Cluster expansion of the wave function. Valence and Rydberg excitations and ionizations of ethylene

Hiroshi Nakatsuji

Division of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 606, Japan

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The symmetry-adapted-cluster (SAC) and SAC-CI theories have been applied successfully to the calculations of the valence and Rydberg excitations and the outer- and inner-valence ionizations of ethylene. Among all, the result for the singlet (π,π^*) excited state is very encouraging, showing the effectiveness of the SAC-CI theory for the descriptions of electron correlations in the excited state. A systematic assignment of the singlet and triplet Rydberg excited states is given. The outer-valence ionization spectra are well reproduced by the SAC-CI theory, though in the inner-valence region, the intensities of the calculated ionization peaks are rather weak in comparison with the experiment.

I. INTRODUCTION

The excited states of ethylene, especially the (π,π^*) singlet excited state, are probably one of the most frequently studied systems by a number of theories for a number of years. Huzinaga[1] found from π-electron calculations that the optimum π^* orbital in the $^1(\pi,\pi^*)$ state might be very diffuse. Dunning *et al.*[2] performed an SCF calculation and reported a Rydberg nature for the $^1(\pi,\pi^*)$ state. Buenker, Peyerimhoff *et al.*[3] studied lower valence and Rydberg excited states and showed an importance of electron correlation. Rose, Shibuya, and McKoy[4] applied the equation of motion method. Fischer–Hjalmars and Kowalewski[5] studied various Rydberg excited states. Buenker, Peyerimhoff *et al.*[6] further reported advanced CI calculations and showed an importance of diffuse *d*-type basis for the description of the $^1(\pi,\pi^*)$ state. They reported excitation energies and oscillator strengths in closer agreement with experiment. McMurchie and Davidson[7] stressed an importance of the $\sigma\rightarrow\sigma^*$ excitations mixing with the $\pi\rightarrow\pi^*$ excitation, as previously noted by Tanaka,[8] Iwata, and Freed.[9] McMurchie and Davidson[7(b)] also reported a systematic study of the singlet Rydberg excited states. Brooks and Schaefer[10] performed accurate CI calculations with a variety of basis set. Buenker, Peyerimhoff, and Shih[11] carried out a large CI (4000–9500 dimensions) with a large basis set (108 CGTO's) for the $^1(\pi,\pi^*)$ state. The calculated excitation energy was 8.04 eV (experimental absorption maximum at 7.65 eV), the second moment in the π direction was 19–20 a.u., and the oscillator strength was 0.34–0.36 (experimental value 0.34). Buenker *et al.* also studied the so-called "sudden polarization" effect[12(a)] and the intensity distributions in the singlet (π,π^*) excitation bands.[12(b)]

On the more experimental side, several review articles[13–15] have been published since the report of the UV spectra by Wilkinson and Mulliken.[16] They show steady advances and yet an incompleteness of our knowledges on the electronic structures of ethylene. The assignment of the singlet Rydberg states seems not yet completely certain.[7(b),15(b)] Moreover, for the triplet Rydberg states, many of the lower excited states were observed only recently by Wilden and Comer[17] by electron energy-loss spectroscopy. Probably by this reason, a systematic theoretical study of the triplet Rydberg states does not yet appear, in contrast to a large number of studies on the singlet excited states.

In this series of articles, we have developed a cluster-expansion formalism for the studies of electron correlations in ground and various excited states.[18–21] The symmetry-adapted-cluster (SAC) expansion[18] was formulated for closed- and open-shell systems, and the SAC-CI theory[19] for excited states, ionized states, and electron-attached states. The theory has been applied successfully to various molecules like H_2O, CH_2, H_2CO, CO_2, N_2O, CS_2, COS, and NO.[18–20] The excited states studied involve both one- and two-electron excited states. We have also studied spin and electron correlations in several organic radicals.[21] It is interesting to apply this theory to the excited states of ethylene to see how well does the theory describe them. We calculate here the valence and Rydberg excited states and the ionized states of ethylene. We want to give a systematic assignment for the singlet and triplet Rydberg states of ethylene.

II. CALCULATIONAL DETAILS

We calculated the ground state of ethylene by the SAC theory[18] and the singlet and triplet excited states and ionized states by the SAC-CI theory.[19] The Hartree–Fock MO's of the closed-shell ground state were used as a reference configuration for all of these states.

The geometry of ethylene in its ground state[22] was used throughout the present calculation. The molecule is in the *yz* plane with the CC bond collinear to the *z* axis. We have used two kinds of basis set. Basis I is composed of [5*s*2*p*/2*s*] CGTO's of Huzinaga–Dunning[23] augmented with *d*-polarization functions on carbon ($\zeta = 0.75$), Rydberg *sp* set on carbon ($\zeta_s = 0.023$, $\zeta_p = 0.021$), and two sets of diffuse $d\pi$ and $d\bar{\pi}$ AO's ($\zeta = 0.022$ and 0.030) on the center of the bond.[6] This set is composed of 52 CGTO's. Basis II is composed of [3*s*2*p*/2*s*] CGTO's, Rydberg *sp* set on carbon ($\zeta_s = 0.023$, $\zeta_p = 0.021$), two sets of diffuse $d\pi$, $d\bar{\pi}$ AO's ($\zeta = 0.022$ and 0.030) on the center of the bond, and two sets of diffuse p_x, p_y AO's on carbons ($\zeta = 0.052$ and 0.083). This set is composed of 46 CGTO's. In both cases, the scale factor for the hydrogen bases were set to 1.2. Basis I is suitable for

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descriptions of valence excited states and ionized states and basis II for Rydberg excited states.

The algorithm for the SAC and SAC-CI calculations[24] was summarized previously.[20,25] The number of linked operators was diminished by the configuration selection technique.[20(a),26] The unlinked terms in the SAC calculation represent the effect of simultaneous binary collisions of electrons.[27] These effects were limited only to such double excitation operators whose coefficients in the SDCI are larger than 1×10^{-2}. The unlinked terms in the SAC-CI calculations represent an assumed transferability of electron correlations between ground and excited states.[19] The main reference configurations are the single and double excited configurations whose coefficients in the smaller CI are larger than 0.1. The double excitation operators applying to these main reference configurations were limited to those whose coefficients in the ground state SDCI are larger than 1×10^{-3}.

When the main reference configurations in the unlinked terms are limited to single excitations, the unlinked terms are actually composed of triple excitations, i.e., double excitations from main reference configurations. They are important for ordinary excitations and ionizations which are essentially one-electron processes. However, when two-electron processes are important as in the inner-valence ionization spectra which involve shake-up (simultaneous ionization-excitation) processes, the corresponding double excitations should be included to the main reference configurations.[28] The unlinked terms are then composed of triple and quadruple excitations. We refer to the former-type calculations as "3-excited" calculations and the latter type as "3,4-excited" calculations.

III. VALENCE AND RYDBERG EXCITED STATES OF ETHYLENE

A. *N*, *T*, and *V* states

A merit of the SAC and SAC-CI theories is that the number of independent variables is smaller than an ordinary CI calculations of similar accuracy. This is especially so for calculations of electron correlations in excited states. In Table I, we compared the dimensions of the independent variables for the calculations of the *N*, *T*, *V*, and lowest ionized states. We see that the dimensions of the present calculations are much smaller than those of the CI calculations due to Buenker *et al.*[11] and Brooks *et al.*[10] For ions, the dimensions of the SAC-CI calculation is very small. The CI calculations due to McMurchie and Davidson[7] are relatively small. In the present calculations, these dimensions are the sizes of the matrices to be diagonalized.

Table II shows the Hartree–Fock energy and the correlation energy of ethylene in its ground state. Basis I gives lower energy than basis II because of an inclusion of the polarization function. The present CI is due to the linked single and double excitation operators. The SAC calculation is due to the nonvariational method.[19(b),25] The cluster effect lowers the energy by 0.005–0.006 a.u.

Table III shows the vertical excitation energy of ethylene in the B_{1u} symmetry. They were calculated with basis I. The present results are relative to the ground state energy −78.280 63 a.u. obtained by the SAC method. The lower 1 $^3B_{1u}$ and 1 $^1B_{1u}$ states are the *T* and *V* states, respectively. For the *T* states, the present theory gives 4.5–4.6 eV which is in close agreement with the experimental value 4.6 eV.[13] For the *V* state, the present theory gives 8.2 eV. The effect of quadruple excitations in the unlinked term is 0.05 eV (the difference between 3-excited and 3,4-excited calculations). The experimental absorption maximum appears at 7.65 eV, but it may reflect a nonadiabatic effect.[12(b)] The best theoretical value so far obtained is 8.06 eV due to Buenker, Peyerimhoff, and Shih.[11] Our result is close to the result of Brooks and Schaefer[10] who used the basis set similar to ours.

TABLE I. Dimension of calculations for the *N*, *T*, *V*, and lowest ionized ($^2B_{3u}$) states.

	SAC, SAC-CI		CI		
	Basis I	Basis II	BPS[a]	MD[b]	BS[c]
NO of AO	52	46	108	68	56
$X\,^1A_g$ *N*	1804	1000	4835	982	4425
$^3B_{1u}$ *T*	1779	1408	7186		5425
$^1B_{1u}$ *V*	980	786	4079–9472	2000	5388
$^2B_{3u}$ ion	93	···	3461	742	···

[a] Reference 11.

[b] Reference 7.

[c] Reference 10.

The second B_{1u} state is a Rydberg excited state with mainly the $3d_{xy}$ nature. For the singlet state, the theoretical value is within 0.2 eV from the experimental value.[16] The effects of quadruple excitations are 0.17 and 0.12 eV for the triplet and singlet excitations, respectively. They are larger for these states than for the lower *T* and *V* states.

Table IV shows the second moment of ethylene in the $\pi(x)$ direction. It shows a size of extension of the electron cloud of the state. The value of the *T* state is very close to that of the ground state. Then, the *T* state is purely valence. The value of the *V* state is calculated twice as large as that of the ground state. The present result agrees well with the best theoretical value due to Buenker *et al.*[11] For the second $^1B_{1u}$ state, which is a Rydberg $3d_{xz}$ state, the second moment is four times as large as that of the ground state. It is, however, smaller than the CI result of McMurchie and Davidson.[7]

Table V shows the transition moment for the $X\,^1A_g \rightarrow 1\,^1B_{1u}$ excitations. For ther $N\rightarrow V$ transition, the present result is 0.419 which is reasonably compared with the experimental value 0.34.[13] It is much larger than that of the Rydberg excitation $X\,^1A_{1g}\rightarrow 2\,^1B_{1u}$; the present value is 0.085 and the result of McMurchie *et al.* is 0.050.

From the results shown in Tables I–V, we conclude that the present SAC-CI method gives an adequate description of the *V* and *T* states of ethylene. Especially, the results for the *V* state are very encouraging, showing the effectiveness of the present theory; the SAC-CI calculations of the dimension 980 compare well with the CI calculations of the order 4000–9500.

TABLE II. Hartree–Fock energy and correlation energy of the ground state of ethylene.

Method	Present Basis I	Present Basis II	BP[a]	MD[b]	BS[c]
Hartree–Fock	− 78.042 43	− 78.012 59	− 78.061 31	− 78.047 46	− 78.050 35
CI	− 0.231 93	− 0.161 40	− 0.332	− 0.116 47	− 0.276 24
SAC-NV	− 0.238 20	− 0.166 49			

[a] Reference 11.
[b] Reference 7.
[c] Reference 10.

TABLE III. Vertical excitatation energy of ethylene in the B_{1u} symmetry (eV).

State	Orbital picture	SAC-CI[a] 3-excited	SAC-CI[a] 3, 4-excited	Expt.[b]	CI BPS[c]	CI MD[d]	CI BS[e]
$1\,{}^3B_{1u}$ T	$\pi \to \pi^*$ $(1b_{3u} \to 2b_{2g})$	4.57	4.54	4.6	4.46	4.49	4.31
$1\,{}^1B_{1u}$ V		8.23	8.17	7.65	8.06	7.96	8.25
$2\,{}^3B_{1u}$	$\pi \to 3d_{xz}$ $(1b_{3u} \to 1b_{2g})$	9.24	9.07				
$2\,{}^1B_{1u}$		9.56	9.44	9.36		9.31	

[a] SAC-CI-V results with basis I. Relative to the SAC energy of the ground state − 78.280 63 a.u.
[b] References 13 and 15.
[c] Reference 11.
[d] Reference 7.
[e] Reference 10.

B. Rydberg excited states

Ethylene has a number of Rydberg excited states. Most of the optically active transitions were observed by Wilkinson and Mulliken.[16] For the triplet states, however, many of the lower excited states were observed only recently by Wilden and Comer[17] by electron energy-loss spectroscopy.

Table VI shows the vertical Rydberg excitation energies of ethylene. They are relative to the ground state energy given in Table II calculated by the SAC method. Between the two basis sets, basis II is more suitable for the description of the Rydberg states, since it includes a larger number of diffuse basis set. The present SAC-CI results agree with the experimental values to within 0.3 eV for both singlet and triplet excitations, as long as the present assignment as discussed below is correct.

We first discuss the singlet Rydberg transitions. In an earlier paper due to Mulliken,[15(a)] the transition observed at 7.45 eV in the energy-loss spectra[29] was assigned to the ${}^1B_{2g}$ state, which is mainly composed of the $3p\sigma$ orbital. Van Veen,[30] on the other hand, assigned this peak to the vibrational level of the ${}^1B_{3u}$ state and suggested to assign the peak observed at 7.83 eV in his electron-impact spectra to the transition to the $3p$ AO. Mulliken assigned[15(b)] in his later paper this peak to the ${}^1B_{1g}$ state which is mainly an in-plane $3p_y$ orbital. For the ${}^1B_{2g}$ state, he attributed the peak at 7.2 eV observed in the magnetic circular dichroism (MCD) spec-

TABLE IV. Second moment $\left\langle \Psi \middle| \sum_i x_i^2 \middle| \Psi \right\rangle$ for ethylene (a.u.).

State	Orbital picture	SAC, SAC-CI[a]	CI BPS[b]	CI MD[c]	CI BS[d]
$X\,{}^1A_g$ N	ground	11.96	11.75	11.8	
$1\,{}^3B_{1u}$ T	${}^3(\pi \to \pi^*)$	12.43	11.90	12.0	
$1\,{}^1B_{1u}$ V	${}^1(\pi \to \pi^*)$	21.51	20.11	17.8	26
$2\,{}^1B_{1u}$	$\pi \to 3d_{xz}$	49.42		67.9	

[a] Results of basis I.
[b] Reference 11.
[c] Reference 7.
[d] Reference 10.

TABLE V. Transition moment for the $X\,{}^1A_g \to {}^1B_{1u}$ excitation.

State	Orbital picture	SAC-CI[a]	Expt.[b]	CI MD[c]	CI BPS[d]
$1\,{}^1B_{1u}$ (V)	$\pi \to \pi^*$	0.419	0.34	0.605	0.362
$2\,{}^1B_{1u}$	$\pi \to 3d_{xz}$	0.085		0.050	

[a] Results of basis I.
[b] Reference 13.
[c] Reference 7.
[d] Reference 11.

TABLE VI. Vertical excitation energy of ethylene to Rydberg excited states.

		SAC-CI[a, b]			CI	
State	Orbital picture	Basis I	Basis II	Expt.	MD[f]	BP[g]
$^3B_{3u}$	$\pi\rightarrow 3s$	7.24	7.17	6.98[d]		6.89[h]
$^1B_{3u}$		7.41	7.33	7.11[c]	7.26	7.13
$^3B_{1g}$	$\pi\rightarrow 3p_y$	7.96	7.85	7.78[d]		7.62[h]
$^1B_{1g}$		7.97	7.86	7.83[e]	7.93	7.89
$^3B_{2g}$	$\pi\rightarrow 3p_\sigma$	7.95	7.85	7.78[d]		
$^1B_{2g}$		8.00	7.93	7.83[e]	8.01	7.86
^3A_g	$\pi\rightarrow 3p_\pi$	8.19	8.12	8.15[d]		
^1A_g		8.42	8.28	8.26[c]	8.36	8.21
$^3B_{3u}$	$\pi\rightarrow 3d_\sigma$	8.91	8.85	8.57[d]		
$^1B_{3u}$		8.98	8.90	8.62[c]	8.80	8.73
^3A_u	$\pi\rightarrow 3d_{yz}$	9.11	8.97			
^1A_u		9.09	9.05	8.90	8.99	8.83
$^3B_{1u}$	$\pi\rightarrow 3d_{xz}$	9.24(9.07)	9.17			
$^1B_{1u}$		9.56(9.44)	9.60	9.36[c]	9.31	9.17

[a] Relative to the SAC energy for the ground state; basis I − 78.280 63 a.u. and basis II − 78.179 08 a.u.

[b] Due to 3-excited calculations, except for those given in parentheses which are due to 3, 4-excited calculations.

[c] References 13 and 15.

[d] Reference 17.

[e] Reference 30.

[f] Reference 7.

[g] Reference 12(b).

[h] Reference 6(b).

trum.[31] In the present calculations, however, the $^1B_{1g}$ and $^1B_{2g}$ states are 7.86 and 7.93 eV above the ground state and both states are close to the experimental peak at 7.83 eV. It is difficult to assign $^1B_{2g}$ peak to 7.2 eV as Mulliken did. Rather, we think that the $^1B_{1g}$ and $^1B_{2g}$ states (i.e., in-plane $3p_\sigma$ and $3p_y$ orbitals) are almost degenerate and their peaks should overlap. Actually, the triplet counterparts, $^3B_{1g}$ and $^3B_{2g}$ states, show an accidental degeneracy. This trend was also observed in earlier theoretical studies by McMurchie–Davidson[7(b)] and by Petrongolo, Buenker, and Peyerimhoff.[12(b)] For the other states, the present assignments agree with those given by Mulliken.[15(b)] We note that we assigned the peak observed at 8.90 eV to the ^1A_u state. This assignment does not contradict with the assignment to the $^1B_{2u}$ and $^1B_{3u}$ states.[15(a)] These states are $3d_{yz}$, $3d_\delta$, and $3d_{xy}$ Rydberg states and all the states are nearly degenerates, as the previous calculations show.[7(b),12(b)] We did not calculate the $^1B_{2u}$ and $^1B_{3u}$ states.

In Table VI, the larger discrepancy (~0.3 eV) between the present and experimental values occur to the $\pi\rightarrow 3d_\sigma$ and $\pi\rightarrow 3d_{xz}$ transitions. For the former, the reason is due to the insufficient basis set; our basis do not include $3d_\sigma$ AO explicitly. The present result is due to a mimetic hybridization of the diffuse *sp* sets on carbons. For the $\pi\rightarrow 3d_{xz}$ transition, which couple with the valence $\pi\rightarrow\pi^*$ transition (Table III), we have also carried out the calculations including double excitations in the main reference configurations of the unlinked term. This 3,4-excited calculation gave 9.07 and 9.44 eV for the $^3B_{1u}$ and $^1B_{1u}$ states, respectively, showing a better agreement with the experiment.

Systematic theoretical studies of the triplet Rydberg excited states seem not to be done before. In Table VI, we have given our SAC-CI results for seven lower states. They are compared with the experimental data reported by Wilden and Comer.[17] They assigned their experimental peaks on the basis of the assignments of the corresponding singlet peaks. For Rydberg excited states, the singlet-triplet separation is small. Their assignments agree with the present theoretical results. For the $^3B_{1g}$ and $^3B_{2g}$ states, which are approximately the $3p_y$ and $3p_\sigma$ states, respectively, the present calculation gave almost identical excitation energies. As discussed before, these in-plane Rydberg orbitals $3p_y$ and $3p_\sigma$ are better understood to be degenerate. The experiments also could not distinguish these two states.[17] The out-of-plane $3p$ orbital ($3p_\pi$), however, lies higher by 0.37 eV for triplet state and 0.43 eV for singlet state than the in-plane $3p$ orbitals. For the transitions to the $3d$-type orbitals, only the lowest triplet excitation was observed. It is assigned here to the $\pi\rightarrow 3d_\sigma$ ($^3B_{3u}$) transition. The larger calculated value is probably due to the lack of the explicit $3d_\sigma$ AO in the basis set. No experimental values seem to exist for the other triplet states. For the $^{1,3}A_u$ ($\pi\rightarrow 3d_{yz}$) states, the results of basis I violate the Hund's rule. This might be due to the mechanism as reported by Kollmar and Staemmler.[32] However, since the result is basis set dependent, more detailed study is necessary for a final conclusion.

IV. IONIZED STATES OF ETHYLENE IN OUTER- AND INNER-VALENCE REGIONS

In Table VII, we summarized the ionization potential of ethylene. The Koopmans values, the present SAC-CI results obtained with basis I, the CI results due to Iwata *et al.*,[33] and the Green's function results with the over-valence-type (OVT) method[34] and with the 2*ph* Tamm–Dancoff approximation (TDA)[35] are compared with experiments.[33,36–39] The

TABLE VII. Ionization potential of ethylene.

State	Ionizing orbital	Koopmans	SAC-CI[a] 3-excited	SAC-CI[a] 3, 4-excited	Expt.[b]	CI[b] Iwata	Green function OVT[d]	Green function TDA[e]
$^2B_{3u}$	$1b_{3u}(\pi)$	10.20	10.44	10.25	10.51	10.22	10.44	9.74
$^2B_{3g}$	$1b_{3g}$	13.88	13.03	12.78	12.85	12.78	13.04	12.13
^2A_g	$3a_g$	15.95	14.78	14.50	14.66	14.55	14.70	13.77
$^2B_{2u}$	$1b_{2u}$	17.54	16.33	15.93	15.87	16.14	16.07	15.02
$^2B_{1u}$	$2b_{1u}$	21.57	19.77	19.32	19.1	19.54	19.44	18.34
^2A_g	$2a_g$	28.11	25.00	24.37	23.7[c]	···	···	23.10

[a] Results of basis I. Relative to the SAC energy of the ground state − 78.280 63 a.u.

[b] Reference 32.

[c] Reference 35.

[d] Reference 33.

[e] Reference 34.

Koopmans values are larger than experiments, as expected, except for the lowest ionization. The present SAC-CI results due to the 3,4-excited calculations agree with the experimental value within 0.3 eV, except for the ionization from the $2a_g$ orbital which is the inner valence 2*s* bonding MO. The effect of the quadruple excitations in the unlinked term is to lower the ionized states by 0.2–0.6 eV. The effect is larger for deeper states which have more chance to mix with the doubly excited ionization-excitation configurations. Between the two Green's function methods, the over valence-type (OVT) method gives more accurate results, though only the 2*ph* TDA method can deal with the inner-valence ionizations.

Figure 1 and Table VIII show the theoretical ionization spectra obtained by the SAC-CI theory with including up to quadruple excitations in the unlinked term. They are due to basis I. The intensity of the peak was calculated with the use of the monopole approximation.[40] In the energy region larger than 23 eV, many satellite peaks with relatively weak intensities are calculated, along with a strong peak at 24.4 eV which corresponds to the ionization from the $2a_g$ orbital. The experimental ESCA spectra of ethylene[36,37] exhibit a strong peak at 23.7 eV, a less intense broad peak at 26–29 eV, and a weak peak at ∼31 eV. The electron impact (*e*, 2*e*) spectra[38] also show a similar feature. In comparison with the experimental peak, the theoretical satellite peaks in the 26–29 eV region seem to be too weak. This might be due to a crudeness of the monopole approximation used here for intensity calculations. Further, as seen from Table VIII, these satellite peaks involve the simultaneous ionization–excitations from the σ and π ($1b_{3u}$) bonding MO's to the $\pi^*(2b_{2g})$ antibonding MO. This could cause a large change in geometry due to the shake-up ionizations. The C–C length would be elongated and the molecule may not be planar as in the (π,π^*) excited states. This effect causes a large change in the intensity calculation and should be a reason of the broadness of the satellite peaks. It tends to shift the overall peaks to lower energy retgion. The present calculation cannot give an unambigous assignment of the peak observed in the 26–29 eV region. It might be a composit of the satellite peaks of the ionization from the $1b_{2u}$ and $2b_{1u}$ MO's. The weak peak observed at ∼31 eV is assigned to the satellite of the ionization from the $2a_g$ orbital.

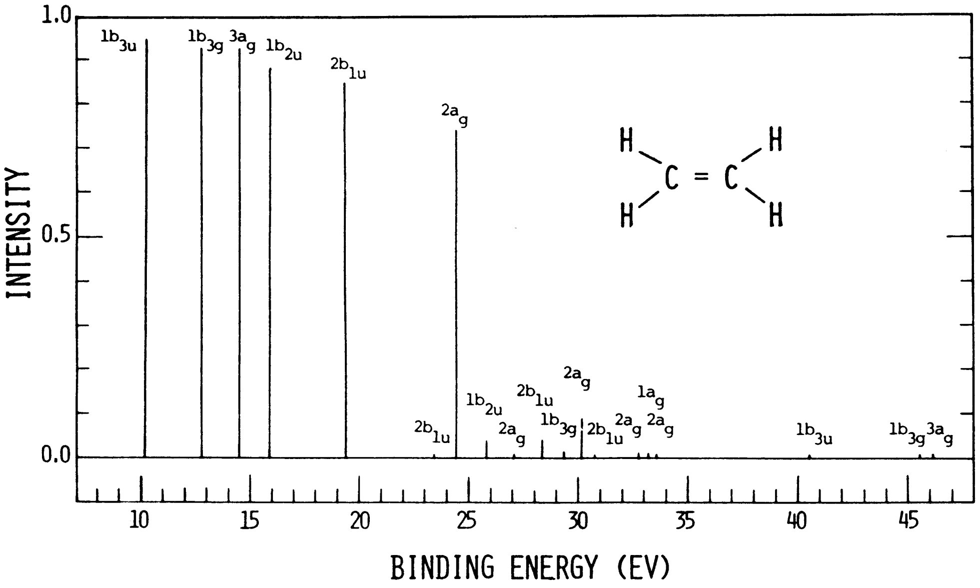

FIG. 1. Theoretical SAC-CI ionization spectra of ethylene due to the 3,4-excited calculations with basis I.

TABLE VIII. Theoretical ionization spectrum of ethylene in the 10–40 eV region calculated by the SAC-CI theory.

Ionization energy (eV)		Orbital assignment	Intensity P	Main configuration[d]
SAC-CI[a, b]	Expt.[c]			
10.25	10.51	$1b_{3u}$	0.95	$0.97(1b_{3u})^{-1}$
12.78	12.85	$1b_{3g}$	0.93	$0.96(1b_{3g})^{-1}$
14.50	14.66	$3a_g$	0.92	$0.96(3a_g)^{-1}$
15.93	15.87	$1b_{2u}$	0.88	$0.93(1b_{2u})^{-1}$
19.32	19.1	$2b_{1u}$	0.85	$0.92(2b_{1u})^{-1}$
23.45		$2b_{1u}$	0.01	$0.79(1b_{3u})^{-1}(3a_g)^{-1}(2b_{2g})^1$
24.37	23.7	$2a_g$	0.74	$0.86(2a_g)^{-1}$
25.86		$1b_{2u}$	0.04	$0.74(1b_{3g})^{-1}(1b_{3u})^{-1}(2b_{2g})^1$
26.97		$2a_g$	0.01	$1.13(1b_{3u})^{-2}(5a_g)^1$
28.31	27.4	$2b_{1u}$	0.04	$0.72(3a_g)^{-1}(1b_{3u})^{-1}(2b_{2g})^1$
29.28		$1b_{3g}$	0.02	$0.64(1b_{2u})^{-1}(1b_{3u})^{-1}(2b_{2g})^1$
30.15	~31	$2a_g$	0.09	$0.63(1b_{3u})^{-2}(6a_g)^1$ $+0.56(1b_{3u})^{-1}(2b_{1u})^{-1}(2b_{2g})^1$
30.73		$2b_{1u}$	0.01	$0.97(1b_{3u})^{-2}(5b_{1u})^1$
32.70		$2a_g$	0.02	$0.74(1b_{3u})^{-1}(3a_g)^{-1}(2b_{3u})^1$
33.13		$3a_g$	0.01	$0.70(3a_g)^{-1}(1b_{3u})^{-1}(2b_{3u})^1$
33.52		$2a_g$	0.02	$0.68(3a_g)^{-1}(1b_{3u})^{-1}(2b_{3u})^1$

[a] Relative to the ground state energy − 78.280 63 a.u.

[b] 3, 4-excited calculations with basis I.

[c] References 32 and 35.

[d] The Hartree–Fock orbital sequence is $(\text{core})^4\ (2a_g)^2\ (2b_{1u})^2\ (1b_{2u})^2\ (3a_g)^2\ (1b_{3g})^2\ (1b_{3u})^2$ (Rydberg) $(2b_{3u})$ $(2b_{2g})\ldots(6a_g)$, where $1b_{3u}$, $2b_{3u}$, $2b_{2g}$, and $6a_g$ MO's are π, $3p_\pi$, π^*, C–H antibonding MO's, respectively.

For ethylene, the theoretical study of the inner-valence ionization was given previously by Martin and Davidson[41] and by Cederbaum *et al.*[35] Martin and Davidson obtained three satellite peaks from a small CI calculations. The satellite peak observed at ~27.4 eV was assigned to the satellite of the ionization from the $2a_g$ MO; the shake-up configuration is $(2b_{1u})^{-1}\ (\pi)^{-1}\ (\pi^*)^1$. Cederbaum *et al.* calculated the ionization spectra by the 2*ph*-TDA Green function method. They obtained similar number of satellite peaks to the present case but with stronger intensity. They assigned the peak observed at ~27.4 eV as the satellite of the ionization from the $2a_g$ MO. Thus, our assignment is different from the assignments of the previous authors. More elaborate calculations seem to be necessary for final conclusion.

V. CONCLUSION

The SAC and SAC-CI theories have been applied to the calculations of the excited and ionized states of ethylene. Both valence and Rydberg excited states were successfully calculated by the SAC-CI theory. Especially, the results for the singlet (π,π^*) excited state (V state) were very encouraging, showing the effectiveness of the SAC-CI theory for the descriptions of the electron correlation in the excited state. The 7.83 eV peak observed in the electron-impact spectra was assigned to the singlet $\pi\rightarrow3p$ transition (either $3p_{\bar{\pi}}$ ($^1B_{2g}$) or $3p_\sigma$ ($^1B_{1g}$) state which are almost degenerate). The present calculation is a first systematic calculation of the triplet Rydberg excited states. The experimental spectra observed by Wilden and Comer[17] were accounted for on the basis of the present calculations. The results of the SAC-CI calculations for the outer-valence ionizations showed satisfactory agreements with experiment. For the inner-valence region, however, the intensities of the calculated peaks were rather weak in comparison with the experiment.

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