

Theoretical study of valence and Rydberg excited states of benzene revisited¹

Tomohiro Hashimoto*, Haruyuki Nakano, Kimihiko Hirao

Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, Tokyo 113, Japan

Received 26 December 1997; accepted 6 January 1998

Abstract

The multireference Møller–Plesset perturbation (MRMP) theory with complete active space self-consistent field (CASSCF) reference functions is applied to the study of the singlet and triplet valence π – π^* excited states and Rydberg excited states of benzene in the ultraviolet region. The overall accuracy of MRMP is surprisingly high. The average deviations of the excitation energies from the available experimental values are 0.1 eV for the valence excited states and 0.15 eV for the Rydberg states. A comparison is made with recent results of single reference-based methods. It is concluded that MRMP is able to describe satisfactorily excited states with a double excitation character, while single reference-based methods are not. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Benzene; Valence excited states; Rydberg excited states

1. Introduction

The ultraviolet (UV) spectrum of the benzene molecule has been a subject of many experimental and theoretical investigations for a long time. There are four excited states in the UV region originating from π – π^* excitation: 1^1B_{2u} , 1^1B_{1u} and the degenerate 1^1E_{1u} and 1^1E_{2g} , states of D_{6h} symmetry. Among them, absorption bands located at 4.90, 6.20, and 6.94 eV are now unambiguously assigned to the states of symmetry 1^1B_{2u} , 1^1B_{1u} and 1^1E_{1u} , respectively [1]. The other valence excited state of 1^1E_{2g} has been observed in the $S_1 \rightarrow S_n$ absorption located at 7.80 eV [2].

Theoretically, some simple parameterized semi-empirical methods work much better than expected.

On the other hand, it has been rather difficult to describe the excited states of benzene accurately with ab initio methods. However, the development of ab initio molecular orbital theories enables us to calculate the excited states with high accuracy. In our previous studies, to clarify the applicability of our methodology, we have applied the multireference Møller–Plesset perturbation (MRMP) theory [3] with complete active space self-consistent field (CASSCF) [4] reference functions to the study of valence and Rydberg excited states with valence double zeta plus single d-type polarization quality basis set [5], followed by the valence π – π^* excited states in a refined theory with valence triple zeta plus double d-type polarization quality basis set [6]. In the latter study, we showed that the approach with pairing properties would be of great value in understanding the valence excited states of the alternant hydrocarbons. These results compare well with experimental results. Some studies [10–12] were

* Corresponding author.

¹ Dedicated to Professor Sigeru Huzinaga on the occasion of his 70th birthday.

published after our work. Christiansen et al. carried out single- and double-coupled cluster (CCSD) calculations using a very large basis set [11]. Their results, with over 400 basis functions, may almost approach the basis set limit. However, the results were slightly higher than the experimental values since they included only single and double excitation effects. Another coupled-cluster calculation with triple excitations by Del Bene et al. had better agreement with the experimental data, although a smaller basis set was used [12]. It seems that the extension of the basis set is less significant than the improvement of many-electron function. It is also noted that these single reference-based methods cannot adequately treat the 1^1E_{2g} state which has the double excitation character.

In this study, we computed again both valence $\pi-\pi^*$ and Rydberg excited states with a larger basis set than our previous studies to investigate the influence of f-function on carbon atoms and to reconfirm the usefulness of the multireference treatment. We also used the same molecular structure as used previously [7, 10, 11], although the difference between the excitation energies at the CASSCF level and the ones calculated with the geometry in our previous work is about only 0.03 eV for singlet valence states.

2. Computational details

The molecule is placed in the xy plane. We used the same molecular structure as in the CASPT2 studies with C–C and C–H bond lengths of 1.395 Å and 1.085 Å, respectively, which are close to the experimental values [7, 10, 11]. The basis set used was Dunning's cc-pVTZ basis set for carbon atoms and cc-pVDZ for hydrogen atoms [8], augmented with Rydberg functions ($8s8p8d/1s1p1d$) placed at the center of molecule. We contracted the ($8s8p8d$) [9] primitive set to a ($1s1p1d$) set by calculating the benzene cation with the primitive functions in the UHF approximation, and selecting the lowest Rydberg-type virtual orbitals of each angular momentum component.

Firstly, we carried out the state-averaged CASSCF calculations. All the valence states of benzene considered here were averaged with 6 π electrons distributed among 12 π orbitals for singlet and triplet states. The 12 valence π orbitals were composed of

6 valence π orbitals and 6 extended π orbitals: two a_{2u} , two e_{1g} , two e_{2u} and two b_{2g} , orbitals. Rydberg states were averaged with the active space by adding appropriate Rydberg orbitals to valence π and π^* orbitals. The added Rydberg orbitals were $3d_\sigma$, $3d_\delta$ and $3s$ orbitals for the description of B_{1g} , B_{2g} and E_{1g} states; $3d_\pi$ for A_{1g} , A_{2g} and E_{2g} ; $3p_\sigma$ for A_{1u} , A_{2u} and E_{2u} ; and $3p_\pi$ for B_{1u} , B_{2u} and E_{1u} states.

Then the second-order MRMP procedure was applied to each individual state to introduce a dynamic $\sigma-\pi$ polarization effect. Oscillator strengths were calculated using the CASSCF transition dipole moments and the MRMP transition energies. All the calculations were performed in D_{2h} symmetry.

3. Results and discussion

3.1. Valence $\pi-\pi^*$ excited states

First we describe pairing properties of the alternant hydrocarbons satisfied for the Hückel and PPP Hamiltonians. Let the occupied π orbitals be designated by $1, 2, \dots$, from the highest one down, and the unoccupied ones by $1', 2', \dots$, from the lowest one up. The orbitals i and i' are called a conjugated pair. In the case of benzene, the symmetry class of the conjugated pair of orbitals (i, i') is (a_{2u}, b_{3g}) or (e_{1g}, e_{2u}) in D_{6h} symmetry. Therefore, the possible valence singly excited states arising from $i \rightarrow j'$ transitions have the symmetry A_{1g} , E_{2g} , B_{1u} , B_{2u} , and E_{2u} . Because of the relationship of the π orbital energy, $\epsilon_i = -\epsilon_{i'} + \text{constant}$, the energy of the singly excited configuration resulting from the $i \rightarrow j'$ transition is equal to that from the $j \rightarrow i'$ transition. The linear combinations of the two degenerate configurations generate the covalent *minus* (–) and ionic *plus* (+) states, which are defined as follows:

$${}^1\Psi^\pm(ij') = |(ij' \pm i'j)(\alpha\beta - \beta\alpha)/2|$$

$${}^3\Psi^\pm(ij') = |(ij' \pm i'j)(\alpha\beta + \beta\alpha)/2|$$

We use the abbreviation (ij') to represent a conjugated pair of one-electron transitions of $i \rightarrow j'$ and $j \rightarrow i'$. The *minus* state is a covalent state while the *plus* state is an ionic state for both singlet and triplet states, which stems from the characteristics of the states in the valence bond description. The covalent *minus*

Table 1
Main configurations in CASSCF wavefunctions of valence excited states of benzene^a

Singlet			Triplet			
State	Transitions	Coefficients	State	Transitions	Coefficients	
$1^1A_{1g}^-(1^1A_g^-)$	$(3)^2(2)^2(1)^2$	0.941	$1^3B_{2u}^+(1^3B_{3u}^+)$			
	$1,2 \rightarrow 1',2'$	-0.162				
	$(1)^2 \rightarrow (1')^2$	-0.134				
	$(2)^2 \rightarrow (2')^2$	-0.134				
$1^1B_{2u}^-(1^1B_{3u}^-)$	$1 \rightarrow 2'$	0.633		$1 \rightarrow 2'$	0.686	
	$2 \rightarrow 1'$	-0.633		$2 \rightarrow 1'$	0.686	
	$1,2 \rightarrow 1',3'$	0.162				
	$1,3 \rightarrow 1',2'$	-0.181				
	$2,3 \rightarrow (1')^2$	0.148				
	$2,3 \rightarrow (2')^2$	-0.148				
$1^1B_{1u}^+(1^1B_{2u}^+)$	$1 \rightarrow 1'$	0.678		$1^3B_{1u}^-(1^3B_{2u}^-)$	$1 \rightarrow 1'$	0.661
	$2 \rightarrow 2'$	0.678			$2 \rightarrow 2'$	0.660
			$3 \rightarrow 3'$		0.188	
$1^1E_{1u}^+(1^1B_{3u}^+)$	$1 \rightarrow 2'$	0.646	$1^3E_{1u}^-(1^3B_{3u}^-)$	$1 \rightarrow 2'$	-0.649	
	$2 \rightarrow 1'$	0.646		$2 \rightarrow 1'$	0.649	
	$2 \rightarrow 4'$	0.144		$1,2 \rightarrow 1',3'$	0.175	
		$1,3 \rightarrow 1',2'$		0.158		
$1^1E_{1u}^+(2^1B_{2u}^+)$	$1 \rightarrow 1'$	0.646	$1^3E_{1u}^-(2^3B_{2u}^-)$	$1 \rightarrow 1'$	-0.649	
	$2 \rightarrow 2'$	-0.646		$2 \rightarrow 2'$	0.649	
	$1 \rightarrow 4'$	-0.144		$1,2 \rightarrow 2',3'$	0.160	
				$2,3 \rightarrow 1',2'$	0.216	
$1^1E_{2g}^-(2^1A_g^-)$	$1 \rightarrow 3'$	-0.383	$1^3E_{2g}^-(1^3A_g^-)$	$1 \rightarrow 3'$	-0.474	
	$3 \rightarrow 1'$	0.577		$3 \rightarrow 1'$	0.668	
	$(1)^2 \rightarrow (1')^2$	-0.434		$1,1' \rightarrow 2,2'$	0.331	
	$1,2 \rightarrow 1',2'$	-0.289			0.252	
		0.167			-0.218	
$(2)^2 \rightarrow (1')^2$	0.199					
$1^1E_{2g}^-(1^1B_{1g}^-)$	$2 \rightarrow 3'$	-0.383	$1^3E_{2g}^-(1^3B_{1g}^-)$	$2 \rightarrow 3'$	-0.474	
	$3 \rightarrow 2'$	0.577		$3 \rightarrow 2'$	0.668	
	$1,2 \rightarrow (2')^2$	-0.448		$1,2 \rightarrow (2')^2$	-0.218	
	$(2)^2 \rightarrow 1',2'$	0.402		$(2)^2 \rightarrow 1',2'$	-0.254	
	$1,2 \rightarrow (3')^2$	0.129		$1,2 \rightarrow (1')^2$	0.218	
	$(3)^2 \rightarrow 1',2'$	-0.154		$(1)^2 \rightarrow 1',2'$	0.254	

^a The six valence π orbitals are in the order of energy: $a_{2u}(1b_{1u})$, $e_{1g}(1b_{2g})$, $e_{1g}(1b_{3g})$, $e_{2u}(2b_{1u})$, $e_{2u}(1a_u)$, and $b_{2g}(2b_{3g})$ in D_{6h} symmetry. The symmetry class in D_{2h} group is given in parentheses. They are designated by 3, 2, 1, 1', 2', 3', respectively. The 4' orbital is one of the extended active orbitals with $a_{2u}(3b_{1u})$ symmetry.

states and the ionic *plus* states exhibit different behavior as far as electron correlation is concerned.

In Table 1, we observe that the above pairing properties are also satisfied to a high degree, even at the CASSCF level [6]. While ionic *plus* states consist

almost entirely of single excitations, covalent *minus* states include a large fraction of doubly excited configurations, especially for *g* states. For example, the second largest contribution in the $1^1E_{2g}^-(2^1A_g^-)$ state is the HOMO \rightarrow LUMO double excitation

whose CI coefficient is -0.434 . The ionic $1^1E_{1u}^+$ state includes a considerable amount of transition to the extended orbital beyond the valence π orbitals designated by $4'$. This means that six active π orbitals are not large enough to treat the dynamic correlation as a perturbation for the ionic *plus* states, as revealed in our previous study [6].

The calculated excitation energies are listed with recent theoretical results in Table 2. CASSCF tends to overestimate the excitation energies as compared to experimental values. The largest deviation, which is more than 1 eV, is found in the ionic *plus* states for both singlet and triplet states. MRMP theory corrects the deficiency and represents a great improvement over CASSCF. The MRMP excitation energies are quite close to the experimental values both for ionic *plus* and covalent *minus* states. For the covalent *minus* states, including the ground state, some of the dynamic σ - π polarization effects cancel each other out due to the pairing properties. Thus, the dynamic σ - π polarization effect of covalent *minus* excited states is usually of the same order as that of the ground state. On the other hand, the dynamic σ - π polarization effect of the ionic *plus* excited states is much more significant than that of a covalent ground state, and lowers the excitation energies by more than 1 eV. The average deviations are 0.06 eV for singlet states and 0.14 eV for triplet states. It is also noted that covalent *minus* states always give lower energy values than the corresponding ionic *plus* states.

Figs. 1 and 2 show the schematic summary of the calculated results of the singlet and triplet states, respectively. SDT π -CI and CASSCF, which include only the π - π correlation, give excitation energies that are too large, especially for the ionic *plus* states. By including the influence of the σ electrons in a perturbation treatment, MRMP energies are in good agreement with experimental data, as mentioned above. Overall, the CCSD method with a very large basis set overestimates, especially the excitation energy for 1^1E_{2g} state, which is more than 1 eV higher than the experimental data [11]. In estimating triple excitation effects, the CCSD(\tilde{T}) results become closer to the experimental results, even when using a smaller basis set, although the molecular structure is different [12]. However, the CCSD(\tilde{T}) method is also unable to give an adequate result for the 1^1E_{2g} state. The effects of higher-body excitations are more important than

those of enlargement of the basis set. Furthermore, since the difference between our previous results [6] on carbon atoms without f-functions and the present ones with f-functions are within 0.1 eV, the improvement in the one-electron function does not have a great influence on the excitation energies of the valence excited states of benzene. Although these single reference-based methods cannot treat the covalent excited states with a double excitation nature such as 1^1E_{2g} and 1^3E_{2g} adequately, our MRMP and CASPT2 can handle these states as well as those characterized as single excitations.

3.2. Rydberg excited states

The main configurations in the CASSCF wavefunctions of Rydberg excited states are listed in Table 3 and the calculated excitation energies are collected in Table 4. The Rydberg states are well characterized as single excitations from the degenerate HOMOs. With D_{6h} symmetry, the Rydberg excited states consist mainly of single dominant, singly excited configurations except the $E_{1g}(3d_\delta)$ states, which have at most two dominant configurations. The Rydberg excitation energies are usually calculated to reasonable accuracy even at the CASSCF level, although they are slightly underestimated. Adding the second-order correlation effects, MRMP excitation energies become larger and closer to the experimental data. Thus, the dynamic correlation effect on Rydberg excited states is less significant than that on the ground state. The magnitude of this effect depends on the character of the Rydberg state. The differences between the CASSCF and MRMP energies are 0.0 eV for $3p_\pi$ and 0.2–0.25 eV for $3s$, $3p_\sigma$, and $3d_\pi$ type states. The largest changes appear in the $E_{2g}(3d_\delta)$, $B_{1g}(3d_\sigma)$ and $B_{2g}(3d_\sigma)$ states (about 0.4 eV). Consequently, the MRMP excitation energies are higher than the experimental values by 0.25 eV for these states. The difference between the present results and the previous ones [5] using Dunning's cc-pVDZ basis set is 0.2 eV. This is due to the problem of how to adopt the ground-state energy rather than the basis set. In applying the MRMP procedure for the ground state, we used the state-averaged CASSCF reference function, while the state-specific CASSCF function was used as a reference in the previous study [5].

Table 2
Valence $\pi-\pi^*$ excitation energies (eV) of benzene with 12 active π orbitals

State	Excitation energy (eV)							Oscillator strength	
	CASSCF ^a	MRMP ^a	Expt. ^b	CASPT2 ^c	SOPPA ^d	CCSD ^e	CCSD(\tilde{T}) ^f	Calculated	Expt.
Singlet									
$1^1B_{2u}^-$	4.94	4.70	4.90	4.84	4.69	5.18	4.74	0.0000	
$1^1B_{1u}^+$	7.55	6.21	6.20	6.30	6.01	6.48	6.17	0.0000	
$1^1E_{1u}^+$	8.77	6.93	6.94	7.03	6.75	7.23	6.99	0.8912	1.25 ^g
$1^1E_{2g}^-$	8.05	7.82	7.80	7.90		9.17		0.0000	Forbidden
Triplet									
$1^3B_{1u}^-$	3.89	3.89	3.95	3.89	3.75				
$1^3E_{1u}^-$	4.85	4.53	4.76	4.50	4.48				
$1^3B_{2u}^+$	6.77	5.54	5.60	5.44	5.50				
$1^3E_{2g}^-$	7.16	7.02	6.83	7.03	7.41				

^a Ground state energy (Hartree): CASSCF (6e,12o) = -230.851943, MRMP = -231.708774; C[4321], H[21], CM[111], 219CGTOs.

^b Ref. [1] for 1^1B_{2u} , 1^1B_{1u} , and 1^1E_{1u} states; Ref. [2] for 1^1E_{2g} state; Ref. [13] for 1^3B_{1u} , 1^3E_{1u} , and 1^3B_{2u} states; Ref. [14] for 1^3E_{2g} state.

^c Ref. [7]; C[431], H[21], CM[111], 147 CGTOs.

^d Ref. [10]; C[431], H[21], CM[111], 147 CGTOs.

^e Ref. [11]; C[5432], H[432], CM[222], 432 CGTOs.

^f Ref. [12]; C[532], H[32], 198 CGTOs.

^g Ref. [15].

3.3. Internal, semi-internal, and external contributions to the second-order correlation

wavefunction in Table 6 is in the range 75–78% and insensitive to the state, indicating that MRMP can give a well-balanced description for each state considered here. The total differential correlation effects

The weight of the respective reference

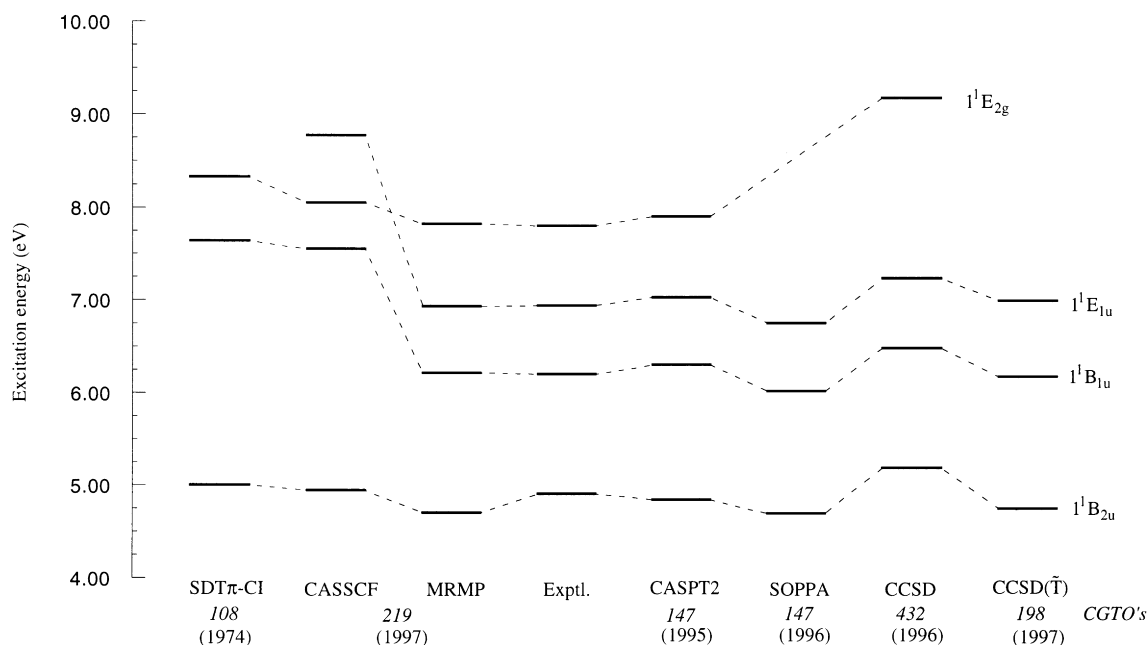


Fig. 1. Schematic summary of the calculated results of the singlet valence $\pi-\pi^*$ excitation energies of benzene.

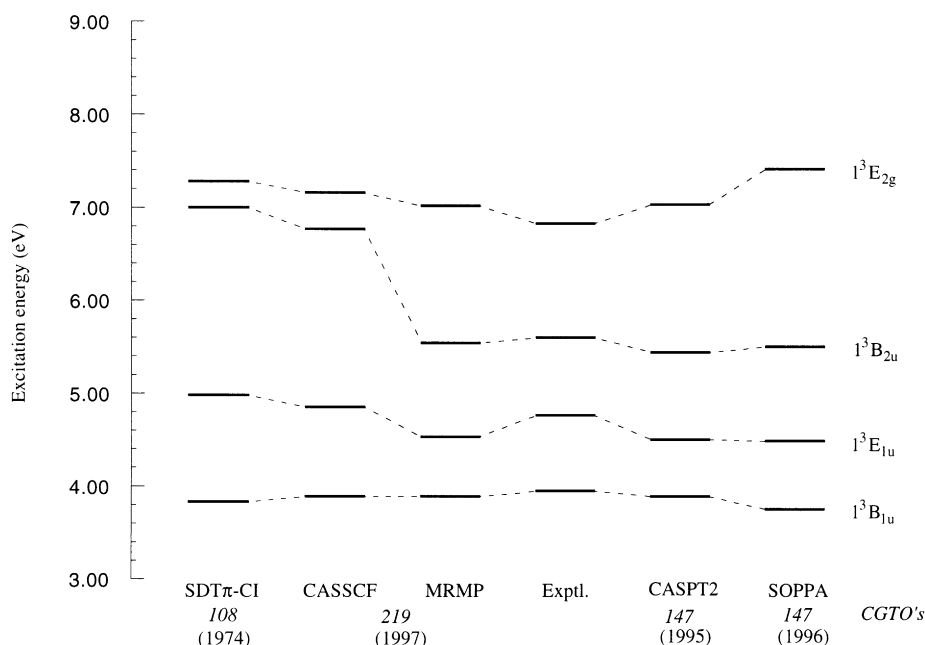


Fig. 2. Schematic summary of the calculated results of the triplet valence $\pi-\pi^*$ excitation energies of benzene.

with respect to the ground state in Table 5 are negative for the valence excited states, and positive for the Rydberg excited states. It means that the second-order correlation is larger in valence excited states and smaller in Rydberg excited states compared to the ground state, as mentioned above. This correlation effect is insensitive to the Rydberg excited state, while

Table 3

Main configurations in CASSCF wavefunctions of singlet Rydberg excited states of benzene

State	Transition	Coefficients
$1^1E_{1g}(3s)$	$e_{1g} \rightarrow 3s$	0.936
$1^1A_{2u}(3p_\sigma)$	$e_{1g} \rightarrow 3p_1$	0.670
$1^1E_{2u}(3p_\sigma)$	$e_{1g} \rightarrow 3p_1$	0.668
$1^1A_{1u}(3p_\sigma)$	$e_{1g} \rightarrow 3p_1$	0.667
$2^1E_{1u}(3p_\pi)$	$e_{1g} \rightarrow 3p_0$	0.944
$2^1E_{1g}(3d_\delta)$	$e_{1g} \rightarrow 3d_2$	0.621
	$e_{1g} \rightarrow 3d_0$	0.349
$1^1B_{1g}(3d_\sigma)$	$e_{1g} \rightarrow 3d_2$	0.621
$1^1B_{2g}(3d_\sigma)$	$e_{1g} \rightarrow 3d_0$	0.689
$3^1E_{1g}(3d_\delta)$	$e_{1g} \rightarrow 3d_0$	0.869
	$e_{1g} \rightarrow 3d_2$	0.244
$2^1A_{1g}(3d_\pi)$	$e_{1g} \rightarrow 3d_1$	0.667
$2^1E_{2g}(3d_\pi)$	$e_{1g} \rightarrow 3d_1$	0.667
$1^1A_{2g}(3d_\pi)$	$e_{1g} \rightarrow 3d_1$	0.667

state-specific for the valence excited states—much larger in magnitude for the ionic *plus* states and of the same order as that of the ground state for the covalent *minus* states.

In terms of the Fermi sea determined by the reference function the first-order corrections to the wavefunction may be classified in terms of the number (0, 1, or 2) of external orbitals introduced as internal, semi-internal, and external. These contributions are summarized in Tables 5 and 6. The internal contribution is expected to be small for all the excited states since we start with the CASSCF reference wavefunction. The external term resembles the dynamical pair correlation of the closed-shell. The sign of the differential external term with respect to the ground state is negative for both the valence and Rydberg states. Note in Table 6 that the weight of the external term is almost constant. The semi-internal contribution represents the dynamical polarization effect. The differential semi-internal terms are negative for the valence excited states but positive for the Rydberg states. Thus, the $\sigma-\pi$ polarization effect is opposite for valence and Rydberg excited states. The semi-internal term cancels out the external term for the Rydberg excited states. Thus, the excitation

Table 4
Singlet Rydberg excitation energies (eV) of benzene

State	Excitation energy (eV)						
	CASSCF ^a	MRMP ^a	Expt. ^b	CASPT2 ^c	SOPPA ^d	CCSD ^e	CCSD(\bar{T}) ^f
$1^1E_{1g}(3s)$	6.34	6.52	6.33	6.38	6.18	6.56	6.25
$1^1A_{2u}(3p\sigma)$	6.75	6.99	6.93	6.86	6.70	7.09	6.80
$1^1E_{2u}(3p\sigma)$	6.81	7.06	6.95	6.91	6.76	7.17	6.88
$1^1A_{1u}(3p\sigma)$	6.88	7.12	–	6.99	6.83	7.26	6.97
$2^1E_{1u}(3p\pi)$	7.29	7.29	7.41	7.16	7.03	7.50	
$2^1E_{1g}(3d\delta)$	7.32	7.69	–	7.57	7.34	7.67	
$1^1B_{1g}(3d\sigma)$	7.33	7.70	7.46	7.58	7.35	7.75	
$1^1B_{2g}(3d\sigma)$	7.33	7.70	7.46	7.58	7.35	7.76	
$3^1E_{1g}(3d\delta)$	7.39	7.81	7.54	7.57	7.40	7.77	
$2^1A_{1g}(3d\pi)$	7.64	7.82	7.80	7.74	7.56	7.98	
$2^1E_{2g}(3d\pi)$	7.61	7.85	7.81	7.77	7.55	7.97	
$1^1A_{2g}(3d\pi)$	7.64	7.87	–	7.81	7.59	8.01	

^a Ground state energy (Hartree): CASSCF (6e,12o) = -230.851943, MRMP = -231.708774; C[4321], H[21], CM[111], 219CGTOs.

^b Ref. [16] for 1^1E_{1g} state; Ref. [17] for 1^1A_{2u} , 2^1A_{1g} , and 2^1E_{2g} states; Ref. [18] for 1^1A_{2u} , 1^1E_{2u} , and 2^1E_{1u} states; Ref. [19] for 1^1B_{1g} and 1^1B_{2g} states; Ref. [20] for 3^1E_{1g} , 2^1A_{1g} , and 2^1E_{2g} states.

^c Ref. [7]; C[431], H[21], CM[111], 147 CGTOs.

^d Ref. [10]; C[431], H[21], CM[111], 147 CGTOs.

^e Ref. [11]; C[5432], H[432], CM[222], 432 CGTOs.

^f Ref. [12]; C[532], H[32], 198 CGTOs.

Table 5
Second-order correlation energy partitioning into internal, semi-internal, and external contributions^a

State	Total	Internal	Semi-internal	External
Ground state				
$1^1A_{1g}^-$	-0.857379	-0.008100	-0.215077	-0.634202
Valence excited states				
$1^1B_{2u}^-$	-8.665	-0.554	-1.168	-6.944
$1^1B_{1u}^+$	-49.314	-2.305	-38.899	-8.109
$1^1E_{1u}^+$	-67.732	-1.985	-58.092	-7.655
$1^1E_{2g}^-$	-8.814	0.173	-0.901	-8.086
$1^3B_{1u}^-$	0.142	0.060	2.655	-2.574
$1^3E_{1u}^-$	-11.733	-0.089	-7.792	-3.852
$1^3B_{2u}^+$	-44.988	-1.086	-40.597	-3.306
$1^3E_{2g}^-$	-4.976	0.354	-0.213	-5.117
Rydberg excited states				
$1^1E_{1g}(3s)$	7.006	0.295	34.280	-27.568
$1^1A_{2u}(3p\sigma)$	9.401	0.280	34.717	-25.595
$1^1E_{2u}(3p\sigma)$	9.619	0.352	34.933	-25.666
$1^1A_{1u}(3p\sigma)$	9.255	0.389	34.616	-25.751
$2^1E_{1u}(3p\pi)$	0.441	1.393	37.248	-38.199
$2^1E_{1g}(3d\delta)$	14.027	0.018	34.757	-20.748
$1^1B_{1g}(3d\sigma)$	14.257	0.039	35.026	-20.808
$1^1B_{2g}(3d\sigma)$	14.056	0.024	34.861	-20.829
$3^1E_{1g}(3d\delta)$	15.980	0.076	36.360	-20.456
$2^1A_{1g}(3d\pi)$	7.436	0.921	38.199	-31.684
$2^1E_{2g}(3d\pi)$	9.144	0.915	39.099	-30.870
$1^1A_{2g}(3d\pi)$	9.051	0.928	38.961	-30.838

^a Energies for ground state are in hartree. Values for excited states are relative energies in millihartree with respect to the ground state.

Table 6

Weight of reference wavefunction, internal, semi-internal, and external contributions (%)

State	Reference	Internal	Semi-internal	External
Valence state				
$1^1A_{1g}^-$	78.0	0.3	7.6	14.1
$1^1B_{2u}^-$	76.9	0.4	8.5	14.3
$1^1B_{1u}^+$	75.3	0.4	10.3	14.0
$1^1E_{1u}^+$	70.8	0.4	15.6	13.2
$1^1E_{2g}^-$	76.6	0.3	8.9	14.2
$1^3B_{1u}^-$	77.5	0.3	7.9	14.2
$1^3E_{1u}^-$	76.9	0.3	8.6	14.2
$1^3B_{2u}^+$	75.7	0.3	10.1	13.9
$1^3E_{2g}^-$	70.4	0.3	15.3	14.0
Rydberg excited states				
$1^1E_{1g}(3s)$	77.3	0.3	7.5	14.9
$1^1A_{2u}(3p\sigma)$	76.6	0.3	8.4	14.7
$1^1E_{2u}(3p\sigma)$	77.3	0.3	7.6	14.8
$1^1A_{1u}(3p\sigma)$	77.4	0.3	7.4	14.8
$2^1E_{1u}(3p\pi)$	76.9	0.3	7.7	15.1
$2^1E_{1g}(3d\delta)$	77.5	0.4	7.6	14.6
$1^1B_{1g}(3d\sigma)$	77.8	0.4	7.2	14.7
$1^1B_{2g}(3d\sigma)$	77.8	0.4	7.2	14.6
$3^1E_{1g}(3d\delta)$	78.0	0.3	7.0	14.7
$2^1A_{1g}(3d\pi)$	77.1	0.3	7.7	14.9
$2^1E_{2g}(3d\pi)$	77.5	0.3	7.3	14.9
$1^1A_{2g}(3d\pi)$	77.5	0.3	7.3	14.9

energies could be reproduced well even at the CASSCF level. For the valence excited states, the semi-internal term is found to be the most important contribution. The effect is also different between the covalent and ionic states. The semi-internal contribution for the ionic excited states is significant, which means that the π ionic configurations strongly polarize the σ space. The accurate description of the excited states, particularly the ionic states, cannot be obtained before the semi-internal contribution is correctly taken into account.

4. Conclusion

The multireference perturbation theory with CASSCF reference functions was reapplied to the study of the valence $\pi-\pi^*$ and Rydberg excited states of benzene using a larger basis set. The present theory satisfactorily describes the low-lying valence $\pi-\pi^*$ excited states as well as the Rydberg excited states. The ionic plus states are dominated by the single excitations but the covalent *minus* states (espe-

cially the *g* states) include a large fraction of doubly excited configurations both for singlet and triplet valence excited states. The Rydberg excited states are characterized as single excitations. The dynamic $\sigma-\pi$ polarization effects on the covalent excited states are usually the same as in the ground state, while this effect is more significant for the ionic excited states than for the ground state. These effects are less significant on the Rydberg excited states than on the ground state. The improvement in one-electron functions beyond the d-functions does not have a great effect on the excitation energies of benzene. It is much more important to include the effect of higher-body excitations. Multireference treatment is necessary to describe states with a double excitation character. It can handle these states as well as those characterized as single excitations, while single reference-based methods cannot. The present approach with pairing properties will be of great value in understanding the general properties of the excitation spectra of the alternant hydrocarbons and even the properties of their substituted and heterocyclic analogues, which will be reported elsewhere.

Acknowledgements

The present research was supported in part by a grant-in-aid from the Ministry of Education, Science, Sports, and Culture. The computations were carried out on an IBM SP2 system at the Intelligent Modeling Laboratory (IML) of the University of Tokyo. The CASSCF reference wavefunctions were obtained using a MOLPRO program [21]. The perturbation calculations were performed with an MR2D program [22].

References

- [1] A. Hiraya, K. Shobatake, *J. Chem. Phys.* 94 (1991) 7700.
- [2] N. Nakashima, H. Inoue, M. Sumitani, K. Yoshihara, *J. Chem. Phys.* 73 (1980) 5976.
- [3] K. Hirao, *Chem. Phys. Lett.* 190 (1992) 374; *Chem. Phys. Lett.* 196 (1992) 397; *Chem. Phys. Lett.* 201 (1993) 59; *Int. J. Quantum Chem.*, S26 (1992) 517.
- [4] P. E. Siegbahn, A. Heiberg, B.O. Roos, B.Levy, *Phys. Scr.* 21 (1980) 323; B.O. Roos, P.R. Taylor, P.E. Siegbahn, *Chem. Phys.* 48 (1980) 157; B.O. Roos, *Int. J. Quantum Chem.* S14 (1980) 175.
- [5] K. Hirao, H. Nakano, T. Hashimoto, *Chem. Phys. Lett.* 235 (1995) 430.
- [6] T. Hashimoto, H. Nakano, K. Hirao, *J. Chem. Phys.* 104 (1996) 6244.
- [7] J. Lorentzon, P.-Å. Malmqvist, M. Fülischer, B.O. Roos, *Theor. Chim. Acta* 91 (1995) 91.
- [8] T.H. Dunning, *J. Chem. Phys.* 90 (1989) 1007.
- [9] K. Kaufmann, W. Baumeister, M. Jungen, *J. Phys. B22* (1989) 2223.
- [10] M.J. Packer, E.K. Dalskov, T. Enevoldsen, H.J.Aa. Jensen, J. Oddershede, *J. Chem. Phys.* 105 (1996) 5886.
- [11] O. Christiansen, H. Koch, P. Jørgensen, T. Helgaker, A.S. de Meris, *J. Chem. Phys.* 105 (1996) 6921.
- [12] J.E. Del Bene, J.D. Watts, R.J. Bartlett, *J. Chem. Phys.* 106 (1997) 6051.
- [13] J.P. Doering, *J. Chem. Phys.* 51 (1969) 2866.
- [14] R. Astier, Y.H. Meyer, *Chem. Phys. Lett.* 3 (1969) 399.
- [15] M.W. Williams, R.A. MacRae, R.N. Hamm, E.T. Arakawa, *Phys. Rev. Lett.* 22 (1969) 1088.
- [16] P.M. Johnson, *J. Chem. Phys.* 64 (1976) 4143.
- [17] R.L. Whetten, S.G. Grubb, C.E. Otis, A.C. Albercht, E.R. Grant, *J. Chem. Phys.* 82 (1985) 1115.
- [18] P.M. Johnson, G.M. Korenowski, *Chem. Phys. Lett.* 97 (1983) 53.
- [19] S.G. Grubb, R.L. Whetten, A.C. Albercht, E.R. Grant, *Chem. Phys. Lett.* 108 (1984) 420.
- [20] R.L. Whetten, K.-J. Fu, E.R. Grant, *J. Chem. Phys.* 79 (1983) 2620.
- [21] H.-J. Werner, P.J. Knowles, *J. Chem. Phys.* 73 (1980) 2342; *Chem. Phys. Lett.* 115 (1985) 259.
- [22] H. Nakano, *J. Chem. Phys.* 99 (1993) 7983; H. Nakano, MR2D Ver. 2, University of Tokyo, 1995.