

# Theoretical study on the ionized states of ethylene by the SAC-CI (general-*R*) method

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## Abstract

The SAC (symmetry adapted cluster)/SAC-CI (configuration interaction) general-*R* method is successfully applied to the photoelectron spectrum of ethylene. The theoretical spectrum satisfactorily reproduces the outer- and inner-valence regions of the spectrum. The exponential generation (EG) algorithm followed by perturbation selection (PS) is shown to be useful in the generation of small and yet effective higher-excitation operators for the SAC-CI general-*R* method. The peak at 23.7 eV is assigned to the ‘twinning’ ionized states, the  $2^2A_g$  and  $3^2A_g$  states, and the peak at 27.4 eV is attributed to the  $6^2A_g$  and  $7^2A_g$  states. In the energy region around 31 eV, some ionized states are suggested to locate with small intensities. The  $1^2B_{2g}$  state obtains its intensity by the initial state configuration interaction. © 1998 Elsevier Science B.V.

## 1. Introduction

Ethylene has long been a key molecule in the experimental [1–9] and theoretical [1,8,10–18] studies of photoelectron spectra. The assignments of the outer-valence ionizations are now well established [1,8,10–18], but some problems still exist in the assignment of the shake-up peaks in the inner-valence region of the spectrum [8,10–18]. Different theoretical assignments [8,10–18] were reported for the peak at 23.7 eV; ‘twinning’ [8,11,12,16–18] (two ionized states compose the peak) and ‘non-twinning’ ones [10,13–15] (single ionized state composes the peak). For the quite small hump at 31 eV, the SAC-CI theoretical assignment was proposed previ-

ously [13,14], but the accuracy of the calculations was not satisfactory, since only the single and double (SD) ionization operators were included in the linked term.

The reason for the complexity in the theoretical calculations of the inner-valence ionization spectra lies in their multi-electron nature: simultaneous ionization and excitation process. For quantitative descriptions of such processes, large computational efforts are generally required since the number of excitation operators increases markedly for higher-order excitations [8,15]. However, we believe that the number of the excitation operators which are really necessary for quantitative calculations should be limited and can be generated by the exponential generation (EG) algorithm [19]. The description of such a state must be improved dramatically by in-

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cluding such excitation operators. In our SAC [20]/SAC-CI [21,22] method [23,24], such important higher-excitation operators are included in the linked terms by the general-*R* (*g-R*) algorithm [25] in addition to the single and double excitation operators in the SD-*R* method.

The spirit of the EG algorithm is that the important higher-excitation operators must be the products of the lower important excitation operators [19]. The EG algorithm is a selective generation method of the higher-excitation operators from the lower-order ones. The SAC-CI calculations including such higher excitation operators (*g-R*) have been shown to give results close to the full-CI ones with small numbers of operators [25–27]. On the other hand, the perturbation selection (PS) procedure [28] is also a reliable method of selection so that we have proposed a combined use of the EG and perturbation selection [27,28]. We first do EG for higher excitation operators and then do PS with respect to the main configurations. PS alone without EG is too time consuming for calculations of moderate-size molecules.

In this report, the SAC-CI (*g-R*) method with the EG + PS for higher-excitation operators is applied to the ionized states of ethylene. Assignments of the photoelectron spectrum in both the outer- and inner-valence regions are given and compared with previous experimental and theoretical results.

## 2. Computational detail

We calculate vertical ionization energies of ethylene using experimental geometry [29]. The basis sets of calculations are as follows: for carbon, Huzinaga–Dunning (9s5p)/[5s3p] set [30] plus d-polarization function ( $\alpha = 0.75$ ) [13] and, for hydrogen, Huzinaga–Dunning (4s)/[3s] set [31] plus p-polarization function ( $\alpha = 0.95$ ), and at the center of the C=C bond, the s, p, and d functions ( $\alpha = 1.4, 0.5$ , and 1.02, respectively) [32] are used. The number of the SCF MOs are 74. The SAC-CI *g-R* calculations are performed within the active space composed of the six occupied and 61 unoccupied MOs: the 1s orbitals of carbon and some higher virtual MOs are eliminated from the active space. In the SAC-CI (*g-R*) method, the EG algorithm [19] is used for

Table 1  
Dimensions of the SAC/SAC-CI (general-*R*) calculations for ethylene

State	Number of configurations (EG <sup>a</sup> + PS <sup>b</sup> /EG <sup>a</sup> )				Total
	Order of excitations				
	1	2	3	4	
Singlet ground state					
A <sub>g</sub>	64/64	3176/9453			3241/9518
Ionized states					
A <sub>g</sub>	2/2	283/340	3516/4481	1005/1823	4806/6646
B <sub>2g</sub>	0/0	185/224	3024/4189	980/1961	4189/6374
B <sub>3g</sub>	1/1	244/324	3392/4518	970/1893	4607/6736
B <sub>1u</sub>	1/1	263/340	3511/4608	854/1842	4629/6791
B <sub>2u</sub>	1/1	247/326	3621/4545	1025/1896	4894/6768
B <sub>3u</sub>	1/1	179/224	2928/4043	859/1940	3967/6208

<sup>a</sup>EG denotes exponential generation.

<sup>b</sup>PS denotes perturbation selection.

generation of the triple and quadruple excitation operators. Preliminary SD-CI calculations were carried out to select the operators and thresholds for the EG,  $\{\lambda_{MM}^S, \lambda_{MM}^D\}$ , are set to  $\{0.005, 0.04\}$ . The superscripts, ‘S’ and ‘D’, denote single and double excitation operators, respectively, and the subscript, ‘MM’, denotes the product of the excitation operators. The excitation operators with SD-CI coefficients larger than the above thresholds are chosen as the operators for EG. In the present calculations, about 6000 operators from single to quadruple excitations are generated for each symmetry. The B<sub>1g</sub> and A<sub>u</sub> states which are known not to exist in the energy region lower than 30 eV of the photoelectron spectrum [8] are excluded from the calculations. The generated configurations are further selected by the perturbation selection procedure with a threshold of  $1 \times 10^{-5}$  hartree for the main configurations chosen from the SD-CI results. Table 1 shows the results of the selections. All single (ionization) operators and selected higher operators (PS for doubles and EG + PS for triples and quadruples) are included in the linked term. Table 1 shows that many of the operators generated by EG are further selected by PS, which shows the effectiveness of the EG algorithm.

The SCF MOs are calculated by the HONDO program, version 8 [33]. For the SAC-CI calculations, the development version [34] of the SAC85 program [35] is used.

### 3. Result and discussion

The SCF MOs of ethylene are expressed as

$$(\text{core})^4(2a_g)^2(2b_{1u})^2(1b_{2u})^2(3a_g)^2(1b_{3g})^2(1b_{3u})^2 \\ \times (1b_{2g})^0(3b_{1u})^0 \dots,$$

where the number in the superscript shows the occupation number. The natures of the  $2a_g$ ,  $2b_{1u}$ ,  $3a_g$  and  $3b_{1u}$  MOs are  $2s\sigma$ ,  $2s\sigma^*$ ,  $2p\sigma$  and  $2p\sigma^*$ , respectively. The  $1b_{2u}$  and  $1b_{3g}$  MOs are in-plane  $2p\pi_i$  and  $2p\pi_i^*$  characters, respectively, and the  $1b_{3u}$  and  $1b_{2g}$  MOs are out-of-plane  $2p\pi_o$  and  $2p\pi_o^*$  characters, respectively, where the subscripts ‘i’ and ‘o’ denote in- and out-of-plane, respectively.

In Table 2, the ionization energies, monopole intensities and main configurations of the ionized states are summarized. The calculated monopole intensity includes both final-state configuration interaction (FSCI) and initial state configuration interaction (ISCI) [36]. The experimental ionization potentials and the previous SAC-CI(SD-*R*) [13], 2ph-TDA [11], and MRSDCI [8] results are also shown. In the previous SAC-CI (SD-*R*) calculations [13], the intensities were calculated including only the FSCI. The ionized states with intensities less than 0.001 are not shown.

In Fig. 1, the experimental photoelectron spectrum (PES) and the present theoretical spectrum are shown. For the experimental spectrum, we adopted the spectra measured by Bieri et al. [7] (10 ~ 25 eV) and Gelius [5] (~ 25 eV; expanded along the vertical axis). The bars connecting among experimental peaks represent the primary-satellite relationships obtained by the present calculations. The present results reproduce well the experimental PES in both the outer- and inner-valence regions.

The primary peaks observed at 10.51, 12.85, 14.66, 15.87 and 19.23 eV [4] are assigned to  $1^2B_{3u}$ ,  $1^2B_{3g}$ ,  $1^2A_g$ ,  $1^2B_{2u}$  and  $1^2B_{1u}$  states calculated at 10.20, 12.75, 14.50, 15.83 and 19.18 eV, respectively. The average discrepancy between the experiment and theory is 0.13 eV. This assignment is the same as the previous one [1,8,10–18]. They represent almost pure one-electron processes. The  $1^2B_{3u}$ ,  $1^2B_{3g}$ ,  $1^2A_g$ ,  $1^2B_{2u}$  states are the ionization of the carbon 2p electrons in the outer-valence orbitals,

$1b_{3u}$ ,  $1b_{3g}$ ,  $3a_g$ , and  $1b_{2u}$ , respectively. The  $1^2B_{1u}$  state is the ionization from the  $2b_{1u}$  orbital ( $2s\sigma^*$ ).

There has been a controversy on the assignment of the peak observed at 23.7 eV as mentioned in Section 1: ‘twinning’ or ‘non-twinning’ [8,10–18]. The present results supports ‘twinning’ proposed in Refs. [8,11,12,16–18]. This peak is assigned to the two ionized states,  $2^2A_g$  and  $3^2A_g$  states calculated at 23.54 and 24.55 eV, respectively. The main configuration of the  $2^2A_g$  state is  $2h-1p$  state,  $(1b_{3u})^{-2}(4a_g)^1$ , to which 1h state,  $(2a_g)^{-1}$ , strongly mixes. The  $3^2A_g$  state is the counterpart of the  $2^2A_g$  state. In addition, many triple-excited configurations also mix as sub-configurations. The origin of the ‘twinning’ state is a strong mixing between the  $2h-1p$  and 1h configurations, and the intensities of these states arises from the  $(2a_g)^{-1}$  configuration. In other words, the primary peak of the ionization from the  $2a_g$  MO splits into two by the mixing of the  $2h-1p$  state  $(1b_{3u})^{-2}(4a_g)^1$ .

A comparison with the previous calculations indicates that the electron correlations take a large part in the ‘twinning’ phenomenon and that inclusion of the small but important higher-excitation operators by the SAC-CI (g-*R*) method greatly improves the description of the states. Recently, a large-scale MRSDCI calculation with a large basis set [8] was reported, in which the ‘twinning’ was reproduced by using state-averaged natural orbitals as a reference function but not by the SCF MOs. Further, the previous ‘non-twinning’ results by the SAC-CI (SD-*R*) method [13,14], in which the  $2^2A_g$  state was calculated to be a one-electron process, are dramatically improved in the present g-*R* calculation by the inclusion of the 3,4-ple excitations as linked term and 5,6-ple excitation as unlinked terms.

The very weak peak observed at the 27 ~ 30 eV region is assigned to  $6^2A_g$  and  $7^2A_g$  states calculated at 28.05 and 29.60 eV, respectively. This assignment is the same as in 2ph-TDA [11] and MRSDCI [8]. The main configuration of these states is  $(2b_{1u})^{-1}(1b_{3u})^{-1}(1b_{2g})^1$  and other double and triple excitations strongly mix in it. The intensity of the states are borrowed from the  $(2a_g)^{-1}$  configuration.

A quite small hump was observed at 31 eV in the PES [5] and the previous 2ph-TDA [11] results showed some  $2^2A_g$  exist in this region. The present result also suggests the existence of some low-inten-

Table 2  
Ionized states of ethylene with intensities larger than 0.001 in the photoelectron spectrum

State	SAC-CI (general- <i>R</i> )		Exptl. <sup>a</sup>		SAC-CI(SD- <i>R</i> ) <sup>b</sup>	2ph-TDA <sup>c</sup>	MRSDCI <sup>d</sup>
	Main configuration ( $ C  \geq 0.3$ )	<i>IP</i> (eV)	Intensity <sup>e</sup>	<i>IP</i> (eV)	<i>IP</i> (eV)	<i>IP</i> (eV)	<i>IP</i> (eV)
1 <sup>2</sup> B <sub>3u</sub>	$-0.96(1b_{3u})^{-1}$	10.20	0.926	10.51(s) <sup>f</sup>	10.25	9.74	10.38
1 <sup>2</sup> B <sub>3g</sub>	$-0.95(1b_{3g})^{-1}$	12.75	0.899	12.85(s) <sup>f</sup>	12.78	12.13	12.91
1 <sup>2</sup> A <sub>g</sub>	$0.93(3a_g)^{-1}$	14.50	0.890	14.66(s) <sup>f</sup>	14.50	13.77	14.66
1 <sup>2</sup> B <sub>2u</sub>	$-0.88(1b_{2u})^{-1} - 0.33(1b_{3g})^{-1}(1b_{3u})^{-1}(1b_{2g})^1$	15.83	0.765	15.87(s) <sup>f</sup>	15.93	15.02	16.02
1 <sup>2</sup> B <sub>2g</sub>	$0.91(1b_{3u})^{-2}(1b_{2g})^1 - 0.34(1b_{3u})^{-2}(2b_{2g})^1$	17.55	0.009				17.2
2 <sup>2</sup> B <sub>2u</sub>	$0.82(1b_{3g})^{-1}(1b_{3u})^{-1}(1b_{2g})^1 + 0.37(1b_{3g})^{-1}(1b_{3u})^{-1}(1b_{2g})^1$	18.53	0.012			17.82	18.32
1 <sup>2</sup> B <sub>1u</sub>	$0.82(2b_{1u})^{-1} - 0.34(2b_{3u})^{-1}(3a_g)^{-1}(1b_{2g})^1$	19.18	0.666	19.23(s) <sup>f</sup>	19.32	18.34	19.24
2 <sup>2</sup> B <sub>1u</sub>	$-0.82(2b_{3u})^{-1}(3a_g)^{-1}(1b_{2g})^1 - 0.32(2b_{3u})^{-1}(3a_g)^{-1}(1b_{2g})^1$ $+ 0.31(2b_{3u})^{-1}(3a_g)^{-1}(2b_{2g})^1$	20.98	0.021	21.4(w) <sup>d</sup>	23.45	20.32	20.34
2 <sup>2</sup> B <sub>3g</sub>	$-0.82(1b_{2u})^{-1}(1b_{3u})^{-1}(1b_{2g})^1 - 0.37(1b_{2u})^{-1}(1b_{3u})^{-1}(1b_{2g})^1$	22.38	0.001				21.91
3 <sup>2</sup> B <sub>2u</sub>	$-0.81(1b_{3g})^{-1}(1b_{3u})^{-1}(1b_{2g})^1 + 0.30(1b_{2u})^{-1}(1b_{3u})^{-2}(1b_{2g})^2$	22.84	0.048		25.86	23.22	22.22
2 <sup>2</sup> A <sub>g</sub>	$0.68(1b_{3u})^{-2}(4a_g)^1 - 0.46(2a_g)^{-1}$	23.54	0.209	23.7(m) <sup>g</sup>	24.37	23.10	23.3
3 <sup>2</sup> B <sub>1u</sub>	$0.86(1b_{3u})^{-2}(3b_{1u})^1$	24.45	0.003				23.44
3 <sup>2</sup> A <sub>g</sub>	$0.72(1b_{3u})^{-2}(4a_g)^1 + 0.42(2a_g)^{-1}$	24.55	0.177	23.7(m) <sup>g</sup>	26.97	23.83	24.5
4 <sup>2</sup> B <sub>1u</sub>	$0.79(2b_{3u})^{-1}(3a_g)^{-1}(1b_{2g})^1$	25.21	0.053			25.58	24.34
3 <sup>2</sup> B <sub>3g</sub>	$0.71(1b_{2u})^{-1}(1b_{3u})^{-1}(1b_{2g})^1 + 0.54(1b_{3g})^{-1}(1b_{3u})^{-2}(1b_{2g})^2$	25.79	0.004				24.21
3 <sup>2</sup> B <sub>3u</sub>	$-0.51(1b_{3u})^{-2}(2b_{3u})^1 - 0.41(1b_{2u})^{-1}(1b_{3u})^{-1}(2b_{2u})^1$ $+ 0.37(3a_g)^{-1}(1b_{3u})^{-1}(4a_g)^1 - 0.37(1b_{3g})^{-1}(1b_{3u})^{-1}(2b_{3g})^1$	26.56	0.001				23.78
4 <sup>2</sup> A <sub>g</sub>	$-0.81(1b_{3u})^{-2}(5a_g)^1 + 0.32(2b_{1u})^{-1}(1b_{3u})^{-1}(1b_{2g})^1$	27.08	0.002				27.06
4 <sup>2</sup> B <sub>3u</sub>	$-0.83(1b_{3u})^{-2}(2b_{3u})^1$	27.46	0.002				
5 <sup>2</sup> B <sub>2u</sub>	$0.84(1b_{3g})^{-2}(2b_{2u})^1$	27.66	0.001				
6 <sup>2</sup> B <sub>1u</sub>	$0.72(1b_{3g})^{-2}(3b_{1u})^1 + 0.37(1b_{3g})^{-2}(4b_{1u})^1$	27.87	0.002				
6 <sup>2</sup> A <sub>g</sub>	$-0.62(2b_{1u})^{-1}(1b_{3u})^{-1}(1b_{2g})^1 - 0.53(1b_{3u})^{-2}(5a_g)^1$	28.05	0.077	27.4(w) <sup>g</sup>		26.95	27.7
5 <sup>2</sup> B <sub>3g</sub>	$-0.81(1b_{3g})^{-1}(1b_{3u})^{-1}(2b_{3u})^1$	29.08	0.002				
6 <sup>2</sup> B <sub>3g</sub>	$-0.50(1b_{3g})^{-1}(1b_{3u})^{-1}(2b_{3u})^1 + 0.40(3a_g)^{-1}(1b_{3g})^{-1}(4a_g)^1$	29.57	0.002				
7 <sup>2</sup> A <sub>g</sub>	$-0.64(2b_{1u})^{-1}(1b_{3u})^{-1}(1b_{2g})^1 - 0.52(3a_g)^{-1}(1b_{3u})^{-2}(1b_{2g})^2$	29.60	0.050	27.4(w) <sup>g</sup>		28.02	28.7
7 <sup>2</sup> B <sub>3g</sub>	$-0.51(1b_{3g})^{-1}(1b_{3u})^{-1}(2b_{3u})^1 - 0.41(1b_{3g})^{-1}(1b_{3u})^{-1}(2b_{3u})^1$ $- 0.37(3a_g)^{-1}(1b_{3g})^{-1}(4a_g)^1 - 0.33(3a_g)^{-1}(1b_{3g})^{-1}(4a_g)^1$	29.79	0.003				
10 <sup>2</sup> B <sub>2g</sub>	$-0.85(1b_{3u})^{-2}(2b_{2g})^1$	30.02	0.008				
7 <sup>2</sup> B <sub>2u</sub>	$0.66(3a_g)^{-1}(1b_{3g})^{-1}(3b_{1u})^1 + 0.34(3a_g)^{-1}(1b_{3g})^{-1}(4b_{1u})^1$ $- 0.33(3a_g)^{-2}(2b_{2u})^1$	30.15	0.001				
8 <sup>2</sup> B <sub>1u</sub>	$-0.55(1b_{3g})^{-2}(3b_{1u})^1 + 0.47(1b_{3g})^{-2}(4b_{1u})^1$ $+ 0.41(1b_{3g})^{-1}(1b_{2u})^{-1}(4a_g)^1$	30.27	0.002				

$8^2 B_{3g}$	$-0.67(3a_g)^{-1}(1b_{3g})^{-1}(4a_g)^1 + 0.38(1b_{3g})^{-1}(1b_{3u})^{-1}(2b_{3u})^1$	30.31	0.002	
$8^2 A_g$	$-0.71(1b_{3g})^{-2}(5a_g)^1 - 0.34(1b_{2u})^{-1}(1b_{3g})^{-1}(3b_{1u})^1$ $+ 0.32(1b_{3g})^{-2}(4a_g)^1$	30.90	0.001	
$9^2 B_{3u}$	$-0.68(1b_{3g})^{-1}(1b_{3u})^{-1}(2b_{3g})^1 + 0.34(3a_g)^{-1}(1b_{3u})^{-1}(5a_g)^1$ $+ 0.31(1b_{2u})^{-1}(1b_{3u})^{-1}(2b_{2u})^1$	30.94	0.002	
$10^2 B_{3u}$	$0.61(1b_{2u})^{-1}(1b_{3u})^{-1}(2b_{2u})^1 - 0.43(1b_{3g})^{-1}(1b_{3u})^{-1}(2b_{3g})^1$ $+ 0.33(1b_{2u})^{-1}(1b_{3u})^{-1}(2b_{2u})^1$	31.11	0.001	
$10^2 B_{1u}$	$-0.70(3a_g)^{-1}(1b_{3g})^{-1}(2b_{2u})^1 + 0.30(1b_{3g})^{-1}(1b_{2u})^{-1}(4a_g)^1$	31.47	0.005	
$10^2 A_g$	$-0.49(3a_g)^{-2}(4a_g)^1 - 0.35(1b_{3g})^{-2}(5a_g)^1$ $+ 0.35(1b_{2u})^{-1}(3a_g)^{-1}(2b_{2u})^1$	31.53	0.003	
$11^2 B_{3u}$	$-0.62(1b_{2u})^{-1}(1b_{3u})^{-1}(2b_{2u})^1 - 0.44(1b_{3g})^{-1}(1b_{3u})^{-1}(2b_{3g})^1$	31.65	0.011	$\sim 31(w)^h$
$10^2 B_{2u}$	$0.74(1b_{3g})^{-2}(3b_{2u})^1$	31.76	0.001	
$11^2 A_g$	$0.83(1b_{3u})^{-2}(6a_g)^1$	31.99	0.003	
$12^2 A_g$	$0.62(1b_{3u})^{-2}(6a_g)^1 - 0.45(1b_{3u})^{-1}(3a_g)^{-1}(2b_{3u})^1$	32.07	0.010	$\sim 31(w)^h$
$11^2 B_{1u}$	$0.62(1b_{3g})^{-2}(4b_{1u})^1 + 0.44(1b_{3g})^{-1}(1b_{2u})^{-1}(4a_g)^1$	32.20	0.004	
$10^2 B_{3g}$	$-0.60(1b_{2u})^{-1}(1b_{3g})^{-1}(2b_{2u})^1 - 0.32(3a_g)^{-1}(1b_{3g})^{-1}(5a_g)^1$ $+ 0.32(3a_g)^{-1}(1b_{3g})^{-1}(5a_g)^1$	32.20	0.002	
$11^2 B_{2u}$	$0.67(1b_{3g})^{-1}(1b_{3u})^{-1}(2b_{2g})^1$	32.21	0.002	
$12^2 B_{2u}$	$-0.42(3a_g)^{-1}(1b_{3g})^{-1}(3b_{1u})^1 - 0.40(3a_g)^{-2}(2b_{2u})^1$ $- 0.33(1b_{3g})^{-2}(3b_{2u})^1 + 0.32(1b_{2u})^{-1}(3a_g)^{-1}(4a_g)^1$	32.75	0.001	
$11^2 B_{3g}$	$0.42(1b_{3g})^{-1}(1b_{3u})^{-2}(1b_{2g})^2$	32.81	0.004	
$13^2 B_{2u}$	$-0.37(3a_g)^{-2}(2b_{2u})^1 - 0.35(1b_{2u})^{-1}(1b_{3u})^{-1}(2b_{3u})^1$ $+ 0.33(1b_{2u})^{-2}(2b_{2u})^1$	33.09	0.002	
$13^2 B_{1u}$	$-0.69(1b_{3u})^{-1}(2a_g)^{-1}(1b_{2g})^1 + 0.40(1b_{2u})^{-2}(2b_{1u})^{-1}(1b_{2g})^2$	33.23	0.003	
$14^2 B_{2u}$	$0.49(1b_{2u})^{-1}(3a_g)^{-1}(4a_g)^1 + 0.33(2b_{1u})^{-1}(1b_{3g})^{-1}(4a_g)^1$ $- 0.31(1b_{2u})^{-1}(1b_{3u})^{-1}(2b_{3u})^1$	33.29	0.005	
$14^2 B_{3g}$	$+ 0.48(1b_{3g})^{-2}(2b_{2u})^1 + 0.40(3a_g)^{-1}(1b_{3g})^{-1}(5a_g)^1$ $- 0.37(1b_{2u})^{-1}(3a_g)^{-1}(3b_{1u})^1$	33.94	0.001	

<sup>a</sup>The characters in the parentheses, ‘s’, ‘m’ and ‘w’ denote the intensities of the peaks (strong, medium, and weak) respectively.

<sup>b</sup>Ref. [13].

<sup>c</sup>Ref. [11].

<sup>d</sup>Ref. [8].

<sup>e</sup>Monopole intensity including the final- and initial-state configuration interactions.

<sup>f</sup>Ref. [4].

<sup>g</sup>Ref. [6].

<sup>h</sup>Ref. [5].

sity ionized states, which belong not only to the  ${}^2A_g$  states but also to the states in the other symmetries. In Fig. 2, the ionized states with intensities larger than 0.001 are shown. The  $10^2B_{1u}$ ,  $11^2B_{3u}$ ,  $12^2A_g$ , and  $14^2B_{2u}$  states are calculated at 31.47, 31.65, 32.07 and 33.29 eV, respectively, and many other ionized states with very small intensities are calculated in this region. The intensities of these states are due to the configuration mixings with the  $1h$  states, although they are small.

In a recent high-resolution PES [8], a new correlation peak was observed at 21.4 eV. In the MRSDCI calculation [8], the four ionized states were carefully attributed to this new peak. Among them, the  $2^2B_{1u}$  and  $3^2B_{2u}$  states calculated at 20.34 and 20.22 eV, respectively, had relatively large intensities [8]. Our result proposes to assign the new peak to  $2^2B_{1u}$

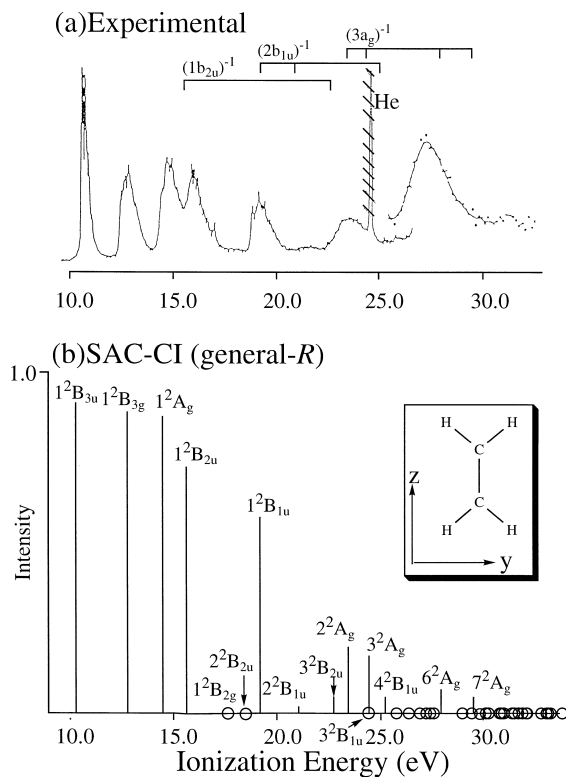


Fig. 1. Ionization spectra for ethylene. (a) Photoelectron spectra from Refs. [7] (10 ~ 25 eV) and [5] (~ 25 eV; expanded along the vertical axis). The bars connecting the observed peaks show the primary-satellite relationships found in the present calculations. (b) Theoretical spectrum calculated by the SAC-CI (general-R) method. Ionized states with intensities  $\geq 0.001$  are shown.

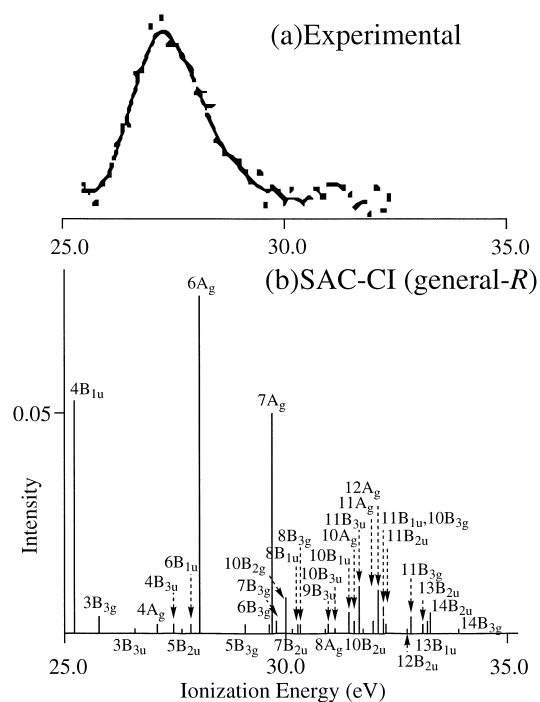


Fig. 2. Inner-valence ionization spectra for ethylene. (a) Photoelectron spectra from Ref. [5] (~ 25 eV). (b) Theoretical spectrum calculated by the SAC-CI (general-R) method. Ionized states with intensities  $\geq 0.001$  are shown.

state calculated at 20.98 eV, a satellite band of the  $1^2B_{1u}$  state. The main configuration is  $(2b_{3u})^{-1}(3a_g)^{-1}(1b_{2g})^1$ . The  $3^2B_{2u}$  state calculated at 22.84 eV is attributed to the lower-energy side shoulder of the primary peak at 23.7 eV as described below. The 2ph-TDA method [11] led to a similar result; the  $2^2B_{1u}$  and  $3^2B_{2u}$  states were calculated at 20.32 eV and 23.22 eV, respectively.

The  $3^2B_{2u}$  and  $4^2B_{1u}$  states calculated at 22.84 and 25.21 eV, respectively, are suggested to be the lower and higher side shoulder of the peak at 23.7 eV. The  $3^2B_{2u}$  and  $4^2B_{1u}$  states are the satellite peaks belonging to the main peaks at 15.87 and 19.23 eV, respectively.

In the present calculation, many other ionized states with small intensities are calculated. The  $1^2B_{2g}$  state is calculated at 17.55 eV and locates at the shoulder of the primary peak at 15.87 eV. The nature of the state is  $(1b_{3u})^{-2}(1b_{2g})^1$ . We note that the  $B_{2g}$  symmetry have no  $1h$  state, which means there is no primary peak to borrow intensity. The observed in-

tensity is a result of the initial state configuration interaction (ISCI) [34]. In the ground-state SAC wave function, the double excitations,  $(1b_{3u})^{-2}(1b_{2g})^2$  and  $(1b_{3u})^{-2}(1b_{2g})^1(2b_{2g})^1$  have relatively large coefficients. The first one is the double excitation from HOMO to LUMO, which often becomes important in  $\pi$ -conjugated systems. The  $(1b_{3u})^{-2}(1b_{2g})^1$  configuration has its intensity from these two configurations. The  $10^2B_{2g}$  state calculated at 30.02 eV also has small intensity through ISCI effect.

In Table 2, the previous results by SAC-CI (SD-*R*) [13], 2ph-TDA [11], and MRSDCI [8] are also shown. The previous SAC-CI (SD-*R*) calculations in 1984 with the basis of [5s2p1d/2s] plus three bond-centered functions were quite efficient, since the dimension of the calculations were less than 100 in each symmetry, and gave accurate results for the primary peaks. However, since the calculations did not include higher-excitation operators and the ISCI effect, the ionization potentials in the inner-valence region were overestimated and ‘non-twinning’ result was led for the peak at 23.7 eV. The 2ph-TDA calculations with the DZP basis were reported in 1978. Although the results underestimated the ionization potentials by about 0.8 eV for the entire spectrum, the energy separations among the ionized states were reproduced well. Recently, a quite large MRSDCI calculations with the basis of [6s7p3d1f/5s2p1d] plus four bond-centered functions was reported. This is the best calculation made so far, and the results reproduced the detailed spectral features. Although the dimensions of the present SAC-CI (*g-R*) calculations are quite small ( $\approx 4000 \sim 5000$  configurations in each symmetry) in comparison with this MRSDCI calculation, the results are comparable as seen from Table 1. This result shows the SAC-CI (*g-R*) method based on the EG + PS algorithm is quite effective for the study of the multi-electron processes involved in the photoelectron spectra.

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