 929
2 ² A ₁ state					
00	0	93	7 ¹ 11 ³	1397	7 240
11 ²	287	2 745	7 ¹ 11 ⁴	1540	15 930
11 ³	431	8 225	7 ¹ 11 ⁵	1684	26 740
11 ⁴	575	17 650	7 ¹ 11 ⁶	1828	35 510
11 ⁵	719	28 850	7 ¹ 11 ⁷	1972	38 240
11 ⁶	862	37 280	8 ¹ 11 ⁹	2089	2 452
11 ⁷	1006	38 980	3 ¹ 11 ³	2121	4 988
11 ⁸	1150	33 500	3 ¹ 11 ⁴	2265	9 811
7 ¹ 11 ²	1253	2 359	5 ¹ 11 ³	2340	2 360
			1 ¹ 11 ⁵	3893	3 176

X¹A₁ ground state, all determined under comparable conditions, are shown in Table IV; the corresponding transition states (TS) are shown in Table V.

We optimized the TS for interconversion of the two D_{2d} structures for COT, using the Synchronous Transit Quasi-Newton (STQN) method in *G-16*,^{29–32} under the QST3 option. Three structures are input, those in Fig. 1, together with a planar mean structure. It is important to use the atomic numbering system consistently in these diagrams. At the Hartree-Fock, MP2, and B3LYP levels, the TS (Table V) lies above the corresponding ground state by 0.5789 eV (4670 cm⁻¹), 0.6529 eV (5266 cm⁻¹), and 0.4241 eV (3420 cm⁻¹), respectively.

The relative energy surface (in cm⁻¹) for the interconversion of COT between these two D_{2d} conformers, is shown in Fig. 7. The principal symmetry z-axis passes through the center of one square of nonadjacent C=C; the angle (θ) is defined from this point to the center of the other pair of C=C bonds, as in Fig. 8; this angle is close to 65° in the equilibrium structure.

TABLE IV. Equilibrium structures (Å/deg) for COT and its cationic states calculated by the TZVP basis set using the MP2 method X¹A₁.

State	X ¹ A ₁	1 ² A ₁	1 ² B ₂	1 ² A ₂	Transition state D _{4h}
AIE (eV)	0.0	7.700	9.339	10.802	0
C ₁ =C ₂	1.3365	1.3653	1.3267	1.3632	1.3416
C ₂ —C ₃	1.4698	1.4356	1.4742	1.4313	1.4598
C ₁ H	1.0879	1.0860	1.0865	1.0749	1.0764
C ₁ C ₂ C ₃	127.6	131.7	119.8	133.4	135.0
C ₁ =C ₂ H	117.4	114.7	122.3	113.9	113.6
C ₂ —C ₃ H	114.9	113.2	117.2	112.5	111.4
C ₁ =C ₂ —C ₃ =C ₄	53.7	−37.6	−66.1	−27.1	0.0
HC ₁ =C ₂ H	0.0	0.0	0.0	0.0	0.0
HC ₂ —C ₃ H	44.0	20.8	60.9	−14.1	0.0

TABLE V. Comparison of the transition state (TS) structures for the X^1A_1 ground state with those for the lower ionic state equilibria, performed under the same conditions. The lowest vibrational mode is shown, including the single imaginary one.

TS symmetry process	C=C	C—C	C—H	C=CH	C—CH	Lowest mode	Relative E (eV)
X^1A_1 (D_{2d}) static	1.3234	1.4778	1.0795	117.7	114.9	+196 (a_1)	0
$X^1A_1 \rightleftharpoons {}^1A_{1g} \rightleftharpoons X^1A_1$	1.3261	1.4791	1.0780	113.9	111.8	−170 (b_{2u})	0.579
${}^2B_{2u}$	1.3572	1.4366	1.0756	113.2	111.8	−100 (b_{2u})	9.047
${}^2B_2 + {}^2B_1$ (C_{2v})	1.3708	1.4923	1.0757	112.3	111.0	−246 (a_1)	12.609
${}^2B_{2g}$ (2B_2 C_{2v})	1.2956	1.5375	1.0837	116.4	108.6	−1020 (a_2)	14.889
${}^2A_{2u}$	1.3453	1.5085	1.0747	114.0	111.0	−1244 (e_g)	15.168
${}^2B_{1g}$	1.3486	1.4441	1.0899	112.6	112.4	−141 (b_{2g})	16.635
${}^2A_{2g}$ (2A_2 D_{2d})	1.3077	1.4518	1.1170	113.4	111.6	−2667 (e)	18.634

We believe that the difference in energy between the calculated lowest energy for each of the ionic states and their corresponding TS gives a measure of the line broadening to be present in the PES. The mean of the values above 0.552 eV (4452 cm^{-1}) is much larger than the vibrational modes (Table II) calculated for the ionic states. Consequentially, given the high density of vibrational states as well, the structural interconversion will overwhelm the contributions from the FC analysis. The FC are only of theoretical value when compared with conventional PES spectra.

FIG. 7. The relative energy surface (in cm^{-1}) for the interconversion of COT between the two D_{2d} conformers. The axis is defined as an angle (θ) between the z-principal axis to the center of one square of nonadjacent C=C, and the center of the other pair of C=C bonds, as shown in Fig. 8. This angle varies with the methods used but is close to 65° as for the H-F method shown. The red and blue lines represent “best” fits to sextic and quartic functions, respectively. The blue line exaggerates the difference between the maximum and minima, while the red line gives effectively exact reproduction of the data points. The polynomial function used was $f(x) = B_2\theta^2 + B_4\theta^4 + B_6\theta^6$. The best fit values, with standard errors in parentheses, are B_2 1991 (79), B_4 0.227 (12), and B_6 1.839×10^{-6} (1.036×10^{-7}). Only even powers contribute. **FIG. 8.** Definition of the angle between the two planes of four carbons, which is varied in Fig. 7, to generate the potential energy surface.

1. Structural analysis

The TS linking the two D_{2d} forms of neutral COT has ${}^1A_{1g}$ symmetry, in agreement with previous studies;¹⁶ it is strongly alternating (D_{4h}) rather than a regular octagon (D_{8h}). This procedure applied to the lower ionic states of COT is shown in Table V. The TS for the A^2A_1 state of COT is typical, corresponding to the structural interchange A^2A_1 (D_{2h}) $\rightleftharpoons$ ${}^2B_{2u}$ (D_{4h}). It shows alternating C=C (1.3572 Å) and C—C (1.4366 Å), with a single imaginary frequency of b_{2u} symmetry. In general, the structural C=C and C—C bond lengths of these TS vary considerably, but the relative energies shown are close to the ionization energies as expected.

IV. DISCUSSION

The similarity in the fragmentation pattern of styrene ($\text{C}_6\text{H}_5\text{—CH=CH}_2$) and COT in mass spectral processes,⁵³ supported by photoion mass spectrometry (PIMS)⁵⁴ and photoion-photoelectron coincidence (PIPECO) spectra,⁵⁵ has led to suggestions that their respective cations rearrange to a common species.⁵⁵ These methods show that the COT^+ cation readily fragments to

$\text{C}_2\text{H}_2 + \text{C}_6\text{H}_6^+$. In the energy range 1.5–2.1 eV above the dissociation threshold, formation of these products from the two isomeric hydrocarbons occurs at identical rates.⁵⁵ However, the various PES studies of these two molecules are completely distinct;^{54,56} the appearance potentials of the two C_8H_8^+ cations also differ.⁵³ Although part of the initial population of C_8H_8^+ ions from the PES spectrum may well occur by these fragmentation processes, the COT and styrene PES spectra retain their unique history. In short, the ionization and fragmentation processes are sequential; the parent is photoionized, and the resulting ion subsequently dissociates.

V. CONCLUSIONS

A synchrotron based PES spectrum of COT showing a very high count rate is presented. We believe that the assignment of this spectrum is the most rigorous to date. Vibrational analyses by the Franck-Condon model indicate that a considerable number of fundamental, overtone, and combination band modes should occur, although they are predicted to be densely packed in the PES band envelopes. The fact that this is not observed is attributed to the ionic state $\text{D}_{2d} \rightleftharpoons \text{D}_{2d}$ equilibria for the various states. Two other processes dominate the energy profile, namely, the twin processes of the $\text{C}-\text{C}/\text{C}=\text{C}$ single/double bond switching process and skeletal inversion.

The bands labeled A–E are one-electron ($1e$) ionization processes, and the orbitals where an electron is lost are $7a_1^{-1} < 5e^{-1} < 6a_1^{-1} < 3a_2^{-1} < 4e^{-1}$. $1e$ -ionization appears to occur up to 14 eV with the PES bands (A–L). The higher energy region contains a multiplicity of states even though some high pole strengths occur up to at least 20.3 eV.

Although none of the PES bands exhibit significant vibrational structure, “subtraction” of broad structure, by use of a series of (symmetric or asymmetric) Gaussian peaks, leaves the RR shown in Fig. 3. Positions of unresolved states are probably also exposed in Fig. 3, and this approach may be of more general value.

The equilibrium structures of several ionic states of COT have been elucidated. Transition states (TS) for these have been compared with the equilibrium structure for the X^1A_1 state. The intrinsic reaction coordinate (IRC) procedure gave a planar TS for the $X^1A_1 (\text{D}_{2d}) \rightleftharpoons ^1A_{1g} (\text{D}_{4h}) \rightleftharpoons X^1A_1 (\text{D}_{2d})$ process; this has a single imaginary frequency of b_{2u} symmetry and shows alternating $\text{C}-\text{C}$ (1.4791 Å) and $\text{C}=\text{C}$ (1.3261 Å) bond lengths, with angles 135.0° ($\text{C}=\text{CH}$) and 111.1° ($\text{C}-\text{CH}$), and $\text{C}-\text{H}$ bond lengths (1.0780 Å). The lowest ionic state of COT (X^2A_1) shows a similar TS for the process $X^2A_1 (\text{D}_{2d}) \rightleftharpoons ^2B_{2u} (\text{D}_{4h})$; again the single imaginary frequency has b_{2u} symmetry. This structure also shows alternating $\text{C}-\text{C}$ (1.4366 Å) and $\text{C}=\text{C}$ (1.3572 Å) bonds, with angles 135.0° ($\text{C}=\text{CH}$) and 111.8° ($\text{C}-\text{CH}$), and $\text{C}-\text{H}$ bonds (1.0756 Å).

SUPPLEMENTARY MATERIAL

The supplementary material contents are as follows: SM1: the wide scan PES studied by the Tamm-Dancoff approximation (TDA) with calculated pole strengths. SM2: Table SM2A—equilibrium structures (Å/deg) for COT and its cationic states calculated by the TZVP basis set using the B3LYP density functional and Table SM2B—equilibrium structures (Å/deg) for COT and its cationic

states calculated by the TZVP basis set using the MCSCF method. SM3: Table SM3—the principal vibrations for the lower ionic states, calculated at the MP2 level with the TZVP basis set.

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REFERENCES

- 1 R. Willstätter and E. Waser, *Ber. Dtsch. Chem. Ges.* **44**, 3423–3445 (1911).
- 2 A. C. Cope and C. G. Overberg, *J. Amer. Chem. Soc.* **70**, 1433 (1948).
- 3 E. R. Lippincott, R. C. Lord, and R. S. McDonald, *J. Amer. Chem. Soc.* **73**, 3370 (1951).
- 4 S. N. Tkachev, M. Pravica, E. Kim, E. Romano, and P. F. Week, *J. Phys. Chem. A* **112**, 11501 (2008).
- 5 M. Traetteberg, *Acta Chem. Scand.* **20**, 1724 (1966).
- 6 K. H. Claus and K. Krueger, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **C44**, 1632 (1988), COT crystal structure.
- 7 Z. Luz and S. Meiboom, *J. Chem. Phys.* **59**, 1077 (1973).
- 8 R. Naor and Z. Luz, *J. Chem. Phys.* **76**, 5662 (1982).
- 9 J. F. M. Oth, *Pure Appl. Chem.* **25**, 573 (1971).
- 10 F. A. L. Anet, *J. Amer. Chem. Soc.* **84**, 671 (1962).
- 11 L. A. Paquette, *Pure Appl. Chem.* **54**, 987 (1982).
- 12 D. S. Kummli, S. Lobsiger, H.-M. Frey, S. Leutwyler, and J. F. Stanton, *J. Phys. Chem. A* **112**, 9134 (2008).
- 13 D. P. Craig, *Non-Benzenoid Aromatic Compounds*, edited by D. Ginsburg (Interscience Publishers, New York, 1959), pp. 1–42.
- 14 L. Salem, *The Molecular Orbital Theory of Conjugated Systems* (W. A. Benjamin, 1966), p. 576.
- 15 M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill Series in Advanced Chemistry (McGraw-Hill, 1969).
- 16 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).
- 17 J. L. Andrés, O. Castaño, A. Morreale, R. Palmeiro, and R. Gomperts, “Potential energy surface of cyclooctatetraene,” *J. Chem. Phys.* **108**, 203 (1998).
- 18 M. K. Cyranski, “Energetic aspects of cyclic pi-electron delocalization: Evaluation of the methods of estimating aromatic stabilization energies,” *Chem. Rev.* **105**, 3773 (2005).
- 19 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).
- 20 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).
- 21 K. C. Prince, R. R. Blyth, R. Delaunay, M. Zitnik, J. Krempasky, J. Slezak, R. Camilloni, L. Avaldi, M. Coreno, G. Stefani, C. Furlani, M. de Simone, and S. Stranges, *J. Synchrotron Radiat.* **5**, 565 (1998).
- 22 N. Mårtensson, P. Baltzer, P. A. Brühwiler, J.-O. Forsell, A. Nilsson, A. Stenborg, and B. Wannberg, *J. Electron Spectrosc. Relat. Phenom.* **70**, 117 (1994).
- 23 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.
- ²⁴M. 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 (2005).
- ²⁵H.-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/>.
- ²⁶H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **82**, 5053 (1985).
- ²⁷P. J. Knowles and H.-J. Werner, *Chem. Phys. Lett.* **115**, 259 (1985).
- ²⁸R. J. Buenker and S. Krebs, "The configuration-driven approach for multireference configuration interaction calculations," *Recent Adv. Comput. Chem.* **4**, 1–29 (1999).
- ²⁹C. Peng and H. B. Schlegel, "Combining synchronous transit and quasi-Newton methods for finding transition states," *Israel J. Chem.* **33**, 449–454 (1993).
- ³⁰P. Y. Ayala and H. B. Schlegel, "A combined method for determining reaction paths, minima, and transition state geometries," *J. Chem. Phys.* **107**, 375 (1997).
- ³¹K. Fukui, "The path of chemical-reactions—The IRC approach," *Acc. Chem. Res.* **14**, 363 (1981).
- ³²J. Sun and K. Ruedenberg, *J. Chem. Phys.* **99**, 5257 (1993).
- ³³J. 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).
- ³⁴V. 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).
- ³⁵J. 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).
- ³⁶T. 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).
- ³⁷R. 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).
- ³⁸F. 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).
- ³⁹F. Weigend, "Accurate Coulomb-fitting basis sets for H to Rn," *Phys. Chem. Chem. Phys.* **8**, 1057–1065 (2006).
- ⁴⁰A. D. Becke, "Density-functional exchange-energy approximation with correct asymptotic behavior," *Phys. Rev. A* **38**, 3098–3100 (1988).
- ⁴¹A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange," *J. Chem. Phys.* **98**, 5648–5652 (1993).
- ⁴²J. H. D. Eland, *Int. J. Mass Spectrom. Ion Phys.* **2**, 471 (1969).
- ⁴³C. Batich, P. Bischof, and E. Heilbronner, "Applications of photoelectron spectroscopy. Photoelectron spectra of cyclooctatetraene and its hydrogenated derivatives," *J. Electron Spectrosc. Relat. Phenom.* **1**, 333 (1973).
- ⁴⁴G. Bieri, F. Burger, E. Heilbronner, and J. P. Maier, "Valence ionization energies of hydrocarbons," *Helv. Chim. Acta* **60**, 2213 (1977).
- ⁴⁵M. Ohno, W. von Niessen, E. Pairaud, J. Heinesch, and J. Delwiche, *J. Electron Spectrosc. Relat. Phenom.* **73**, 261 (1995).
- ⁴⁶T. Kobayashi, "Photoelectron angular distribution measurements of 1,3,5-triazine and 1,3,5,7-cyclooctatetraene," *Phys. Lett. A* **70**, 292 (1979).
- ⁴⁷L. S. Cederbaum and W. Domcke, *Adv. Chem. Phys.* **36**, 205 (1977).
- ⁴⁸J. Schirmer and L. S. Cederbaum, *J. Phys. B: At. Mol. Phys.* **11**, 1889 (1978).
- ⁴⁹L. S. Cederbaum, W. Domcke, J. Schirmer, and H. Koppel, *J. Chem. Phys.* **72**, 1348 (1980).
- ⁵⁰W. von Niessen, J. Schirmer, and L. S. Cederbaum, *Comput. Phys. Rep.* **1**, 57 (1984).
- ⁵¹A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Theory*, 1st revised edition (McGraw-Hill Publishing Co., New York, 1989), p. 466.
- ⁵²J. J. Yeh and I. Lindau, "Atomic subshell photoionization cross sections and asymmetry parameters: $1 \leq Z \leq 103$," *At. Data Nucl. Data Tables* **32**, 1–155 (1985). Available at <https://vuo.elettra.trieste.it/services/elements/WebElements.html>.
- ⁵³J. L. Franklin and S. R. Carroll, *J. Amer. Chem. Soc.* **91**, 5940 (1969).
- ⁵⁴H. W. Jochims, E. Rühl, H. Baumgartel, S. Tobita, and S. Leach, "VUV peaks in absorption spectra and photoion yield curves of polycyclic aromatic hydrocarbons and related compounds," *Int. J. Mass Spectrom. Ion Processes* **167/168**, 35 (1997).
- ⁵⁵D. Smith, T. Baer, G. D. Willett, and R. C. Ormerod, "Dissociation rates of internal-energy-selected metastable $C_8H_8^+$ ions," *Int. J. Mass Spectrom. Ion Phys.* **30**, 155 (1979).
- ⁵⁶K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules* (Halsted Press, New York, 1981), p. 195.