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Valence ionization spectra of 4π-electron molecules with low-lying satellites involving n–π* and π–π* transitions§

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The valence ionization spectra up to 25–30 eV of the 4π-electron molecules, butadiene, acrolein, glyoxal, methylenecyclopropene and methylenecyclopropane were investigated by the SAC-CI method. Accurate theoretical assignments of the spectra were given and further the natures of the low-lying satellites were examined. Acrolein and glyoxal have the low-lying satellites of $n^{-1}\pi^{-1}\pi^*$ and $n^{-2}\pi^*$ states and the outermost satellites are lower than the $\pi^{-2}\pi^*$ state of butadiene. However, their intensities are very small, since they do not effectively interact with the main peaks. The $\pi^{-2}\pi^*$ state of methylenecyclopropene with constrained π-conjugation was calculated to be much higher than that of butadiene, though the first IP is lower. In these spectra, some split peaks were calculated at 15–16 eV and the continuous shake-up states were obtained in the region higher than ~18 eV.

1. Introduction

Satellite peaks appear even in the low-energy region of the valence ionization spectra for p conjugated molecules. These satellites are of special interest, since they reflect the electron correlations in molecules [1, 2]. Although the satellites usually have small intensity in the valence ionization spectra, they often play an important role in the energy relaxation processes like Auger decay; these satellites can be directly observed as a spectator Auger process. However, fine analyses of these states require precise theoretical information with the highly accurate method.

Low-lying satellites of the π-conjugated hydrocarbons are attributed to the two-electron process accompanied by the π–π* transition. *Trans*-butadiene constitutes a fundamental linear π-conjugation unit and its valence ionization spectrum has been extensively investigated. Experimentally, the He I [3] and He II [4] potential energy surface (PES), high-resolution XPS [5, 6] and electron momentum spectroscopy [7] were observed for this important molecule. Theoretical calculations were also performed; in particular, the outermost

satellites of polyenes concentrated on Green's function calculations [8, 9]; their ionization potential (IP) shifts to a lower level, as the π-conjugation becomes longer, while the intensity becomes larger.

Another possibility for the low-lying satellite may be found in systems including lone pair electrons in π-conjugation; the n–π* transition is usually as low as the π–π* transition and therefore, low-lying $n^{-1}\pi^{-1}\pi^*$ and $n^{-2}\pi^*$ shake-up states may appear. Acrolein and glyoxal have oxygen atoms in π-conjugation and their ionization spectra are good candidates for having the low-lying satellites. Their outer-valence ionization spectra were measured by the He I [3] and He II [10] PES and the spectrum of acrolein was interpreted using some theoretical calculations [10–12]. Penning ionization electron spectroscopy was also applied to assign the peaks in the outer-valence region [13].

The valence ionized states of methylenecyclopropene and methylenecyclopropane are also of interest, since these molecules have constrained molecular structure and methylenecyclopropene has another pattern for π-conjugation. Their spectra were measured by the He I [3, 14] and the He II [15] PES, however, the experimental measurement in the higher-energy region is still not sufficient. For the theoretical assignment, CI calculation was performed for methylenecyclopropane, however, the results were limited up to 17 eV [3].

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§Dedicated to Professor Michael A. Robb on the occasion of his 60th birthday.

We have extensively investigated the wide variety of molecular spectroscopy by the SAC (Symmetry-Adapted-Cluster) [16]/SAC-CI (Configuration Interaction) [17–21] method. The SAC-CI method is a useful quantum-chemical method for studying molecular ground, excited, ionized and electron attached states of molecules in singlet to septet spin-multiplicities [22]. For ordinary single electron excitation and ionization processes, we use SAC-CI SD(singles and doubles)-*R* method, but for multiple-electron processes like those involved in shake-up satellite peaks, the SAC-CI general-*R* method [23–26] has been shown to be a powerful tool. By using the general-*R* method, we can describe accurately the multiple electron processes and calculate plenty of states appearing in the ionization spectra [27, 28].

Recently, we have systematically applied the general-*R* method to the valence ionization spectra of molecules [28–34]. In the present work, we investigate the valence ionization spectra of some characteristic 4π-electron systems and examine the possibility of the low-lying satellites accompanied by the $\pi–\pi^*$ and $n–\pi^*$ transitions.

2. Computational details

Flexible basis sets were adopted to describe the electron correlations of the valence ionized states; the valence triple zeta of Ahlrichs and co-workers [35] was used, namely, [5s3p] GTOs augmented with d-type polarization function of $\zeta_d = 0.75$ and 0.85 for C and O [36], respectively, and [3s] for the H atom. The resultant SCF dimensions were 94, 88, 82, 88 and 94 for 1,3-*trans*-butadiene, s-*trans* acrolein, s-*trans* glyoxal, methylenecyclopropene and methylenecyclopropane, respectively. Geometries of these molecules were due to the experimental ones [37].

The SAC-CI general-*R* and SD-*R* calculations were performed for the valence ionization spectra. The 1s orbitals of C and O were taken as the core molecular orbitals (MOs) and all the other MOs were included in the active space. The resultant SAC-CI active spaces were 11 occupied and 79 unoccupied MOs (11 occ.×79 unocc.) for butadiene, 11 occ.×73 unocc. for acrolein, 11 occ.×67 unocc. for glyoxal, 10 occ.× 74 unocc. for methylenecyclopropene, and 11 occ.× 79 unocc. for methylenecyclopropane. In the present general-*R* calculations, *R*-operators were included up to triples; the effect of quadruples was minor for the shape of theoretical spectra in the energy region up to 25 eV in the preliminary calculations. In order to reduce the computational effort, perturbation selection was performed [38]. The threshold of the linked terms for the ground state was set to $\lambda_g = 1 \times 10^{-5}$. The unlinked

terms were described as the products of the important linked terms whose SDCI coefficients were larger than 0.005. For the ionized state, the thresholds of the linked doubles and triples were set to $\lambda_e = 1 \times 10^{-6}$. The thresholds of the CI coefficients for calculating the unlinked operators in the SAC-CI method were 0.1 and 0.0 for the *R* and *S* operators, respectively.

The ionization cross-sections were calculated using the monopole approximation [39, 40] to estimate the relative intensities of the peaks. For the calculations of monopole intensities, the correlated SAC/SAC-CI wave functions were used for the ground and ionized states to include both the initial-state and final-ionic-state correlation. The general-*R* spectra were convoluted with the Gaussian envelope taking account of the Franck–Condon widths and the resolution of the spectrometer; the FWHM (Full width at Half Maximum) of Gaussian was adopted as 0.08 (in eV).

The SAC/SAC-CI calculations were executed using the SAC-CI program system, which has been incorporated into the distributed Gaussian 03 suite of programs [22].

3. Results and discussions

3.1. *Butadiene*

The valence orbital sequence of 1,3-*trans* butadiene is

$$(\text{core})^8 (3b_u)^2 (3a_g)^2 (4a_g)^2 (4b_u)^2 (5b_u)^2 (5a_g)^2$$
$$\times (6a_g)^2 (6b_u)^2 (7a_g)^2 (1a_u)^2 (1b_g)^2,$$

where $1a_u$ and $1b_g$ MOs are π orbitals and $4b_u$ to $7a_g$ MOs describe the C–H and CC σ-bonding. The $3b_u$, $3a_g$ and $4a_g$ MOs correspond to 2s orbitals and the ionizations from these orbitals appear in the inner-valence region. Since the XPS spectrum was observed up to about 30 eV [6], the present calculations were performed to simulate the spectrum in this region; for this purpose, 60, 10, 10 and 40 solutions were calculated for A_g, B_g, A_u and B_u symmetry, respectively. In figure 1 the calculated spectrum was compared with the He I PES [3] and XPS [6] spectra. Table 1 summarizes the ionization potentials (IPs), monopole intensities and the dominant configurations calculated by the SAC-CI method with the experimental IPs. Note that we show the ionized states whose intensity is larger than 0.02 and there are many other states with small intensity.

The thirteen and eight peaks were measured by XPS and He I PES, respectively; this work follows the peak numbers of XPS [6]. In the energy region up to $\sim$14 eV, the peaks are in the order of Koopmans' states.
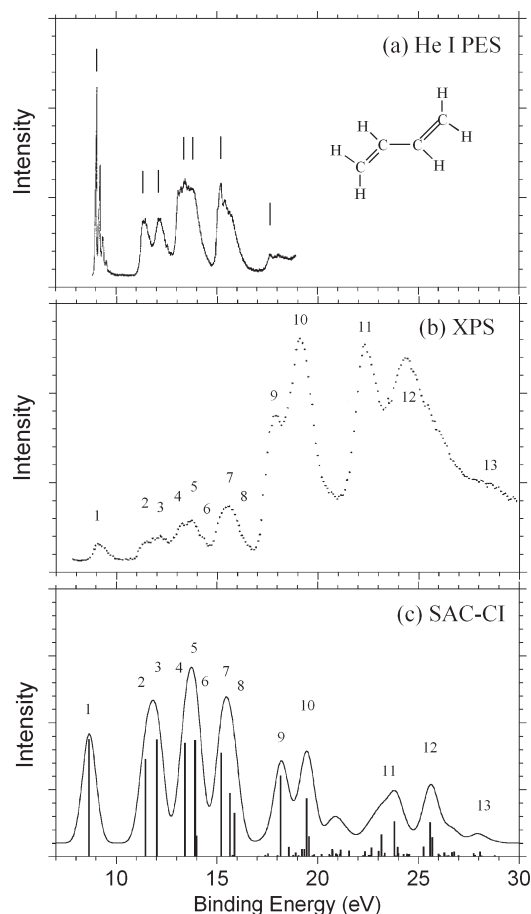
Figure 1. Valence ionization spectra of 1,3-*trans* butadiene by (a) He I PES [3], (b) XPS [6] and (c) SAC-CI method.

In this region, the lowest shake-up state, $\pi^{-2}\pi^*(1b_g^{-2}1a_u)$ of A_u symmetry, was calculated at 13.98 eV with a pole strength of 0.16. The intensity is distributed by the interaction with the ionization from next highest occupied molecular orbital (HOMO) calculated at 11.46 eV. In XPS [6], peak 6 was observed as the shoulder of the higher energy side of peak 5; this shake-up state is one candidate of this shoulder. This state was also discussed in the Green's function calculation [8, 9].

Next, peaks 7 and 8 were observed at 15.59 and 16.29 eV as a continuous asymmetric band. These peaks correspond to the ionizations from $5a_g$ and $5b_u$ MOs. In the present results, the $5b_u$ state splits into two peaks by the interaction with the $\sigma^{-1}\pi^{-1}\pi^*$, $(7a_g^{-1}2a_u1b_g^{-1})$ shake-up state; this splitting explains the asymmetric shape of the observed band. We assign these three states calculated at 15.22, 15.64 and 15.87 eV to this band.

The prominent peaks of the ionizations from the $4b_u$ and $4a_g$ MOs were calculated at 18.16 and 19.46 eV, respectively; they were attributed to the peaks observed at 18.00 and 19.19 eV. Many shake-up states appear from this energy region. In particular, the intensity due to the $4a_g$ component characterized as 2s orbital distributes to many shake-up states through final-ionic-state interaction. In the higher-energy region of these two peaks, the shake-up states whose intensities are due to $4a_g$ MOs continue up to ~25 eV. These shake-up states are dominantly characterized as $\sigma^{-1}\pi^{-1}\pi^*$ states.

Peaks 11 and 12 correspond to the ionizations from $3a_g$ and $3b_u$ MOs. Although the orbital picture is not valid for these states, Koopmans' ordering of these ionizations reverses. In this energy region, many shake-up states, characterized as the ionizations from $5a_g$ or $6b_u$ MOs accompanied by the π–π^* transition, were calculated. For peak 13, some shake-up states having a $3b_g$ component were obtained.

3.2. *Acrolein*

The Hartree–Fock orbital sequence of s-*trans* acrolein is

$$(core)^8(5a')^2(6a')^2(7a')^2(8a')^2(9a')^2(10a')^2$$
$$\times(11a')^2(12a')^2(1a'')^2(13a')^2(2a'')^2,$$

where two a″ orbitals are π MOs and the 13a′ MO is due to the lone pairs of the O atom. The 5a′ to 7a′ MOs correspond to 2s orbitals of C and other MOs represent CH, CC and CO σ-bonding. The outer-valence region of acrolein has been intensively investigated experimentally and theoretically [10–13] as noted in section 1. In the present work, our method was applied to the spectrum up to ~25 eV; 40 and 20 solutions were calculated for A′ and A″ symmetry, respectively. Table 2 summarizes the calculated results with the experimental values and figure 2 compares the present theoretical spectrum with the He I [3] and He II [10] PES.

The low-lying peaks up to ~15 eV can be regarded as main peaks with the intensity larger than 0.7. For the first two peaks observed at 10.10 and 10.92 eV [3], we assign 13a′ and 2a″ states, respectively, in agreement with other works. Koopmans' ordering reverses for these peaks. It should be noted that the effect of electron correlations in the ionized states originating from the n orbital is larger than the π orbital. This feature can be also found in other π-conjugated systems including lone pair electrons like *p*-benzoquinone [41]. For the next overlapping peaks 3 and 4 at 13.7 eV, the 1a″ and 12a′ states were calculated at 13.69 and 13.88 eV, respectively. At the foot of the 12a′ state, the lowest shake-up state was calculated at 13.74 eV, however, the intensity was very small at 0.02. This state is characterized as $n^{-1}\pi^{-1}\pi^*$ $(13a'^{-1}3a''2a''^{-1})$. Note that neutral acrolein

Table 1. Valence ionized states of 1,3-butadiene; ionization potentials (IPs) (in eV), monopole intensities (in parenthesis), and main configurations calculated by the SAC-CI method. Ionized states whose intensity is larger than 0.02 are shown.

| | Exptl. | | SD-R | general-R | |
| | | | | SAC-CI | |
State	XPS[a] IP	HeIPES[b] IP	IP (Intensity)	IP (Intensity)	Main configurations
1bg	9.09	9.09	8.72 (0.84)	8.64 (0.88)	$0.92(1b_g^{-1})$
1a$_u$	11.49	11.55	11.40 (0.80)	11.46 (0.73)	$0.84(1a_u^{-1})$
	14.29		15.99 (0.04)	13.98 (0.16)	$0.80(1b_g^{-2}2a_u)$
7a$_g$	12.19	12.35	11.80 (0.82)	12.02 (0.88)	$0.90(7a_g^{-1})$
6b$_u$	13.29	13.70	13.15 (0.81)	13.41 (0.85)	$0.89(6b_u^{-1})$
6a$_g$	13.76	(14.00)	13.54 (0.82)	13.92 (0.87)	$0.90(6a_g^{-1})$
5a$_g$	15.59	15.31	15.12 (0.79)	15.22 (0.78)	$0.86(5a_g^{-1})$
				18.91 (0.03)	$0.83(1b_g^{-2}8a_g)$
				19.23 (0.04)	$0.82(5b_u^{-1}1a_u1b_g^{-1}) + 0.60(6a_g^{-1}2a_u1a_u^{-1})$
5b$_u$	15.59	15.31	15.57 (0.79)	15.64 (0.47)	$0.67(5b_u^{-1}) - 0.66(7a_g^{-1}2a_u1b_g^{-1}) - 0.44(1b_g^{-1}2a_u7a_g^{-1})$
	16.29			15.87 (0.33)	$0.55(5b_u^{-1}) + 0.79(7a_g^{-1}2a_u1b_g^{-1})$
				17.53 (0.02)	$1.0(6a_g^{-1}2a_u1b_g^{-1}) - 0.50(1b_g^{-1}2a_u6a_g^{-1})$
4b$_u$	18.00	17.70	18.14 (0.76)	18.16 (0.61)	$0.75(4b_u^{-1})$
			22.10 (0.03)	18.57 (0.07)	$0.83(1b_g^{-1}7b_u1b_g^{-1})$
			22.39 (0.03)	19.21 (0.05)	$0.55(1b_g^{-2}8b_u) - 0.54(1b_g^{-1}2a_u7a_g^{-1})$
				19.34 (0.06)	$0.66(1b_g^{-2}8b_u) + 0.44(1b_g^{-1}2a_u7a_g^{-1})$
				20.72 (0.06)	$0.58(1b_g^{-1}2a_u6a_g^{-1}) + 0.42(1b_g^{-2}9b_u)$
				20.73 (0.05)	$0.58(1b_g^{-2}9b_u) - 0.48(1b_g^{-1}2a_u6a_g^{-1})$
				22.35 (0.04)	$0.62(5b_u^{-1}2b_g1b_g^{-1}) - 0.62(5b_u^{-1}2a_u1a_u^{-1})$
				23.03 (0.04)	$0.63(6a_g^{-1}2b_g1a_u^{-1})$
4a$_g$	19.19		19.54 (0.65)	19.46 (0.43)	$0.64(4a_g^{-1})$
			19.82 (0.10)	19.57 (0.15)	$0.47(1b_g^{-1}2a_u6b_u^{-1}) + 0.44(1b_g^{-1}2b_g7a_g^{-1})$
				20.90 (0.02)	$0.83(1b_g^{-2}11a_g)$
				21.11 (0.02)	$0.55(1b_g^{-2}9a_g) + 0.45(1a_u^{-1}8b_u1b_g^{-1})$
				21.14 (0.05)	$0.40(1a_u^{-1}2a_u6a_g^{-1})$
				21.55 (0.04)	$0.71(1b_g^{-1}2b_g7a_g^{-1})$
				22.67 (0.07)	$0.70(1a_u^{-1}2a_u7a_g^{-1})$
				24.01 (0.02)	$0.56(1b_g^{-1}2b_g6a_g^{-1})$
				24.43 (0.02)	$0.43(1b_g^{-2}12a_g)$
				25.27 (0.07)	$0.61(1b_g^{-1}2a_u5b_u^{-1})$
3a$_g$	24.53			25.58 (0.26)	$0.51(3a_g^{-1}) + 0.39(1b_g^{-1}2b_g5a_g^{-1})$
				25.69 (0.14)	$0.38(3a_g^{-1}) - 0.58(1a_u^{-1}2a_u5a_g^{-1})$
				26.29 (0.03)	$0.58(1b_g^{-1}9b_u2a_u^{-1}) + 0.52(2a_u^{-1}9b_u1b_g^{-1})$
3b$_u$	22.44		23.45 (0.42)	23.18 (0.16)	$0.4(3b_u^{-1}) + 0.39(2a_u^{-1}11a_g1b_g^{-1})$
			23.66 (0.16)	23.33 (0.03)	$0.64(1b_g^{-1}2b_g6b_u^{-1})$
			23.77 (0.04)	23.80 (0.26)	$0.50(3b_u^{-1}) - 0.47(1b_g^{-2}11b_u)$
			23.79 (0.04)	23.97 (0.07)	$0.55(1a_u^{-1}2a_u6b_u^{-1}) + 0.52(1b_g^{-1}2a_u5a_g^{-1})$
				26.77 (0.04)	$0.40(1b_g^{-1}3a_u7a_g^{-1})$

[a] From [6].
[b] From [3].

has the n–π* excited state at 3.29 eV. The 11a′ state was obtained at 14.71 eV in accordance with peak 5 observed at 14.60 eV [3].

In the higher-energy side of peak 5, the correlation peak was measured by He I [3] and He II [10] PES at 15.4 eV. In this energy region, the 9a′ and 10a′ states strongly interact with the two-electron process of n^{-1}π^{-1}π* (2a″$^{-1}$3a″13a′$^{-1}$). We assigned the lower peak calculated at 15.68 eV with the intensity of 0.41 to this correlation peak. For the overlapping peaks 6 and 7 observed at 16.3 eV, we attributed two A′ states calculated at 16.13 and 16.60 eV; these states are described by the linear combination of the 10a′ and 9a′ states. At the higher energy side of this band, a satellite state whose intensity is due to the 1a″ orbital was obtained at 16.81 eV; this state was characterized

Table 2. Valence ionized states of *trans* acrolein; ionization potentials (IPs) (in eV), monopole intensities (in parenthesis) and main configurations calculated by the SAC-CI method. Ionized states whose intensity is larger than 0.02 are shown.

| | Exptl. | | SD-*R* | general-*R* | |
State	He II PES[a] IP	He I PES[b] IP	IP (Intensity)	IP (Intensity)	Main configurations
13a′	10.1	10.10	9.65 (0.81)	9.56 (0.83)	$0.89(13a'^{-1})$
2a″	11.0	10.92	10.57 (0.85)	10.43 (0.89)	$0.93(2a''^{-1})$
1a″	13.8	13.70	13.67 (0.78)	13.69 (0.72)	$0.84(1a''^{-1})$
			19.20 (0.03)	16.11 (0.00)	$0.74(13a'^{-2}3a'')$
				16.81 (0.09)	$0.80(2a''^{-1}3a'')$
				19.03 (0.07)	$0.63(2a''^{-1}3a''1a''^{-1}) - 0.50(2a''^{-2}4a'')$
12a′				13.74 (0.02)	$1.00(13a'^{-1}3a''2a''^{-1})$
	13.8	13.70	13.58 (0.83)	13.88 (0.83)	$0.86(12a'^{-1})$
11a′	14.8	14.60	14.31 (0.81)	14.71 (0.83)	$0.87(11a'^{-1})$
9a′ + 10a′	15.4			15.68 (0.41)	$0.40(10a'^{-1}) - 0.54(2a''^{-1}3a''13a'^{-1})$
9a′ + 10a′	16.2	16.30	15.94 (0.81)	16.13 (0.78)	$0.67(9a'^{-1}) - 0.50(10a'^{-1})$
9a′ + 10a′	16.2	16.30	16.01 (0.80)	16.60 (0.49)	$0.56(10a'^{-1})$
8a′	18.8		19.23 (0.80)	19.15 (0.42)	$0.63(8a'^{-1}) - 0.40(13a'^{-1}3a''1a''^{-1})$
			19.67 (0.03)	19.36 (0.32)	$0.54(8a'^{-1}) - 0.52(12a'^{-1}3a''2a''^{-1})$
			20.87 (0.04)	19.90 (0.08)	$0.70(2a''^{-1}4a''13a'^{-1}) - 0.44(2a''^{-1}3a''13a'^{-1})$
				20.57 (0.02)	$0.68(9a'^{-1}3a''2a''^{-1}) - 0.50(2a''^{-1}3a''9a'^{-1})$
7a′	20.9		21.23 (0.59)	21.02 (0.21)	$0.38(7a'^{-1}) + 0.38(2a''^{-1}3a''11a'^{-1})$
			21.41 (0.13)	21.33 (0.24)	$0.47(7a'^{-1}) - 0.46(10a'^{-1}3a''2a''^{-1})$
			24.32 (0.02)	21.34 (0.16)	$0.48(10a'^{-1}3a''2a''^{-1})$
			24.44 (0.03)	21.72 (0.06)	$0.50(2a''^{-1}3a''12a'^{-1})$
				21.94 (0.05)	$0.63(11a'^{-1}4a''2a''^{-1}) - 0.57(11a'^{-1}4a''1a''^{-1})$
				22.64 (0.04)	$0.47(1a''^{-1}3a''12a'^{-1})$
				23.05 (0.02)	$0.37(9a'^{-1}4a''2a''^{-1})$
				23.65 (0.02)	$0.45(10a'^{-1}4a''2a''^{-1})$
				23.83 (0.07)	$0.38(1a''^{-1}3a''11a'^{-1})$
				24.56 (0.03)	$0.39(1a''^{-1}3a''12a'^{-1})$
				24.94 (0.07)	$0.45(2a''^{-1}3a''10a'^{-1})$

[a]From [10].
[b]From [3].

as the $\pi^{-2}\pi^*$ state. Accordingly, the experimental spectra have the shoulder at the higher energy side of peaks 6 and 7.

The He II PES observed two bands centred at 18.8 and 20.9 eV [10]. For the band at 18.8 eV, many shake-up states were calculated with the distributed intensities like in butadiene. The prominent split peaks originating from the 8a′ orbital were obtained at 19.15 and 19.36 eV with intensities of 0.42 and 0.32, respectively. These states also strongly interact with the two-electron processes of $n^{-1}\pi^{-1}\pi^*$ ($13a'^{-1}3a''1a''^{-1}$) and $\sigma^{-1}\pi^{-1}\pi^*$ ($12a'^{-1}3a''1a''^{-1}$). In the energy region of the band at 20.9 eV, many shake-up satellite states characterized as the ionizations from σ orbitals (12a′, 10a′, 9a′) accompanied by the π–π* excitation were calculated with considerable intensities. The prominent peaks were obtained at 21.02, 21.33 and 21.34 eV and the satellite states whose intensities are due to the 7a′ orbital continue up to ∼25 eV.

3.3. Glyoxal

The s-*trans* glyoxal has two O atoms in π conjugation and its Hartree–Fock orbital sequence is written as

$$(\text{core})^8(3a_g)^2(3b_u)^2(4a_g)^2(4b_u)^2(5a_g)^2(5b_u)^2$$
$$\times (6a_g)^2(1a_u)^2(6b_u)^2(1b_g)^2(7a_g)^2,$$

where $1b_g$ and $1a_u$ orbitals are π MOs; $7a_g$ and $6b_u$ orbitals correspond to the lone pairs of O atoms. The outer-valence region of glyoxal was measured by the He II PES with the theoretical assignments by Green's function calculation [10]. In the present work, for calculating the spectrum up to ∼25 eV, 40, 10, 10 and 40 states were solved for A_g, B_g, A_u and B_u symmetry, respectively. The detailed SAC-CI results were summarized in table 3 and the theoretical spectrum was compared with the experimental spectra by the He I PES [3] and He II PES [10].
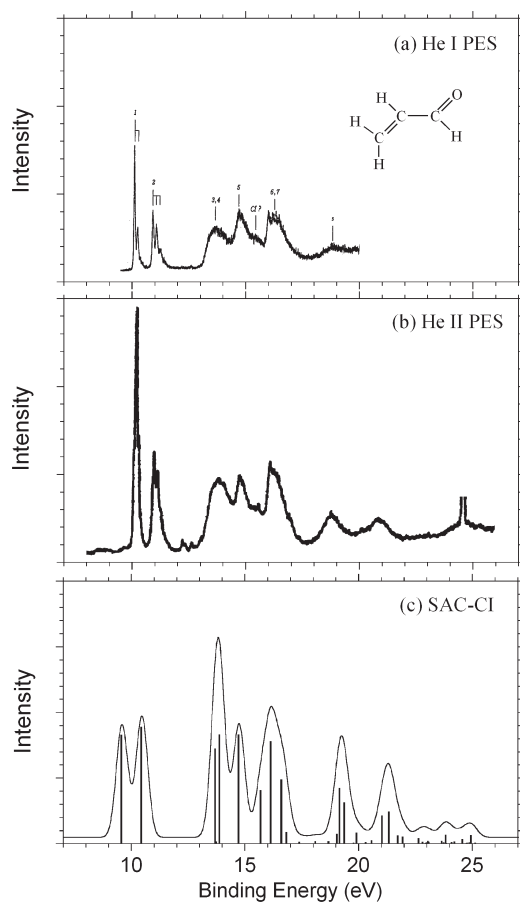
Figure 2. Valence ionization spectra of *trans* acrolein by (a) He I PES [3], (b) He II PES [10] and (c) SAC-CI method.

Figure 3. Valence ionization spectra of s-*trans* glyoxal by (a) He I PES [3], (b) He II PES [10] and (c) SAC-CI method.

The peaks in the outer-valence region up to ~17 eV were calculated to be main peaks with the intensity larger than 0.75. The electron correlations of the ionized states due to n orbitals were also calculated to be large as in acrolein; Koopmans' ordering reversed between $6b_u$ and $1b_g$ states. The first two peaks were ionizations from n orbitals, $7a_g$ and $6b_u$ states, calculated at 10.26 and 12.26 eV, respectively. The π orbitals exist in the higher energy region compared with butadiene and acrolein; they were calculated at 13.86 and 15.54 eV. In the PES, vibrational structure is remarkable in the observed peaks 2 and 3, namely, ionizations from n and π orbitals; the structure relaxation of these states is interesting. The overlapping bands were observed at ~16.9 eV. For this band, $5a_g$ and $5b_u$ states were calculated at 16.67 and 16.92 eV, respectively. Some shake-up states were calculated in the energy region of 13–17 eV, although their intensities were small. The lowest shake-up state was calculated at 12.91 eV and was characterized as $n^{-2}\pi^*$. On the other hand, the lowest $n^{-1}\pi^{-1}\pi^*$ and $\pi^{-2}\pi^*$ shake-up states were obtained at 14.14 and
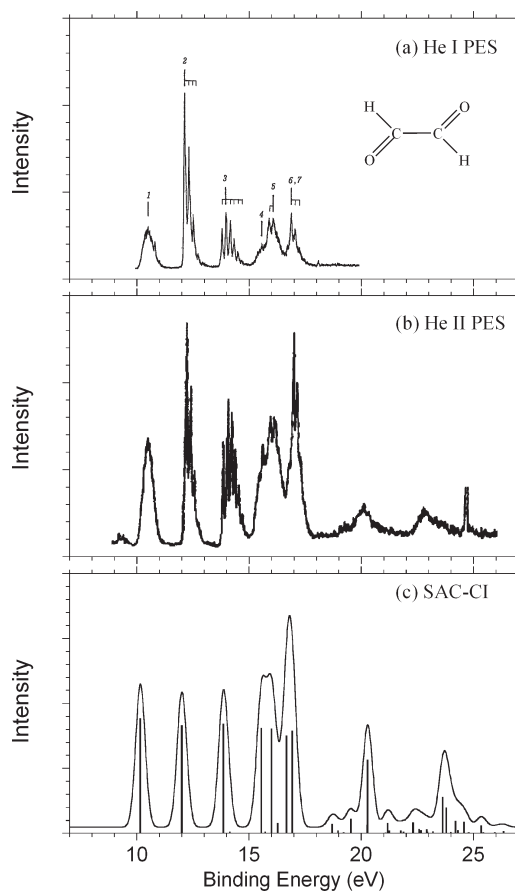
17.96 eV, respectively. Among peaks 5 and 6, a shake-up state with the considerable intensity of 0.08 was calculated at 16.28 eV.

Two continuous bands centred at 20.0 and 22.8 eV were observed in the inner-valence region by the He II PES. In this energy region, many shake-up states with the intensities due to $4b_u$ and $4a_g$ orbitals were calculated. For the broad peak centred at 20.0 eV, the continuous shake-up states exist; prominent peaks were obtained at 18.71, 19.54, 20.28 and 21.17 eV. These shake-up states are mainly characterized as the two-electron processes of $n^{-1}\pi^{-1}\pi^*$. For the peak at 22.8 eV, continuous shake-up states were also obtained at 23.62 and 23.80 eV with intensities of 0.28 and 0.20, respectively. Two-electron processes in this energy region are the ionizations from $5a_g$, $6a_g$ and $7a_g$ orbitals accompanied by the $\pi^{-1}\pi^*$ transition.

3.4. *Methylenecyclopropene*

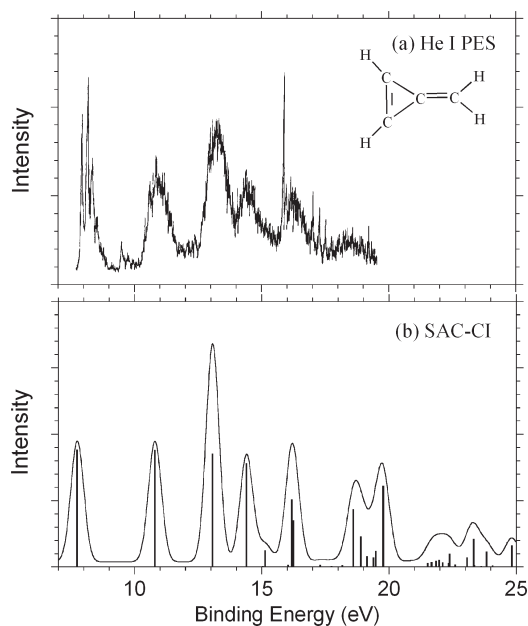Methylenecyclopropene has a different π conjugation pattern with the constrained molecular structure.

Figure 4. Valence ionization spectra of methylenecyclopropene by (a) He I PES [14] and (b) SAC-CI method.

Its valence electronic structure is similar to butadiene, while the first IP of this molecule is lower than butadiene. The Hartree–Fock orbital sequence is written as

$$(\mathrm{core})^8(4a_1)^2(5a_1)^2(2b_2)^2(6a_1)^2(7a_1)^2(3b_2)^2$$
$$\times (8a_1)^2(1b_1)^2(4b_2)^2(2b_1)^2,$$

where $1b_1$ and $2b_1$ orbitals are π MOs, $6a_1$ to $4b_2$ orbitals are CH and CC σ-bonding MOs. The $4a_1$ to $2b_2$ MOs correspond to 2s orbitals of C. For this molecule, little information is available for the valence electronic structure; the outer-valence region of this molecule was measured by the He I PES with the assignments of Koopmans' picture [14]. For calculating the spectrum up to ~25 eV, 40, 10, 10 and 40 states were solved for A_1, A_2, B_1 and B_2 symmetry, respectively. The SAC-CI results of the ionized states of this molecule are summarized in table 4 and the theoretical spectrum is compared with the He I PES [14].

Similar to butadiene, the valence ionized states up to ~15 eV are main peaks. The first IP observed at 8.4 eV is lower than that of butadiene at 9.1 eV, and the energy separation between the first and second peaks ~5 eV is much larger than that of butadiene, ~2 eV. Therefore, the low-lying satellite, $\pi^{-2}\pi^*$ state, is anticipated from this first IP. However, this shake-up state was calculated to be 15.13 eV. For this shake-up state, a shoulder was observed in the higher energy region of the peak at 14.3 eV [14]. The third peak consists of the ionizations

from $1b_1$ and $8a_1$ orbitals. These two states are almost degenerate. The $1b_1$ state interacts with the shake-up states distributing the intensity.

The $7a_1$ state interacts with $\pi^{-1}\pi'^{-1}\pi^*$ ($2b_1^{-1}1a_24b_2^{-1}$) and splits into two peaks. These two peaks were calculated at 16.18 and 16.24 eV and the experimental band is centred at 15.90 eV. The $6a_1$ state also interacts with the $\pi^{-2}\sigma^*$ ($2b_1^{-2}9a_1$) shake-up state and splits into three peaks. Just above this peak, the $2b_2$ state was calculated at 19.48 and 19.78 eV, though there is no experimental information for this energy region of this molecule. In the energy region of 21.5–25 eV, many shake-up states with small intensity continue as in butadiene.

3.5. *Methylenecyclopropane*

Methylenecyclopropane has 2π electrons and the effect of π-conjugation in methylenecyclopropene can be analysed by a comparison between these molecules. The MO sequence of this molecule is written as

$$(\mathrm{core})^8(4a_1)^2(5a_1)^2(2b_2)^2(6a_1)^2(1b_1)^2(7a_1)^2$$
$$\times (3b_2)^2(1a_2)^2(8a_1)^2(4b_2)^2(2b_1)^2,$$

where the $2b_1$ orbital is a π MO and the other orbitals describe CH and CC σ-bonding MOs and 2s orbitals. For this molecule, He I [3] and He II [15] PESs were observed and the theoretical assignment was done with CI calculations up to 17.0 eV [3]. For obtaining the spectrum up to ~25 eV, twenty solutions were calculated for each symmetry. In figure 5, the He I PES [3] and the present SAC-CI spectra are compared. In table 5, the results were summarized with the IPs observed by the photoelectron spectroscopies [3, 15].

The first π^{-1} state is observed at 9.57 eV, which is much higher than that of methylenecyclopropene. First three peaks were assigned to the ionizations from the outer three MOs, $2b_1$, $4b_2$ and $8a_1$. The next continuous four peaks at 13.1, 14.5, 15.8 and 16.3 eV in the He I PES [3] were attributed to the $1a_2$, $3b_2$, $7a_1$ and $1b_1$ states, respectively. These seven ionizations are described by the one-electron process; Koopmans' ordering is valid for these states. The $3b_2$ state calculated at 14.58 eV was contributed by a two-electron process. In the higher-energy region of this state, the outermost shake-up state, $\sigma^{-1}\pi^{-1}\pi^*$ was predicted at 15.57 eV, which was slightly higher than methylenecyclopropene. This peak exists among the intense main peak and was not addressed in the previous experimental works.

In the energy region higher than 17 eV, two peaks were suggested at about ~17.5 and ~19.7 eV [15]. For these peaks, we calculated the $6a_1$ and $2b_2$ states

Table 3. Valence ionized states of s-*trans* glyoxal; ionization potentials (IPs) (in eV), monopole intensities (in parenthesis) and main configurations calculated by the SAC-CI method. Ionized states whose intensity is larger than 0.02 are shown.

| | Exptl. | | SAC-CI | | |
| | | | SD-R | general-R | |
State	He II PES[a] IP	He I PES[b] IP	IP (Intensity)	IP (Intensity)	Main configurations
$7a_g$	10.6	10.60	10.25 (0.82)	10.23 (0.88)	$0.90(7a_g^{-1})$
$6b_u$	12.4	12.20	12.01 (0.79)	12.26 (0.83)	$0.88(6b_u^{-1})$
$1bg$	14.0	14.03	13.99 (0.81)	13.86 (0.84)	$0.90(1b_g^{-1})$
$1a_u$				12.74 (0.00)	$1.00(7a_g^{-2}2a_u)$
$1a_u$	15.3	15.55	15.62 (0.81)	15.54 (0.81)	$0.88(1a_u^{-1})$
			23.13 (0.02)	20.26 (0.07)	$0.67(7a_g^{-2}2a_u) - 0.54(6b_u^{-2}2a_u)$
$6a_g$	16.5	16.07	15.89 (0.81)	16.00 (0.81)	$0.86(6a_g^{-1})$
				16.28 (0.08)	$0.80(7a_g^{-1}2a_u6b_u^{-1}) - 0.57(6b_u^{-1}2a_u7a_g^{-1})$
$5a_g$	–	(16.90)	16.75 (0.79)	16.67 (0.75)	$0.83(5a_g^{-1})$
$5b_u$	17.0	16.88	16.90 (0.79)	16.92 (0.79)	$0.86(5b_u^{-1})$
				18.71 (0.07)	$0.67(1b_g^{-1}2a_u7a_g^{-1}) - 0.50(1a_u^{-1}2a_u6b_u^{-1})$
$4b_u$				19.54 (0.11)	$0.74(6b_u^{-1}2a_u1a_u^{-1})$
	20.0		20.07 (0.77)	20.28 (0.57)	$0.71(4b_u^{-1})$
				21.17 (0.08)	$0.66(7a_g^{-2}7b_u)$
				22.58 (0.03)	$0.44(1a_u^{-1}2b_g7a_g^{-1})$
				23.79 (0.02)	$0.47(1b_g^{-1}2a_u6a_g^{-1}) - 0.46(1a_u^{-1}2a_u5b_u^{-1})$
				24.31 (0.02)	$0.51(1a_u^{-1}2a_u6b_u^{-1}) + 0.45(1b_g^{-1}2b_g6b_u^{-1})$
$4a_g$				21.76 (0.02)	$0.41(5a_g^{-1}2a_u6b_u^{-1})$
				22.31 (0.08)	$0.50(7a_g^{-2}9a_g) + 0.40(1b_g^{-1}2b_g7a_g^{-1})$
				22.66 (0.02)	$0.42(7a_g^{-1}8b_u6b_u^{-1}) - 0.40(6b_u^{-1}8b_u7a_g^{-1})$
			23.12 (0.03)	22.91 (0.03)	$0.48(7a_g^{-2}9a_g) - 0.40(6b_u^{-1}8b_u7a_g^{-1})$
	22.8		23.45 (0.71)	23.62 (0.28)	$0.48(4a_g^{-1}) + 0.51(1b_g^{-1}2a_u5b_u^{-1})$
				23.80 (0.20)	$0.42(4a_g^{-1}) + 0.45(5a_g^{-1}2a_u1a_u^{-1})$ $+ 0.42(1a_u^{-1}2a_u5a_g^{-1})$
				24.19 (0.10)	$0.69(5a_g^{-1}2a_u1a_u^{-1})$
				24.57 (0.09)	$0.45(1a_u^{-1}2a_u6a_g^{-1}) + 0.45(1b_g^{-1}2a_u6b_u^{-1})$
				25.34 (0.06)	$0.59(6a_g^{-1}2b_g1b_g^{-1}) + 0.58(5b_u^{-1}2a_u1b_g^{-1})$

[a]From [10].
[b]From [3].

at 18.02 and 20.57 eV, respectively. Among these two prominent peaks, two shake-up states were obtained at 19.42 and 19.57 eV. However, the orbital picture is valid up to high energy region about 20 eV in contrast to other molecules studied in the present work, since this molecule has only a single π-bond. Above these two peaks, breakdown of the orbital picture was clear in the region of ~23 eV; many correlation peaks continued in 22–25 eV. The cluster of these peaks, whose intensity is due to the $5a_1$ component, was attributed to the peak observed at ~22.2 eV; the ionization dominantly from the $5a_1$ MO was calculated at 23.05 eV with an intensity of 0.36.

3.6. Outermost satellites

The position and intensity of the low-lying shake-up states of the present molecules are interesting, since they have characteristic π-conjugation. In figure 6,

the calculated IPs of the valence ionized states of these molecules are compared; main peaks and outermost satellites are shown. For the peaks in the inner-valence region, their positions are represented by the most intense peak.

In the present systems, we can discuss the effect of the pattern of π-conjugation and the n–π* transitions on the position and intensity of the satellite peaks. Firstly, as the π-conjugation becomes longer, the IP of the outermost satellite peak becomes lower. The IPs of the outermost satellites were calculated to be 17.55 [29], 13.98 and 11.92 eV by the SAC-CI method, for ethylene, 1,3-*trans* butadiene and 1,3,5-*trans* hexatriene, respectively. For hexatriene, only some main peaks and the outermost satellite were calculated for comparison. The intensity of these satellites is dominantly due to the final-ionic-state interaction with the next HOMO for butadiene and hexatriene. The intensity of these satellites becomes larger as the π-conjugation becomes

Table 4. Valence ionized states of methylenecyclopropene; ionization potentials (IPs) (in eV), monopole intensities (in parenthesis) and main configurations calculated by the SAC-CI method. Ionized states whose intensity is larger than 0.02 are shown.

		SAC-CI		
		SD-R	general-R	
State	He I PES[a]	IP (Intensity)	IP (Intensity)	Main configurations
$2b_1$	8.41	7.89 (0.83)	7.84 (0.88)	$0.92(2b_1^{-1})$
$4b_2$	10.95	10.70 (0.82)	10.79 (0.88)	$0.91(4b_2^{-1})$
$1b_1$	13.10	13.03 (0.79)	13.06 (0.73)	$0.84(1b_1^{-1})$
		17.59 (0.04)	15.13 (0.13)	$0.81(2b_1^{-2}3b_1)$
			21.67 (0.04)	$0.92(2b_1^{-1}3b_11b_1^{-1})$
$8a_1$	13.10	12.81 (0.81)	13.06 (0.85)	$0.90(8a_1^{-1})$
$3b_2$	14.30	14.10 (0.79)	14.40 (0.78)	$0.85(3b_2^{-1})$
		18.92 (0.02)	19.13 (0.08)	$0.66(2b_1^{-2}5b_2) - 0.45(2b_1^{-2}6b_2)$
$7a_1$	15.90	15.85 (0.79)	16.18 (0.51)	$0.69(7a_1^{-1}) - 0.52(2b_1^{-1}1a_24b_2^{-1})$
			16.24 (0.35)	$0.54(7a_1^{-1}) + 0.65(2b_1^{-1}1a_24b_2^{-1})$
$6a_1$	18.10	18.10 (0.66)	18.60 (0.44)	$0.64(6a_1^{-1}) - 0.44(2b_1^{-2}9a_1)$
		18.79 (0.05)	18.90 (0.23)	$0.46(6a_1^{-1}) + 0.50(2b_1^{-2}9a_1) - 0.48(2b_1^{-2}11a_1)$
		20.61 (0.07)	19.40 (0.07)	$0.59(2b_1^{-2}12a_1) - 0.48(2b_1^{-2}11a_1)$
$2b_2$		19.15 (0.66)	19.48 (0.12)	$0.82(2b_1^{-1}3b_14b_2^{-1})$
		20.09 (0.04)	19.78 (0.61)	$0.76(2b_2^{-1})$
		20.90 (0.04)	22.11 (0.03)	$0.72(6a_1^{-1}1a_22b_1^{-1}) - 0.57(8a_1^{-1}1a_21b_1^{-1}) + 0.50(2b_1^{-1}1a_26a_1^{-1})$
			22.34 (0.03)	$0.60(2b_1^{-1}1a_26a_1^{-1})$
$5a_1$		22.31 (0.15)	21.52 (0.03)	$0.59(2b_1^{-2}14a_1)$
		22.86 (0.37)	21.68 (0.04)	$0.75(2b_1^{-1}3b_18a_1^{-1})$
		22.96 (0.02)	21.85 (0.04)	$0.49(1b_1^{-1}1a_24b_2^{-1})$
		23.50 (0.13)	21.98 (0.05)	$0.47(2b_1^{-2}14a_1)$
		24.87 (0.03)	22.39 (0.10)	$0.65(7a_1^{-1}3b_12b_1^{-1})$
		25.71 (0.02)	23.06 (0.07)	$0.62(2b_1^{-1}1a_23b_2^{-1}) - 0.50(1b_1^{-1}1a_24b_2^{-1})$
			23.33 (0.21)	$0.44(5a_1^{-1}) - 0.40(2b_2^{-1}1a_22b_1^{-1})$
			23.84 (0.12)	$0.43(2b_1^{-1}1a_22b_2^{-1})$
			24.83 (0.16)	$0.59(2b_1^{-1}3b_17a_1^{-1}) - 0.47(1b_1^{-1}3b_18a_1^{-1})$

[a]From [14].

longer; monopole intensities were calculated as 0.01, 0.16 and 0.20, respectively. These results agree with the ADC(3) calculations [8, 9].

The n–π* transition is usually as low as the π–π* transition in the excitation spectra of molecules, and therefore, lower satellites accompanied by the n–π* transitions are expected for the π-conjugated molecules with lone-pair electrons. Actually, the outermost satellites of acrolein and glyoxal were calculated to be lower than butadiene; they were obtained at 13.76 and 12.91 eV, respectively. However, the intensities of these states were very small such as 0.02 and 0.00. This is because these shake-up states do not effectively interact with the main peaks. The outermost satellite of glyoxal is the A_u state at 12.91 eV and the main peak of A_u symmetry exists at 15.54 eV.

Finally, the effect of constraining the molecular structure of the π-conjugation is considered by the shake-up states of methylenecyclopropene. As noted above, the IP of π^{-1} state of this molecule is lower than butadiene, therefore, the low-lying $\pi^{-2}\pi^*$ satellite is anticipated. The IP of the outermost satellite, however, is 15.13 eV with an intensity of 0.13, which is much higher than that of butadiene, 13.98 eV. This position is almost the same as methylenecyclopropane without π-conjugation.

4. Summary

The valence ionization spectra of some 4π-electron systems, *trans* butadiene, s-*trans* acrolein, s-*trans* glyoxal and methylenecyclopropene, were investigated by the SAC-CI method. Besides the detailed characterization for both main peaks and satellite peaks, the low-lying shake-up states accompanied by the π–π* and n–π* transitions were examined.
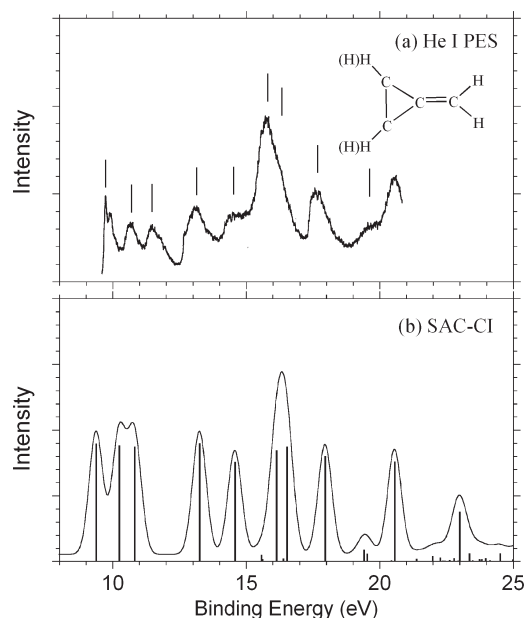
Figure 5. Valence ionization spectra of methylenecyclo-propane by (a) He I PES [3] and (b) SAC-CI method.

The spectrum up to ∼30 eV was calculated for butadiene for which the XPS spectrum is available, and for other molecules, the spectra up to ∼25 eV were studied. The present method has well reproduced the spectra of these molecules and given the detailed assignments for both main peaks and satellite peaks. For these molecules, some split peaks were calculated at around 15–16 eV. In the energy region higher than ∼18 eV, the remarkable breakdown of the orbital picture occurs and the continuous shake-up states have been obtained.

The effect of extending the π-conjugation, introducing the n–π* transition and constraining the molecular structure on the IP and the intensity of the satellites was examined. Acrolein and glyoxal have the outer-most satellites of $n^{-1}\pi^{-1}\pi^*$ and $n^{-2}\pi^*$ states, respectively. Their IPs were calculated to be low, but the intensities were very small, since they do not effectively interact with main peaks. Methylenecyclopropene has constrained molecular structure with a different pattern for the π-conjugation.

Table 5. Valence ionized states of methylenecyclopropane; ionization potentials (IPs) (in eV), monopole intensities (in parenthesis) and main configurations calculated by the SAC-CI method. Ionized states whose intensity is larger than 0.02 are shown.

| | Exptl. | | SD-R IP (Intensity) | SAC-CI general-R | |
| | | | | | |
State	He I PES[a]	He I PES[b]		IP (Intensity)	Main configurations
$2b_1$	9.57	9.76	9.48 (0.84)	9.43 (0.90)	$0.93(2b_1^{-1})$
				16.39 (0.02)	$0.83(2b_1^{-2}3b_1)$
$4b_2$	10.47	10.72	10.32 (0.83)	10.24 (0.88)	$0.92(4b_2^{-1})$
$8a_1$	11.35	11.44	10.83 (0.83)	10.95 (0.88)	$0.92(8a_1^{-1})$
$1a_2$	13.08	13.10	12.98 (0.83)	13.26 (0.90)	$0.93(1a_2^{-1})$
$3b_2$	14.52	14.50	14.50 (0.80)	14.58 (0.76)	$0.85(3b_2^{-1})$
				15.57 (0.05)	$0.94(4b_2^{-1}3b_12b_1^{-1})$
				19.42 (0.09)	$0.83(2b_1^{-1}3b_14b_2^{-1})$
$7a_1$	15.75	15.80	15.78 (0.82)	16.21 (0.86)	$0.90(7a_1^{-1})$
$1b_1$		16.30	16.11 (0.82)	16.53 (0.88)	$0.91(1b_1^{-1})$
$6a_1$	17.45		17.77 (0.80)	18.02 (0.80)	$0.87(6a_1^{-1})$
			22.91 (0.13)	19.57 (0.06)	$0.90(2b_1^{-1}3b_18a_1^{-1})$
				21.39 (0.02)	$0.64(7a_1^{-1}3b_12b_1^{-1}) - 0.41(2b_1^{-2}10a_1)$
				22.02 (0.04)	$0.59(2b_1^{-2}10a_1) - 0.44(2b_1^{-2}9a_1)$
				22.31 (0.03)	$0.53(4b_2^{-1}7b_28a_1^{-1}) - 0.48(4b_2^{-1}5b_28a_1^{-1})$
$2b_2$	19.72		20.36 (0.79)	20.57 (0.76)	$0.84(2b_2^{-1})$
			22.96 (0.03)	22.78 (0.02)	$0.40(4b_2^{-2}6b_2)$
				23.97 (0.02)	$0.57(1a_2^{-1}10a_12b_1^{-1}) + 0.44(1a_2^{-1}11a_12b_1^{-1})$
$5a_1$	22.2		23.22 (0.60)	23.05 (0.36)	$0.59(5a_1^{-1})$
				23.38 (0.08)	$0.60(2b_1^{-2}11a_1)$
				23.79 (0.02)	$0.51(1a_2^{-1}5b_22b_1^{-1}) - 0.47(2b_1^{-1}6b_21a_2^{-1})$

[a]From [15].
[b]From [3].
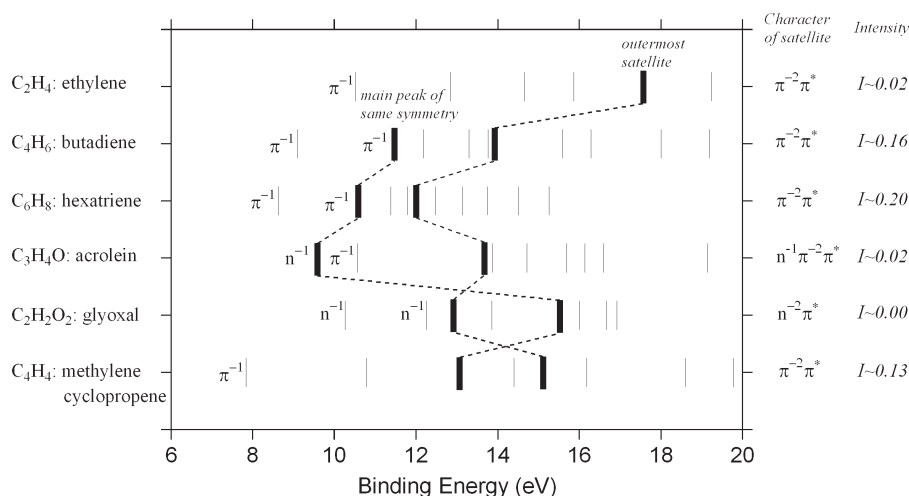
Figure 6.   Comparison of the main peaks and the outermost satellites for the π-conjugated molecules.

The outermost satellite of this molecule was calculated to be higher, although the first IP of the π^{-1} state is lower than that of butadiene.

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