

Theoretical study of the excitation spectra of five-membered ring compounds: Cyclopentadiene, furan, and pyrrole

Haruyuki Nakano, Takao Tsuneda, Tomohiro Hashimoto, and Kimihiko Hirao
Department of Applied Chemistry, School of Engineering, University of Tokyo, Tokyo 113, Japan

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Multireference perturbation theory with complete active space self-consistent field (CASSCF) reference functions was applied to the study of the valence and Rydberg excited states in the range of 5–8 eV of five-membered ring compounds, cyclopentadiene, furan, and pyrrole. The spectra of these molecules have been studied extensively for many years but characterization is far from complete. The present approach can describe all kinds of excited states with the same accuracy. The calculated transition energies are in good agreement with corresponding experimental data. We were able to predict the valence and Rydberg excited states with an accuracy of 0.27 eV or better except for the B_2^+ of pyrrole. The valence excited states of five-membered ring compounds were interpreted in terms of the covalent *minus* states and ionic *plus* states of the alternate symmetry. The unobserved $1A_1 \rightarrow A_1^-$ transition with very weak intensity, which is hidden under the strong $1A_1 \rightarrow B_2^+$ transition, is also discussed. Overall, the present theory supports the assignments recently made by Serrano-Andres *et al.* based on the CASSCF plus second-order perturbation results. However, there remain some discrepancies in the assignment of the spectrum of pyrrole. © 1996 American Institute of Physics. [S0021-9606(96)02706-9]

I. INTRODUCTION

The many body perturbation method has been used as a convenient way to take into account electron correlation. The single reference version like Møller–Plesset (MP n , $n=2-4$) is a well-defined theory that can be applied safely to the ground state of closed-shell molecules around equilibrium geometry but it fails badly to describe the nondynamical correlation due to the quasidegeneracy. The multireference Møller–Plesset (MRMP) perturbation theory¹ using the complete active space self-consistent field (CASSCF) (Ref. 2) reference function has proved to be a useful method for obtaining reliable potential surfaces of chemical reactions and accurate transition energies. It has many attractive features: (1) it can dissociate a molecule correctly into its fragments, (2) it is applicable to open-shells and excited states, (3) it is almost size-consistent, (4) it is very computationally efficient (neither iteration nor diagonalization of a large matrix is necessary in the calculation). We have also proposed a quasidegenerate perturbation theory with multiconfigurational SCF reference functions (MCQD).³ MCQD has the additional features; (5) it can be applied to degenerate and quasidegenerate systems and (6) the interstate property such as the transition dipole moment can be handled in the same way as in obtaining the effective Hamiltonian.

In this paper, we clarify the applicability of the multireference perturbation theory to the calculation of accurate excitation spectra of five-membered ring compounds, 1,3-cyclopentadiene (CP), furan, and pyrrole. Furan and pyrrole are aromatic compounds where the hetero atom supplies two π electrons and the four carbon atoms supply one π -electron each, whereas CP does not (cyclopentadienide ion is aromatic sextet). These molecules are of importance in synthetic organic chemistry and in biochemistry. Experimental work on the electronic spectrum of these molecules has a long

history but a full characterization is a long way off. The spectrum has a very complex structure with many overlapping Rydberg series. Knowledge of the location and Franck–Condon profiles of electronic excitations in these molecules is of considerable importance in interpreting the results of photochemical experiments.

In Sec. II we summarize the computational details. Calculated results are presented and discussed in Sec. III. Conclusions are presented in the final section.

II. COMPUTATIONAL DETAILS

The calculations were carried out for the ground and low-lying singlet excited states of CP, furan, and pyrrole. Experimental geometries were used for all the molecules. Thus, the calculated excitation energies are vertical in nature. The molecules were placed in the yz -plane. The basis sets used for first-row atoms (C, N, and O) are Dunning's cc-pVTZ.⁴ The polarization functions were taken from those of cc-pVDZ. The Rydberg functions ($2s2p2d$) were also placed on the charge center of each molecule. The primitive Rydberg functions for C, N, and O determined by Dunning and Hay⁵ were weight-averaged and split into two with splitting factors of 1.9 and 0.75. The exponents obtained in this way were 0.0437(s), 0.0173(s), 0.0399(p), and 0.0158(p) for CP, 0.0456(s), 0.0180(s), 0.0414(p), and 0.0164(p) for pyrrole, and 0.0471(s), 0.0186(s), 0.0426(p), and 0.0168(p) for furan. We used the same Rydberg d exponents, 0.0285 and 0.0113, for all three molecules. The cc-pVDZ was used for hydrogen atoms (no polarization on H).

First we carried out the state-averaged CASSCF calculations in each symmetry. For CP, four π electrons were treated as active electrons and distributed among two bonding π ($2b_1$ and $1a_2$) and two antibonding π^* ($3b_1$ and $2a_2$) orbitals. For pyrrole and furan, six π electrons were distrib-

TABLE I. Types of transitions in cyclopentadiene, furan, and pyrrole.

State	Coefficients	Main Configurations								Character
		π					Rydberg			
		($1b_1$)	($2b_1$) 2	($1a_2$) 1	($3b_1$) 1'	($2a_2$) 2'	($3pb_1$)	($3db_1$)	($3da_2$)	
Cyclopentadiene										
1^1A_1	0.957	2	2	2	0	0	0	0	0	
$1^1B_2^+$	0.967	2	2	1	1	0	0	0	0	ionic
$1^1A_1^-$	0.482	2	1	2	1	0	0	0	0	covalent
	-0.467	2	2	1	0	1	0	0	0	
	0.504	2	2	0	2	0	0	0	0	
	-0.375	2	2	1	0	0	0	0	1	
$1^1A_1^+$	0.405	2	1	2	1	0	0	0	0	ionic
	0.660	2	2	1	0	1	0	0	0	
	0.333	2	2	2	0	0	0	0	0	
	0.405	2	2	0	2	0	0	0	0	
Furan										
1^1A_1	0.962	2	2	2	0	0	0	0	0	
$1^1B_2^+$	0.908	2	2	1	1	0	0	0	0	ionic
	-0.317	2	2	1	0	0	0	1	0	
$1^1A_1^-$	0.614	2	1	2	1	0	0	0	0	covalent
	-0.479	2	2	1	0	1	0	0	0	
	0.309	2	2	0	2	0	0	0	0	
	-0.296	2	1	1	1	1	0	0	0	
	0.288	2	2	1	0	0	0	0	1	
$1^1A_1^+$	0.605	2	1	2	1	0	0	0	0	ionic
	0.446	2	2	1	0	1	0	0	0	
	-0.226	1	2	2	1	0	0	0	0	
	-0.439	2	2	0	2	0	0	0	0	
Pyrrole										
1^1A_1	0.966	2	2	2	0	0	0	0	0	
$1^1B_2^+$	0.687	2	2	1	1	0	0	0	0	ionic
	0.291	2	1	2	0	1	0	0	0	
	-0.488	2	2	1	0	0	1	0	0	
$1^1A_1^-$	0.671	2	1	2	1	0	0	0	0	covalent
	-0.524	2	2	1	0	1	0	0	0	
	0.206	2	2	0	2	0	0	0	0	
	0.340	2	1	1	1	1	0	0	0	
$1^1A_1^+$	0.567	2	1	2	1	0	0	0	0	ionic
	0.568	2	2	1	0	1	0	0	0	
	-0.238	1	2	2	1	0	0	0	0	
	-0.397	2	2	0	2	0	0	0	0	

uted among five valence π orbitals. For the calculations of excited states, we extended the active space by adding appropriate Rydberg orbitals in addition to valence π and π^* orbitals. We added an a_2 orbital with $3d$ character to describe the 1^1A_1 transitions arising from HOMO ($1a_2$). Similarly we added four a_1 ($3s$, $3p$, and two $3d$), two b_2 ($3p$ and $3d$), and two b_1 ($3p$ and $3d$) orbitals for the description of 1^1A_2 , 1^1B_1 , and 1^1B_2 excited states, respectively. In a similar way, the Rydberg orbitals were added to describe the excited states corresponding to transitions from the second HOMO ($2b_1$).

Perturbation calculations were performed with the MRMP and MCQD methods. MRMP was applied to each individual state. In the calculations with MCQD, the Rydberg states in the same symmetry were treated simultaneously but the valence excited states were computed separately. Oscillator strengths were calculated by using

transition moments computed at the CASSCF level and the MRMP transition energies.

III. CALCULATED RESULTS AND DISCUSSION

The CASSCF configurations for the ground and low-lying valence excited states of three molecules are given in Table I in terms of C_{2v} symmetry orbitals. Calculated vertical excitation energies and oscillator strengths with the experimental data available are summarized in Tables II–IV and Figs. 1–3. The present results have been compared to the previous calculations; the CI based on the symmetry-adapted cluster expansion method (SAC-CI) by Kitao and Nakatsuji⁶ and the CASSCF plus second-order perturbation theory (CASPT2) by Serrano-Andres *et al.*⁷ The CASPT2 is similar to our MRMP and MCQD in the sense that they are all second-order perturbation methods based on the CASSCF

TABLE II. Excitation energies and oscillator strengths in cyclopentadiene (eV).

State	Excitation energy			Oscillator strength					
	MRMP ^a	MCQD ^a	Expt.	CASSCF ^a	SACCI ^b	CASPT2 ^c	MRMP	SACCI ^b	CASPT2 ^c
1 ¹ B ₂ ⁺ (Valence)	5.19	5.27	5.26, ^d 5.34 ^e	7.74	5.75	5.27	1.46×10 ⁻¹	1.13×10 ⁻¹	1.48×10 ⁻¹
1 ¹ A ₂ (1a ₂ →3s)	5.62	5.66	5.63 ^f	5.62	5.76	5.65	0.0	0.0	0.0
1 ¹ B ₁ (1a ₂ →3pb ₂)	6.24	6.29	6.25 ^g	6.10	6.33	6.24	1.74×10 ⁻²	3.10×10 ⁻²	3.10×10 ⁻²
2 ¹ B ₂ (1a ₂ →3pb ₁)	6.25	6.31	6.31 ^g	6.35	5.97	6.24	1.49×10 ⁻²	3.62×10 ⁻²	2.48×10 ⁻¹
2 ¹ A ₂ (1a ₂ →3pa ₂)	6.27	6.32	6.26 ^g	6.11	6.38	6.30	0.0	0.0	0.0
2 ¹ A ₁ ⁻ (Valence)	6.42	6.47	5.8–6.2 ^h	7.21	7.05	6.31	3.91×10 ⁻³	1.82×10 ⁻³	3.×10 ⁻⁴
3 ¹ A ₂ (1a ₂ →3da ₁)	6.81	6.86		6.60		6.85	0.0		0.0
2 ¹ B ₁ (1a ₂ →3db ₂)	6.86	6.91		6.61		6.87	1.75×10 ⁻⁶		3.×10 ⁻⁴
4 ¹ A ₂ (1a ₂ →3da ₁)	6.88	6.93		6.63		6.91	0.0		0.0
3 ¹ B ₂ (1a ₂ →3db ₁)	6.91	6.97	6.80 ^d	6.95	6.65	6.86	1.05×10 ⁻²	1.52×10 ⁻³	1.01×10 ⁻²
3 ¹ A ₁ (1a ₂ →3da ₂)	6.89	6.95	7.05 ^d	7.20	6.67	6.93	3.32×10 ⁻⁴	1.22×10 ⁻⁴	2.08×10 ⁻²
3 ¹ B ₁ (2b ₁ →3s)	7.80	7.81	7.85 ⁱ	8.10	8.17	7.95	2.17×10 ⁻²	1.41×10 ⁻⁵	2.52×10 ⁻²
4 ¹ A ₁ ⁺ (Valence)	8.11	8.16	8.03, ^j 8.06 ^h	11.05	7.81	7.89	5.02×10 ⁻¹	2.02×10 ⁻²	4.42×10 ⁻¹

^aThe ground state energy is -193.469 178 a.u. (MRMP), -193.472 613 a.u. (MCQD), and -192.860 519 a.u. (CASSCF).

^bReference 6.

^cReference 7.

^dReference 12.

^eReference 10.

^fReference 14.

^gReference 15.

^hReference 13.

ⁱReference 11.

^jReference 9.

reference functions. The difference is in the way of defining the zeroth order wave functions. In the CASPT2, the first-order wave functions are constructed with the internally contracted scheme (in other words, the zeroth order wavefunctions are linear combinations of CSFs), and thus some sets of

linear equations must be solved in obtaining the second-order energy. On the other hand, our MRMP and MCQD are, respectively, the single- and multistate perturbation methods using the *single CSFs* as the basis of first-order wave functions. In these methods, the second-order energy (or effective

TABLE III. Excitation energies and oscillator strengths in furan (eV).

State	Excitation energy			Oscillator strength					
	MRMP ^a	MCQD ^a	Expt.	CASSCF ^a	SACCI ^b	CASPT2 ^c	MRMP	SACCI ^b	CASPT2 ^c
1 ¹ A ₂ (1a ₂ →3s)	5.84	5.84	5.91 ^{d,e}	5.67	6.27	5.92	0.0	0.0	0.0
1 ¹ B ₂ ⁺ (Valence)	5.95	5.99	6.06 ^{f,i}	8.52	6.60	6.04	1.58×10 ⁻¹	5.52×10 ⁻²	1.54×10 ⁻¹
2 ¹ A ₁ ⁻ (Valence)	6.16	6.19	7.09	6.96	6.96	6.16	3.49×10 ⁻³	3.53×10 ⁻⁴	1.5×10 ⁻³
1 ¹ B ₁ (1a ₂ →3pb ₂)	6.40	6.40	6.48 ^{g,j,k}	6.10	6.74	6.46	1.52×10 ⁻²	4.26×10 ⁻²	3.09×10 ⁻²
2 ¹ B ₂ (1a ₂ →3pb ₁)	6.50	6.51	6.48 ^{g,j,k}	6.42	6.19	6.48	2.66×10 ⁻²	9.59×10 ⁻²	4.71×10 ⁻²
2 ¹ A ₂ (1a ₂ →3pa ₁)	6.53	6.54	6.61 ^{l,h}	6.20	6.96	6.59	0.0	0.0	0.0
3 ¹ A ₂ (1a ₂ →3da ₁)	6.98	6.98		6.64		7.00	0.0		0.0
2 ¹ B ₁ (1a ₂ →3db ₂)	7.10	7.12		6.71		7.15	3.71×10 ⁻⁵		0.0000
4 ¹ A ₂ (1a ₂ →3da ₁)	7.18	7.19		6.77		7.22	0.0		0.0
3 ¹ B ₂ (1a ₂ →3db ₁)	7.18	7.21		7.05		7.13	1.03×10 ⁻²		7.4×10 ⁻³
3 ¹ A ₁ (1a ₂ →3da ₂)	7.26	7.29	7.28 ⁱ	7.34	7.00	7.31	7.29×10 ⁻⁵	2.20×10 ⁻⁵	3.×10 ⁻⁴
3 ¹ B ₁ (2b ₁ →3s)	7.31	7.25	7.38 ^{g,j,l}	6.81	7.62	7.21	1.49×10 ⁻²	3.09×10 ⁻²	1.92×10 ⁻²
4 ¹ A ₁ ⁺ (Valence)	7.69	7.72	7.82 ^j	10.51		7.74	4.94×10 ⁻¹		4.16×10 ⁻¹

^aThe ground state energy is -229.390 926 a.u. (MRMP), -229.390 926 a.u. (MCQD), and -228.714 660 a.u. (CASSCF).

^bReference 6.

^cReference 7.

^dReference 23.

^eReference 27.

^fReference 18.

^gReference 19.

^hReference 24.

ⁱReference 25.

^jReference 22.

^kReference 28.

^lReference 20.

TABLE IV. Excitation energies and oscillator strengths in pyrrole (eV).

State	Excitation energy			Oscillator strength					
	MRMP ^a	MCQD ^a	Expt.	CASSCF ^a	SACCI ^b	CASPT2 ^c	MRMP	SACCI ^b	CASPT2 ^c
1 ¹ A ₂ (1a ₂ →3s)	4.92	4.91	4.96, ^d 5.22 ^{e,f,g}	4.46	5.20	5.08	0.0	0.0	0.0
1 ¹ B ₁ (2b ₁ →3s)	5.70	5.65		4.97	6.13	5.97	2.22×10 ⁻⁴	1.57×10 ⁻⁵	6.×10 ⁻⁴
2 ¹ A ₂ (1a ₂ →3pa ₁)	5.74	5.74		5.18	5.95	5.83	0.0	0.0	0.0
1 ¹ B ₂ (1a ₂ →3pb ₁)	5.87	5.88	5.86 ^{d,h}	5.48	5.54	5.78	2.42×10 ⁻²	4.55×10 ⁻²	3.99×10 ⁻²
2 ¹ B ₁ (1a ₂ →3pb ₂)	5.81	5.80	5.88 ^{g,h,i}	5.18	5.85	5.85	1.46×10 ⁻²	3.22×10 ⁻²	2.39×10 ⁻²
2 ¹ B ₂ ⁺ (Valence)	6.51	6.51	5.98 ^{g,h,j}	8.93	6.63	6.00	9.97×10 ⁻²	4.21×10 ⁻²	1.25×10 ⁻¹
2 ¹ A ₁ ⁻ (Valence)	5.98	6.01		6.78	6.63	5.92	9.79×10 ⁻³	2.34×10 ⁻²	1.95×10 ⁻²
3 ¹ A ₂ (1a ₂ →3da ₁)	6.38	6.37		5.71		6.42	0.0		0.0
4 ¹ A ₂ (1a ₂ →3da ₁)	6.44	6.43		5.77		6.51	0.0		0.0
3 ¹ B ₁ (1a ₂ →3db ₂)	6.45	6.44	6.43 ^d	5.74		6.40	6.33×10 ⁻⁴		1.17×10 ⁻²
4 ¹ B ₁ (2b ₁ →3pa ₁)	6.48	6.50	6.50 ⁱ	5.74		6.62	1.77×10 ⁻²		1.61×10 ⁻²
3 ¹ A ₁ (2b ₁ →3pb ₁)	6.52	6.52	6.50 ⁱ	6.32	6.50	6.65	2.33×10 ⁻²	7.64×10 ⁻³	1.27×10 ⁻²
3 ¹ B ₂ (1a ₂ →3db ₁)	6.61	6.62	6.78 ⁱ	6.12	6.20	6.53	1.21×10 ⁻⁴	1.08×10 ⁻²	1.1×10 ⁻³
4 ¹ A ₁ (1a ₂ →3da ₂)	6.62	6.64	6.78 ⁱ	6.12	6.88	6.54	1.22×10 ⁻⁴	2.44×10 ⁻³	1.0×10 ⁻³
5 ¹ A ₂ (2b ₁ →3pb ₂)	6.70	6.65		5.82	6.85	6.77	0.0	0.0	0.0
5 ¹ B ₁ (2b ₁ →3da ₁)	7.14	7.13	7.26 ^g	6.28		7.32	2.47×10 ⁻⁴		5.×10 ⁻⁵
5 ¹ A ₁ (2b ₁ →3db ₁)	7.20	7.20	7.43 ^g	6.74		7.36	3.04×10 ⁻²		4.7×10 ⁻³
6 ¹ B ₁ (2b ₁ →3da ₁)	7.23	7.21	7.43 ^g	6.35		7.39	1.80×10 ⁻³		2.5×10 ⁻³
6 ¹ A ₂ (2b ₁ →3db ₂)	7.25	7.22		6.32		7.31	0.0		0.0
4 ¹ B ₂ (2b ₁ →3da ₂)	7.36	7.39	7.43 ^g	7.85	7.52	7.43	5.09×10 ⁻⁴	8.74×10 ⁻²	5.×10 ⁻⁴
5 ¹ A ₁ ⁺ (Valence)	7.48	7.51	7.54 ^g	9.76	7.20	7.46	5.62×10 ⁻¹	2.14×10 ⁻²	3.26×10 ⁻¹

^aThe ground state energy is -209.536 360 a.u. (MRMP), -209.538 641 a.u. (MCQD), and -208.877 219 a.u. (CASSCF).

^bReference 6.

^cReference 7.

^dReference 32.

^eReference 23.

^fReference 24.

^gReference 25.

^hReference 30.

ⁱReference 31.

^jReference 21.

Hamiltonian) is obtained just through the sum of the products of molecular integrals and energy denominator $(E_0 - H_0)^{-1}$.

The pairing properties satisfied in the Huckel and PPP Hamiltonians for alternant hydrocarbons serve as a valuable tool for the qualitative interpretation of the excited states calculated with the sophisticated *ab initio* methods even of

heterocyclic analogs.⁸ Let us consider the *cis*-butadiene. The four valence π -orbitals in *cis*-butadiene are in the order of energy, $1b_1$, $1a_2$, $2b_1$, and $2a_2$. The first two are occupied orbitals. They are designated by 2, 1, 1', and 2', respectively. The orbitals i and i' are called a conjugated pair, and the well-known pairing properties are satisfied. The HOMO-LUMO ($1 \rightarrow 1'$) excitation gives rise to the lowest $^1B_2^+$ state

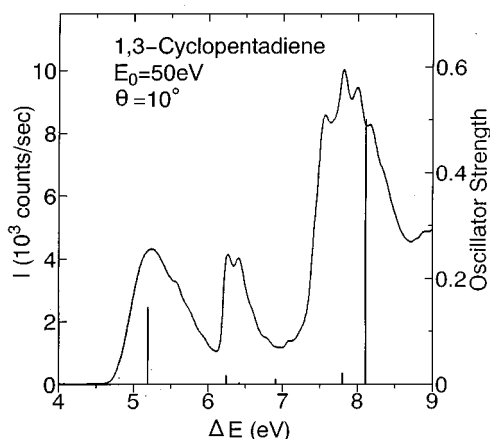


FIG. 1. Calculated transition energies and oscillator strengths are plotted with the experimental spectrum (Ref. 12) of 1,3-cyclopentadiene.

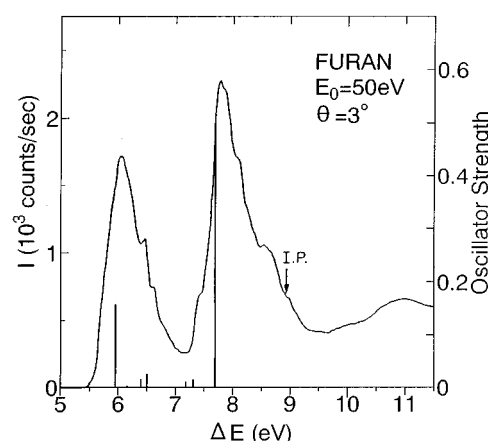


FIG. 2. Calculated transition energies and oscillator strengths are plotted with the experimental spectrum (Ref. 25) of furan.

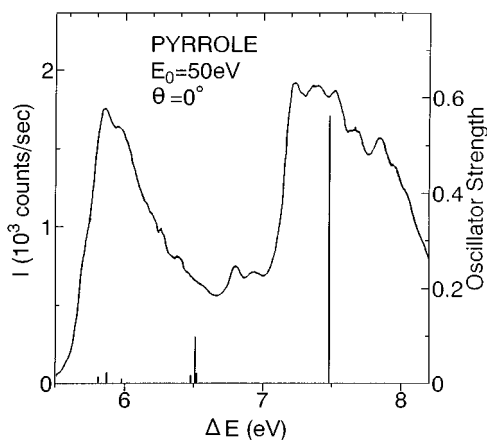


FIG. 3. Calculated transition energies and oscillator strengths are plotted with the experimental spectrum (Ref. 25) of pyrrole.

with the ionic nature. The two single excitations of $1 \rightarrow 2'$ and $2 \rightarrow 1'$ result in a pair of covalent ${}^1A_1^-$ and ionic ${}^1A_1^+$ states. The transition to the ${}^1A_1^-$ state is pseudoparity forbidden while transitions to the ${}^1B_2^+$ and ${}^1A_1^+$ states are dipole allowed. A double excitation of $(1')^2 \rightarrow (1')^2$ also gives rise to the ${}^1A_1^-$ state, which we believe lies in this energy range. If such a state exists, it interacts with the singly excited ${}^1A_g^-$ state. The double excitations are expected to have a profound effect on the description of the dipole-forbidden ${}^1A_1^-$ state of *cis*-butadiene. The simple consideration of possible interactions suggests that the experimentally observed A_1 state is the A_1^+ state. The transition to the A_1^- has very weak intensity and is hidden under the strong $1A_1 \rightarrow B_2^+$ transition, making it difficult to detect it in absorption spectra. The transition of $2 \rightarrow 2'$ gives the second B_2^+ state with ionic character but it is predicted to lie at rather high energy.

The five valence π -orbitals in the five-membered ring compounds are in the order of energy, $1b_1$, $2b_1$, $1a_2$, $3b_1$, and $2a_2$. The first three are occupied orbitals and the $1b_1$ π -orbital (pseudo π -orbital) originated from the hetero atoms (CH_2 group). Thus, $2b_1$, $1a_2$, $3b_1$, and $2a_2$ correspond roughly to the 2, 1, $1'$, and $2'$ orbitals of *cis*-butadiene. Due to the introduction of the hetero atoms (CH_2 group), the pairing properties for the alternant hydrocarbons are no longer satisfied in the five-membered ring compounds but they still behave like alternant hydrocarbons and the situation is similar to that encountered in *cis*-butadiene. Note, however, that the ground state and the doubly excited state like $(\text{HOMO})^2 \rightarrow (\text{LUMO})^2$ behave like minus states in the alternant hydrocarbons but this is not the case for the five-membered ring compounds due to the breakdown of the alternant symmetry. Thus, the low-lying doubly excited state of $(\text{HOMO})^2 \rightarrow (\text{LUMO})^2$ is also expected to interact with the singly excited states of ${}^1A_1^-$ and ${}^1A_1^+$ states.

Rydberg transitions from the highest occupied π ($1a_2$) into diffuse *s*, *p*, *d* orbitals give rise to the *R*-series states, and the second series of Rydberg transitions out of the second highest π orbital ($2b_1$) is called the *R'*-series. The energy differences of the $1a_2$ and $2b_1$ ionization potentials are 1.9, 1.5, and 1.0 eV for CP, furan, and pyrrole, respectively. Thus,

we can expect the spectra, particularly for pyrrole, to have a rich structure of *R*- and *R'*-series Rydberg bands.

A. 1,3-cyclopentadiene (CP)

CP is more similar to polyenes than to aromatic molecules, particularly with its structure resembling that of *cis*-butadiene. The optical spectrum of CP has been studied by many researchers.^{9–15} The first singlet–singlet transition was designated $N \rightarrow V_1 ({}^1A_1 \rightarrow {}^1B_2)$ by Mulliken.¹⁶ Absorption bands begin at about 4.75 eV and continue to 5.90 eV with the absorption maximum located at 5.34 eV.¹⁰ Frueholz *et al.*¹² observed an intensity maximum of a broad transition at 5.26 eV by using electron impact spectroscopy and assigned the peak as the ${}^1A_1 \rightarrow {}^1B_2$ transition. The lowest singlet excited state is computed to be ${}^1B_2^+$. Table I shows that the ${}^1B_2^+$ state is well described by a single $\pi \rightarrow \pi^*$ configuration of $1(1a_2) \rightarrow 1'(3b_1)$ and we cannot see any mixture of Rydberg character. MRMP predicts it to appear at 5.19 eV and MCQD predicts it to appear at 5.27 eV. Both show good agreement with the experiment. The oscillator strength was computed to be 0.146. The ${}^1B_2^+$ state is an ionic state. Previous studies on benzene and ozone¹ showed that the excitation energy of an ionic state is overestimated considerably at the CASSCF level and the introduction of dynamic σ – π polarization effect through the second-order perturbation reduces the excitation energy drastically. The transition energy to ${}^1B_2^+$ state is estimated to be 7.74 eV at the CASSCF level. CASSCF overestimates its energy by as much as 2.5 eV. The unreliable excitation energy of CASSCF was pointed out by Zgierski and Zerbetto¹⁷ and they stressed the need for dynamical correlation. CASPT2 (Ref. 7) also gave a similar trend and predicted the transition energy to be 5.27 eV, which is very close to the present results. SAC-CI (Ref. 6) is a method that provides very accurate transition energies of the singly excited states. SAC-CI is based on the assumption that the dynamical correlation determined in the ground state can be transferred to excited states. This is the case for the covalent and Rydberg excited states dominated by single excitations but it cannot necessarily be applied to the ionic states. SAC-CI placed the ${}^1B_2^+$ state at 5.75 eV, which is slightly too high compared to the experiment.

The second valence excited state was identified as ${}^1A_1^-$. This state comes mainly from the two single $\pi \rightarrow \pi^*$ excitations of $1(1a_2) \rightarrow 2'(2a_2)$ and its conjugate $2(2b_1) \rightarrow 1'(3b_1)$ and the double excitation of $(\text{HOMO})^2 \rightarrow (\text{LUMO})^2$ but also contains Rydberg excited configurations (see Table I). The $1 \rightarrow 2'$ and $2 \rightarrow 1'$ configurations have the nearly same weight with a different sign in the CASSCF wave function. Thus, the ${}^1A_1^-$ is a covalent state but has a multireference nature. The state was predicted to be located at 6.42 eV and 6.47 eV at the MRMP and MCQD levels, respectively. As mentioned above, the transition is pseudoparity forbidden. The computed oscillator strength is very low as expected. The location of the unobserved ${}^1A_1^-$ state in cyclic dienes is open to dispute. McDiarmid *et al.*¹³ predicted from the study of the optical absorption and electron energy loss spectra that the ${}^1A_1^-$ state lies at or below

5.8–6.2 eV. CASPT2 predicted that the ${}^1A_1^-$ state would appear at 6.31 eV, which is very close to the present value. Due to the multiconfigurational character of this state, the theoretical difficulties encountered in SAC-CI procedure, placing this transition at a higher energy of 7.05 eV above the ground state.

The third valence excited state is the ${}^1A_1^+$ state due to the strong optically allowed transitions of $1 \rightarrow 2'$ and $2 \rightarrow 1'$ with a significant contribution from the Hartree–Fock and the double excitation of $(1a_2)^2 \rightarrow (3b_1)^2$ configurations. This state is an ionic state with multireference nature (see Table I), and CASSCF significantly overestimates the transition energy. The CASSCF excitation energy of 11.05 eV is reduced to 8.11 and 8.16 eV by the addition of the dynamic σ – π polarization effect through MRMP and MCQD, respectively. The oscillator strength is computed to be 0.502, which is the strongest of all the transitions in CP treated here. Pickett *et al.*⁹ determined that the state lies at 8.06 eV from an analysis of the optical absorption spectrum, while Frueholz *et al.*¹² observed that the transition occurs at 8.03 eV by an electron impact study. Both are very close to our results. CASPT2 and SAC-CI computed the transition energy to the ${}^1A_1^+$ state to be 7.89 and 7.81 eV, respectively.

In addition to the valence excited states, there are many Rydberg transitions arising from excitations out of the highest $1a_2$ orbital. A weak feature around 5.63 eV has been characterized as the 1A_2 state corresponding to the dipole-forbidden $1a_2 \rightarrow 3s$ Rydberg excitation.¹⁴ The present results, 5.62 eV (MRMP) and 5.66 eV (MCQD), are in good agreement with the assignment.

The next region of absorption occurs from 6.20 to 6.90 eV. These values are probably members of a Rydberg series converging to the first ionization potential of CP, 8.566 eV. Sabljic *et al.*¹⁵ provided experimental assignments for all three $3p$ -Rydberg origins from a careful analysis of the polarized-selected two-photon resonant multiphoton ionization spectra, 6.25 eV for $3p B_1$, 6.26 eV for $3p A_2$, and 6.31 eV for $3p B_2$. On the other hand, Derrick *et al.*¹¹ identified the 1B_1 $3p$ -Rydberg state at 6.255 eV from the study of photoelectron spectroscopy. The present results, 6.24 eV (MRMP) and 6.29 eV (MCQD) for $3p B_1$, 6.27 eV (MRMP) and 6.32 eV (MCQD) for $3p A_2$, and 6.25 eV (MRMP) and 6.31 eV (MCQD) for $3p B_2$, are very close to their assignments. However, the ordering is not necessarily the same as in their assignment. This is understandable because of the small energetic separation (0.06 eV) between the three states. The transitions to $3p B_1$ and $3p B_2$ are dipole-allowed and both were calculated to have relatively strong intensities, while the transition to $3p A_2$ is dipole-forbidden.

Frueholz *et al.*¹² observed another feature with resolvable peaks at 6.80 and 7.05 eV. These must correspond to the $3d$ -Rydberg transitions. From the computed oscillator strength, we assigned these peaks as $3d {}^1B_2$ and $3d {}^1A_1$ transitions, respectively. Our calculations suggest that the transition to $3d {}^1B_2$ occurs at 6.91 eV (MRMP) and 6.97 eV (MCQD) and that to $3d {}^1A_1$ at 6.89 eV (MRMP) and 6.95 eV (MCQD), respectively. The transition to $3d {}^1B_2$ is computed to have a relatively strong intensity but that to $3d {}^1A_1$

is rather weak. Theory also suggests there is little splitting of the five $3d$ -Rydberg transitions, spanning 0.1 eV.

Derrick *et al.*¹¹ assigned the transition at 7.852 eV to the first $3s$ -Rydberg transition from the second highest π orbital. The calculated $3 {}^1B_1$ state is located around 7.80 eV with the oscillator strength of 0.0217. This is also close to the experiment. The corresponding CASPT2 value is 7.95 eV. However, Serrano-Andres *et al.*⁷ assigned the transition as the observed peak at 8.03 eV.¹²

B. Furan

Furan, as well as pyrrole, is of considerable importance in synthetic organic chemistry, the preparation of various drugs and polymers, and in biochemistry. Though furan differs from CP only by the substitution of an O atom for the CH_2 group, its electronic spectrum^{10,18–28} is rather different from that of CP. First we will discuss the valence excited states.

The first band in the absorption spectrum appears at 6.06 eV.^{18,19} Flicker *et al.*^{24,25} assigned the optically allowed transition at 6.06 eV as the ${}^1A_1 \rightarrow {}^1B_2$ excitation from the study of electron impact spectroscopy. Theory shows that the ${}^1B_2^+$ state is the lowest valence state of ionic nature. MRMP predicts that the ${}^1B_2^+$ state lies at 5.95 eV and MCQD predicts it to be at 5.99 eV. These values are improved from the 8.52 eV calculated at the CASSCF level by considering the σ – π polarization effect. The state is well represented by a single $\pi \rightarrow \pi^*$ excitation of $1(1a_2) \rightarrow 1'(3b_1)$ as in the case of CP. The oscillator strength is computed to be 0.158, which is comparable to the experimental value 0.12.¹⁹

The second valence excited state is $2 {}^1A_1^-$. Transition to the A_1^- state is pseudoparity forbidden. There is no experimental evidence for this transition. MRMP predicts that the $2 {}^1A_1^-$ state lies at 6.16 eV and MCQD at 6.19 eV with weak intensity. CASPT2 also predicted the $2 {}^1A_1^-$ state to be at 6.16 eV. SAC-CI prediction of 6.96 eV may be slightly too high due to the multireference nature of the ${}^1A_1^-$ state. Flicker *et al.*²⁵ assigned the peaks at 6.44 and 6.61 eV as the transition to the ${}^1A_1^-$ state, but these are peaks due to Rydberg transitions as discussed below.

The most intense feature of the absorption spectrum with a maximum at 7.79 (Ref. 18) is due to the transition to the third valence excited state, $4 {}^1A_1^+$. The electron impact investigation located the state at 7.82 eV.²⁵ MRMP placed the $4 {}^1A_1^+$ state at 7.69 eV and MCQD placed it at 7.72 eV with high intensity of 0.494. CASPT2 also predicted that the transition occurs at 7.74 eV.

Now let us discuss the Rydberg transitions. The first singlet–singlet excitation of furan is the $3s$ -Rydberg series. Robin²³ assigned the weak peak at 5.94 eV to the dipole-forbidden 1A_2 Rydberg transition. Roebber *et al.*²⁷ also assigned the peak at 5.91 eV to the $1a_2 \rightarrow 3s$ Rydberg state using the multiphoton ionization spectroscopy. The computed excitation energy is 5.84 eV. CASPT2 and SAC-CI predicted that the transition occurs at 5.92 and 6.27 eV, respectively.

The second band system observed in the absorption

spectrum of furan shows sharp bands that could be analyzed to reveal vibrational frequencies of the excited molecule.¹⁸ Derrick *et al.*²² assigned the band at 6.475 eV as the transition $1a_2 \rightarrow 3pb_2$. Cooper *et al.*²⁸ measured the resonantly enhanced multiphoton ionization spectra. Their assignment of 6.47 eV to the $3p$ Rydberg states supported the results of Derrick *et al.* The computed $3p$ 1B_1 transition energy is 6.40 eV, which is in good agreement with the experiment. Theory predicts that another dipole-allowed $3p$ -Rydberg state, 1B_2 , lies above 1B_1 . Both have relatively strong intensities. The dipole-forbidden $3p$ -Rydberg transition to 1A_2 has not been observed explicitly but theory predicts that the state exists around 6.54 eV, slightly above the $3p$ 1B_2 and $3p$ 1B_1 states.

The states following the three $3p$ -Rydberg states are five $3d$ -Rydberg states. The present theory predicts that five states lie in the range of 6.98–7.29 eV with low intensities except for 3 1B_2 (the oscillator strength of the transition to 3 1B_2 is computed to be 0.0103). Derrick *et al.*²² assigned the absorption at 7.284 eV as the 3 1A_1 transition. Cooper *et al.*²⁸ assigned the peak 7.43 eV to the $3d$ Rydberg states. The 3 1A_1 state is predicted to be located at 7.26 eV (MRMP) and at 7.29 eV (MCQD) with very weak intensity.

A band at 7.39 eV with high intensity among the third band system of the absorption spectrum was first observed by Pickett.¹⁸ Watanabe and Nakayama²⁰ suggested that the transition at 7.38 is due to the Rydberg excitation arising from excitations out of the highest occupied $1a_2$ orbitals. Derrick *et al.*,²² however, suggested from a study of the photoelectron spectroscopy that the peak appearing at 7.380 eV is due to the transition from the second highest $2b_1$ to $3s$ Rydberg orbitals. The calculated $2b_1 \rightarrow 3s$ transition energies are 7.31 eV (MRMP) and 7.25 eV (MCQD). CASPT2 predicted the slightly lower excitation energy of 7.21 eV while SAC-CI predicted a slightly higher value of 7.62 eV. The transition is predicted to have a relatively high intensity of 0.015.

C. Pyrrole

The electronic absorption spectrum of pyrrole has been investigated by many researchers.^{10,21,29,30,32} In the range of 5–8 eV, it has a very complex structure with many overlapping Rydberg series. Several other techniques^{24–26,28,31} have been used to study the molecule in the near and ultraviolet regions. However, no complete assignment exists.

The first dipole-allowed transitions were observed at 5.88 and 5.96 eV in the optical spectrum³⁰ and at 5.89 and 5.98 eV in the electron energy-loss spectrum²⁵ of pyrrole. Horvath and Kiss²¹ assigned the peak at 5.97 eV as the valence $\pi \rightarrow \pi^*$ transition. Mullen and Orloff³⁰ assigned the first discrete system beginning at 5.86 eV as a valence transition to 1B_2 . Derrick *et al.*³¹ made a thorough revision of the assignment based on the photoelectron results, reaching the conclusion that the band can be rationalized in terms of Rydberg series. They assigned the peak at 5.87 eV as the first member of the Rydberg series $1a_2 \rightarrow npb_2$ leading to the first ionization potential of 8.21 eV. Bavia *et al.*³² studied the

spectrum of pyrrole in the vapor and crystal and confirmed Dirreck's assignment that the transition at 5.86 eV is due to the Rydberg excitation. On the other hand, Flicker *et al.*^{24,25} suggested that one of the peaks at 5.89 and 5.98 eV is due to the transition to valence-type 1B_2 state. Cooper *et al.*²⁸ studied the resonant multiphoton ionization spectra and also suggested that the band at 5.86 eV is a valence transition. The congested electronic structure of pyrrole has led to several contradictory interpretations of the data.

Early theoretical attempts to assign the observed spectrum assumed that the lowest energy states were $\pi \rightarrow \pi^*$ transitions, but most theories find them to be the Rydberg transition. Butscher and Thunemann³³ calculated the position of the first valence excited state, 1B_2 , to be at 7.70 eV using the multireference CI with doubles (MRD-CI) based on natural orbitals. Rawlings and Davidson³⁴ applied the second-order Rayleigh–Schrödinger B_k method to pyrrole and predicted no valence excited 1B_2 state below 8 eV. On the other hand, the recent SAC-CI (Ref. 6) and CASPT2 (Ref. 7) computed the valence type 1B_2 excitation energy to be 6.63 eV and 6.00 eV, respectively. Thus, theoretical results are also conflicting.

Therefore we performed careful calculations changing the active space of CASSCF and also using a variety of basis sets. All calculations showed similar results, and we concluded that the valence-type $^1B_2^+$ state lies around 6.51 eV. This value is too high compared to the experimental value and the calculated value by CASPT2. The difference from the CASPT2 result is as much as 0.5 eV. Table I shows that the valence type $^1B_2^+$ state is represented by a mixture of the valence type transitions of $1(1a_2) \rightarrow 1'(3b_1)$ and its conjugate of $2(2b_1) \rightarrow 2'(2a_2)$ and includes a large fraction of Rydberg configurations. The valence type $^1B_2^+$ state of pyrrole is somewhat different in character from that in CP and furan. The oscillator strength was computed to be 0.100, which is weaker than that in CP and furan. The $^1B_2^+$ state is expected to be among the Rydberg bands of $1a_2 \rightarrow 3p$, $1a_2 \rightarrow 3d$, and $2b_1 \rightarrow 3p$ transitions. The reason for the relatively large discrepancy in the calculated excitation energy is that CASSCF may have overestimated the contribution of the Rydberg configuration. In general, the second-order energy originated from the Rydberg configurations is rather small compared to that originated from the valence configurations with ionic character.

There are three $1a_2 \rightarrow 3p$ Rydberg transitions in the energy range of 5.74–5.88 eV. The first Rydberg 1 1B_2 state is computed at 5.87 eV (MRMP) and 5.88 eV (MCQD) with relatively high intensity. The 1B_2 state is represented by a Rydberg configuration of $1a_2 \rightarrow 3pb_1$. Below the 1B_2 state, there is also a Rydberg type 1B_1 state. This Rydberg transition $1a_2 \rightarrow 3pb_2$ also has rather high intensity. Thus, we tentatively assigned both two peaks observed in the absorption spectrum as the Rydberg transitions.

The first valence singlet state is the $^1A_1^-$, which comes above the Rydberg states and is represented by a conjugated configurations of $1(1a_2) \rightarrow 2'(2a_2)$ and $2(2b_1) \rightarrow 1'(3b_1)$. There has been little discussion on the position of the pseudoparity forbidden transition to the $^1A_1^-$. The present theory predicts that it exists around 6.0 eV with weak inten-

sity, which is consistent with the CASPT2 prediction of 5.92 eV. Natural orbital CI placed $^1A_1^-$ state at 6.51 eV with DZ plus diffuse orbitals³⁵ and at 6.73 eV with DZP plus diffuse orbitals.³³ SAC-CI also located the $^1A_1^-$ state at 6.96 eV. Due to the multireference nature of the state, these previous methods placed this state at considerably higher energies. Flicker *et al.*²⁵ tentatively assigned the peak at 5.22 eV as $^1A_1^-$ but this seems to be somewhat smaller compared to the theory. The transition at 5.22 eV is due to the Rydberg excitation as discussed below.

The most intense bands in the spectrum appear in the range of 7.26–7.86 eV. This is mainly due to the $^1A_1^+$ transition although many Rydberg series are expected to occur in this energy range. The $^1A_1^+$ excitation energies were computed to be 7.48 eV (MRMP) and 7.51 eV (MCQD), respectively. The oscillator strength is 0.562, which is the most intense transition in pyrrole.

A weak transition at 5.22 eV in pyrrole was assigned as the lowest singlet–singlet dipole forbidden transition in that molecule.^{23–25} The theory suggests that the lowest excitation in pyrrole is the $1a_2 \rightarrow 3s$ Rydberg transition. The present theory, however, predicts it to occur at 4.91 eV. The difference between theory and experiment is 0.3 eV, which is somewhat beyond the error of the present theory in estimating the Rydberg transition energy. The $1a_2 \rightarrow 3s$ transition energy was computed to be 5.08 eV at the CASPT2 level. Bavia *et al.*³² determined by best fitting the experimental $3s$ Rydberg-type terms that the origin of the weak system is around 4.96 eV. Theoretical results are close to the value estimated by Bavia *et al.*

The $3s$ Rydberg transition from the second highest $2b_1$ is expected to occur around 5.65 eV with very weak intensity. However, there is no experimental evidence. Derrick *et al.*³¹ surmised that the 6.23 eV and 6.32 eV peaks correspond to the origin and the ν_1 vibration of the Rydberg series $2b_1 \rightarrow ns$. Their assignment, however, was insufficient to explain the theoretical results.

The Rydberg states following the three $1a_2 \rightarrow 3p$ Rydberg transitions are $1a_2 \rightarrow 3d$ which overlap with the $2b_1 \rightarrow 3p$ Rydberg transitions. Theory suggests that the five $3d$ -Rydberg transitions should occur in the range of 6.37–6.64 eV while three $3p$ Rydberg transitions from the second highest π orbital should appear in 6.48–6.70 eV. All the transitions in the $3d$ -Rydberg transitions are dipole-forbidden or very weak while two of the three $3p$ -Rydberg transitions have considerable intensity. The peak at 6.78 eV is, according to Derrick *et al.*,³¹ the origin of the Rydberg series $1a_2 \rightarrow nda_2$ while the peak at 6.43 eV was characterized as the Rydberg transition $1a_2 \rightarrow 3db_2$.³²

The $3d$ Rydberg transitions from the second highest $2b_1$ are predicted to lie in the range of 7.12–7.36 eV, slightly below the valence $^1A_1^+$ state. Flicker *et al.*²⁵ observed five peaks in the energy range of 7.26–7.86 eV. The main peak must be due to the most intense valence transition to the $^1A_1^+$ state but others may come from the $R'(3d)$ Rydberg transitions. Derrick *et al.*³¹ explained the observed bands in the region of 7.1–7.9 eV by Rydberg transition with quantum number of $n > 3$ arising from $1a_2$ orbitals. This may be an

alternative explanation of the bands but we did not calculate such Rydberg transition in the present study.

IV. CONCLUSIONS

MRMP and MCQD were used to study the valence and Rydberg excited states in the range of 5–8 eV of five-membered ring compounds, cyclopentadiene, furan, and pyrrole. Both methods gave very similar transition energy with a difference of less than 0.05 eV although MRMP gave slightly lower values than MCQD. Both methods can describe all kinds of excited states with the same accuracy. The calculated results agree well with experimentally measured spectra. Valence excited states were interpreted in term of the pairing properties for the alternant hydrocarbons. We discussed the unobserved $1A_1 \rightarrow A_2^-$ transition with very weak intensity, which is hidden under the strong $1A_1 \rightarrow B_2^+$ transition. Overall, the present theory supports the assignments recently made by Serrano-Andres *et al.* based on the CASPT2 results. However, there remain some discrepancies in the assignment of the spectrum of pyrrole. The present theory has proved to be of great utility in predicting and interpreting experimental electronic spectra of medium-sized molecules.

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