# Fine theoretical spectroscopy using symmetry adapted cluster-configuration interaction general-*R* method: Outer- and inner-valence ionization spectra of CS$_2$ and OCS

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Fine theoretical spectroscopy has been presented by the SAC-CI (symmetry adapted cluster-configuration interaction) general-*R* method for the outer- and inner-valence ionization spectra of CS$_2$ and OCS. The SAC-CI general-*R* method simulated the experimental spectra quite accurately and the detailed assignments of the satellite peaks were given. For CS$_2$, four outer-valence satellites $^2\Pi_u$ states were calculated, one of which was attributed to the recently observed peak (1′). Numerous $^2\Sigma_u^+$ and $^2\Sigma_g^+$ satellite peaks were obtained in the inner-valence region and some of them were dominantly described by triple electron processes; the quadruple *R*-operators were found to be important for describing these states in the general-*R* method. For OCS, the relative position of the main peaks was correctly reproduced and the higher *R*-operators were found to be important for the ordering of *A* and *B* states. In the energy region of 24–36 eV, continuous spectra of numerous $^2\Sigma^+$ satellites were obtained, which reproduced the feature of the photoelectron spectrum. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1492798]

## I. INTRODUCTION

Multiple-electron processes observed in ionization spectra have attracted considerable attention since they directly reflect the electron correlations of the molecules. They are called "satellites" and usually appear in the inner-valence region. But, for the strongly correlated system, they even appear in the outer-valence region. Recently, fine analyses of these peaks on peak positions, intensities, and ionization characters have become possible due to the cooperative interplays between qualified theoretical and experimental works. The developments in the high-resolution spectroscopies are remarkable as seen for synchrotron radiation photoelectron spectroscopy (SRPES), x-ray PES, electron momentum spectroscopy (EMS), and Penning ionization electron spectroscopy (PIES).

Among the extensive works on the satellite peaks, special attention has been paid to the correlation effects in the valence ionized states of CS$_2$.[1–9] Allan *et al.*[1] observed both the outer- and inner-valence region using MgK$\alpha$ PES. The He II PES[2,3] was recorded and the theoretical assignment was given by the 2ph-TDA Green's function method.[3] The dipole $(e,2e)$[4] and binary $(e,2e)$[5] electron impact spectroscopy were also applied. Later, the details of the valence satellites were studied by the high-resolution SRPES using the photon energy dependence of the partial cross sections and asymmetry parameter and also with the help of theoretical spectrum of CIPSI method.[7] In particular, it was pointed out that some of the satellite peaks were described by the three-electron processes. Recently, fine structure of the satellite peaks was analyzed by the He I PES, He II PES and SRPES combined with the algebraic diagrammatic construction (ADC) calculation.[8] However, there are still some discrepancies in the assignments of the satellite peaks. It should also be noted that the precise positions of the main peaks were determined by the high-resolution He II PES[10] and the double ionization spectrum was investigated.[11]

The valence ionized states of OCS have also been intensively studied by various spectroscopies, for examples, He I PES,[10] He II PES,[2] MgK$\alpha$ PES,[1] and dipole $(e,2e)$ for impact energies up to 40 eV.[12–14] The latest experimental work is due to the SRPES[15] with photon energies up to 110 eV. However, theoretical studies on the detailed analysis of the satellites have been very limited for this compound; only the SAC-CI (symmetry adapted cluster-configuration interaction) method[9] and 2ph-TDA method[12] were applied to the inner-valence region. It was also criticized that theoretical spectra did not reproduce the experimental PES; the calculated inner-valence satellite peaks clustered separately against the experimental observation. Thus, it is worth presenting the accurate theoretical spectra and detailed assignments for the correlation peaks of these molecules.

In the series of the studies, we have investigated the valence ionization spectra of various molecules using the SAC-CI method. The SAC/SAC-CI method[16–21] has been successfully applied to a number of molecular spectroscopies including ionization spectra.[20–27] In particular, the SAC-CI general-*R* method[28–31] has been shown to be a powerful tool for describing the multiple electron processes in high accuracy and in studying the large numbers of states appearing in the ionization spectra.[32–38] Recently, we applied the general-*R* method to both the outer- and inner-valence ionization spectra of Group V and VI hydrides and gave the detailed characterizations of the satellite peaks.[36,37] In this work, we investigate the valence ionization spectra of CS$_2$ and OCS by the SAC-CI general-*R* method aiming at the detailed and quantitative assignments of the satellite peaks appearing in the outer- and inner-valence regions.

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## II. COMPUTATIONAL DETAILS

The basis set was selected as flexible as possible to describe the electron correlations of shake-up states, namely valence triple zeta (VTZ) of Ahlrichs;[39] $(10s6p)/[6s3p]$ for C and O and $(12s9p)/[7s5p]$ Gaussian type orbitals (GTOs) for S augmented with two polarization $d$-functions of $\zeta_d = 2.314$, 0.645 for O, $\zeta_d = 1.097$, 0.318 for C, and $\zeta_d = 0.819$, 0.269 for S.[40,41] The present basis set was examined for the low-lying valence ionized states with the additional polarization function and diffuse functions, and was confirmed to be sufficient as shown in the Appendix. The resultant SCF dimensions were 89 and 82 for CS$_2$ and OCS, respectively. The vertical ionization process was studied in this work and, therefore, molecular geometries were fixed to the experimental values;[42] namely $R_{CS} = 1.555\,45$ Å for CS$_2$ and $R_{OC} = 1.16$ Å and $R_{CS} = 1.56$ Å for OCS.

The valence ionization spectra of CS$_2$ and OCS were calculated by the SAC-CI general-$R$ method in both outer- and inner-valence regions up to around double ionization thresholds. In the preliminary calculations, several shake-up states in the inner-valence region of CS$_2$ were found to be described by triples with considerable intensity; this feature was also pointed out in the CIPSI work.[7] For producing the reliable spectrum in this energy region, we included $R$-operators up to quadruples in the general-$R$ calculation and utilized the exponentially generated CI (EGCI) method[29–31] for the reference-CI. In the case of OCS, most of the shake-up states were dominantly described by the doubles until around the double ionization threshold and, therefore, $R$-operators were included up to triples. The $1s$ orbitals of C and O and $1s$, $2s$, and $2p$ orbitals of S were kept as frozen core and all the other MOs were included in the active space; the active space of the SAC-CI consisted of 8 occupied and 70 unoccupied MOs for CS$_2$ and 8 occupied and 67 unoccupied MOs for OCS.

In order to reduce the computational effort, perturbation selection[22] was performed in the state-selection scheme. The thresholds were determined so as to achieve the calculations including the sufficient order of $R$-operators yet with appropriate computational cost. For CS$_2$, the threshold of the linked terms for the ground state was set to $\lambda_g = 5 \times 10^{-6}$ and the unlinked terms were adopted as the products of the important linked terms whose SDCI coefficients were larger than 0.005. For ionized state, the threshold of the double linked term was set to $\lambda_e = 1 \times 10^{-7}$ and those of the triples and quadruples were $\lambda_e = 1 \times 10^{-6}$ and $5 \times 10^{-6}$, respectively. The reference-EGCI calculations were performed to determine the primary states using small active space; triples were generated by the exponential-generation algorithm.[29–31] The threshold of the exponential generation was set to $\lambda_{AA} = 0.1$. For the main peaks of CS$_2$, better thresholds were used. For OCS, better thresholds were adopted, namely, $\lambda_g = 1 \times 10^{-7}$ for SAC and $\lambda_e = 1 \times 10^{-7}$ and $1 \times 10^{-6}$ for doubles and triples of SAC-CI, respectively. The thresholds of the CI coefficients for calculating the unlinked operators in the SAC-CI method are 0.01 and $1 \times 10^{-8}$ for the $R$ and $S$ operators, respectively.

Ionization cross-sections were calculated using the monopole approximation[43,44] to estimate the relative intensi-

TABLE I. The reference-EGCI and SAC-CI general-$R$ dimensions for the ionized states of CS$_2$ and OCS.

| State | Total | Singles | Doubles | Triples | Quadruples |
|---|---|---|---|---|---|
| CS$_2$ | | | | | |
| Reference-EGCI dimension | | | | | |
| $^2\Sigma_g^+$ | 5617 | 2 | 228 | 5387 | $\cdots$ |
| $^2\Pi_g$ | 5679 | 1 | 200 | 5478 | $\cdots$ |
| $^2\Sigma_u^+$ | 5650 | 2 | 228 | 5420 | $\cdots$ |
| $^2\Pi_u$ | 5586 | 1 | 200 | 5385 | $\cdots$ |
| | | | | | |
| SAC-CI dimension after perturbation selection | | | | | |
| $^2\Sigma_g^+$ | 86 399 | 2 | 608 | 42 523 | 43 266 |
| $^2\Pi_g$ | 82 227 | 1 | 518 | 35 630 | 46 078 |
| $^2\Sigma_u^+$ | 84 319 | 2 | 601 | 42 130 | 41 586 |
| $^2\Pi_u$ | 83 758 | 1 | 515 | 35 730 | 47 512 |
| | | | | | |
| OCS | | | | | |
| SAC-CI dimension after perturbation selection | | | | | |
| $^2\Sigma^+$ | 97 117 | 4 | 1164 | 95 949 | $\cdots$ |
| $^2\Pi$ | 83 562 | 2 | 986 | 82 574 | $\cdots$ |

ties of the peaks. Both initial- and final-state correlation effects were included.

The SAC/SAC-CI calculations were executed using the SAC96 program system,[45] which has been incorporated into the development version of the Gaussian suite of programs.[46]

## III. RESULTS AND DISCUSSION

### A. CS$_2$

The outer- and inner-valence regions of the ionization spectra of CS$_2$ up to c.a. 28 eV were studied by the SAC-CI general-$R$ method. The valence electronic configuration of CS$_2$ is described by

$$(\text{core})^{22}(5\sigma_g)^2(4\sigma_u)^2(6\sigma_g)^2(5\sigma_u)^2(2\pi_u)^4(2\pi_g)^4.$$

As noted in the previous section, several states in the inner-valence region were found to be substantially dominated by triples; namely ionization accompanied by two-electron ex-
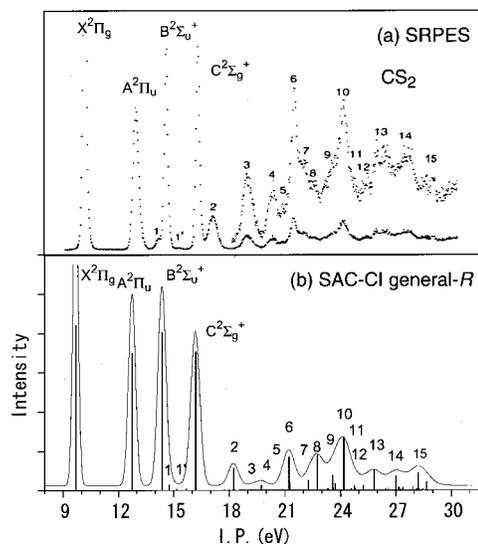


FIG. 1. Valence ionization spectra of CS$_2$ by (a) SRPES (Ref. 8) and (b) SAC-CI general-$R$ method.

TABLE II. Ionization potential (I.P.) (in eV), monopole intensity and main configuration of the valence ionized states of $CS_2$.

| | Experimental I.P. | | | | | SAC-CI general-R | | | |
|---|---|---|---|---|---|---|---|---|---|
| No. | SRPES[a] | PES[b] | PES[c] | HeII[d] | $(e,2e)$[e] | State | I.P. (eV) | Intensity | Main configurations ($|C|>0.3$) |
| X | 10.00 | 10.11 | ... | ... | ... | $^2\Pi_g$ | 9.70 | 0.841 | $0.89(2\pi_g^{-1})$ |
| A | 12.90 | 12.89 | ... | ... | ... | $^2\Pi_u$ | 12.76 | 0.693 | $0.80(2\pi_u^{-1})-0.33(2\pi_g^{-2}3\pi_u)$ |
| B | 14.46 | 14.49 | ... | ... | ... | $^2\Sigma_u^+$ | 14.38 | 0.804 | $0.86(5\sigma_u^{-1})$ |
| 1 | 14.1 | 14.09 | 14.1 | 14.06 | ... | $^2\Pi_u$ | 14.75 | 0.027 | $0.52(2\pi_g^{-2}3\pi_u)+0.44(2\pi_g^{-2}3\pi_u)-0.39(2\pi_g^{-2}3\pi_u)$ |
| | | | | | | $^2\Pi_u$ | 15.19 | 0.005 | $0.78(2\pi_g^{-2}3\pi_u)+0.56(2\pi_g^{-2}3\pi_u)+0.39(2\pi_g^{-2}3\pi_u)$ |
| 1′ | ... | 15.2 | ... | ... | ... | $^2\Pi_u$ | 15.69 | 0.009 | $0.57(2\pi_g^{-2}3\pi_u)-0.56(2\pi_g^{-2}3\pi_u)-0.48(2\pi_g^{-2}3\pi_u)+0.42(2\pi_g^{-2}3\pi_u)$ |
| C | 16.15 | 16.20 | ... | ... | ... | $^2\Sigma_g^+$ | 16.19 | 0.705 | $0.81(7\sigma_g^{-1})$ |
| 2 | 17.2 | 17.0 | 17.1 | 17.06 | ... | $^2\Pi_u$ | 18.24 | 0.115 | $0.32(2\pi_u^{-1})+0.67(2\pi_g^{-2}3\pi_u)+0.43(2\pi_g^{-2}3\pi_u)-0.20(2\pi_g^{-2}3\pi_u^2 2\pi_u^{-1})$ |
| 3 | 19.15 | 18.81 | 18.36 | 18.97 | 19.1 | $^2\Sigma_g^+$ | 19.20 | 0.006 | $0.48(2\pi_g^{-2}8\sigma_g)+0.48(2\pi_g^{-2}8\sigma_g)-0.39(5\sigma_u^{-1}3\pi_u2\pi_g^{-1})-0.37(5\sigma_u^{-1}3\pi_u2\pi_g^{-1})$ |
| | | | | | | $^2\Sigma_g^+$ | 19.74 | 0.026 | $0.54(5\sigma_u^{-1}3\pi_u2\pi_g^{-1})+0.53(5\sigma_u^{-1}3\pi_u2\pi_g^{-1})+0.44(5\sigma_u^{-1}3\pi_u2\pi_g^{-1})$ |
| 4 | 20.4 | 20.17 | 19.91 | 20.22 | 20.2 | $^2\Pi_g$ | 20.15 | 0.001 | $0.44(2\pi_u^{-1}3\pi_u2\pi_g^{-1})+0.35(2\pi_g^{-1}3\pi_u2\pi_u^{-1})+0.34(2\pi_u^{-1}3\pi_u2\pi_g^{-1})+0.31(2\pi_g^{-1}3\pi_u2\pi_u^{-1})-0.60(2\pi_g^{-3}3\pi_u^2)$ |
| | | | | | | $^2\Pi_g$ | 20.23 | 0.0002 | $0.46(2\pi_g^{-1}3\pi_u2\pi_u^{-1})+0.43(2\pi_g^{-1}3\pi_u2\pi_u^{-1})-0.42(2\pi_u^{-1}3\pi_u2\pi_g^{-1})+0.38(2\pi_u^{-1}3\pi_u2\pi_g^{-1})+0.38(2\pi_u^{-1}3\pi_u2\pi_g^{-1})-0.36(2\pi_g^{-1}3\pi_u2\pi_u^{-1})+0.39(2\pi_g^{-3}3\pi_u^2)+0.22(2\pi_g^{-3}3\pi_u^2)$ |
| 5 | 20.8 | ... | 20.96 | ... | ... | $^2\Sigma_u^+$ | 20.88 | 0.005 | $0.53(5\sigma_u^{-1}3\pi_u2\pi_u^{-1})+0.51(5\sigma_u^{-1}3\pi_u2\pi_u^{-1})+0.50(7\sigma_g^{-1}3\pi_u2\pi_g^{-1})+0.50(7\sigma_g^{-1}3\pi_u2\pi_g^{-1})$ |
| | | | | | | $^2\Pi_u$ | 20.97 | 0.001 | $0.39(2\pi_u^{-2}3\pi_u)+0.38(2\pi_u^{-2}3\pi_u)+0.92(2\pi_g^{-1}3\pi_u^2 2\pi_u^{-2})+0.29(2\pi_g^{-1}3\pi_u^2 2\pi_u^{-2})+0.25(2\pi_g^{-1}3\pi_u^2 2\pi_u^{-2})$ |
| | | | | | | $^2\Sigma_u^+$ | 21.10 | 0.003 | $0.49(2\pi_g^{-1}3\pi_u7\sigma_g^{-1})-0.46(2\pi_g^{-1}3\pi_u7\sigma_g^{-1})-0.45(2\pi_u^{-2}3\pi_u)+0.44(7\sigma_g^{-1}3\pi_u2\pi_g^{-1})-0.44(5\sigma_u^{-1}3\pi_u2\pi_u^{-1})-0.41(7\sigma_g^{-1}3\pi_u2\pi_g^{-1})+0.41(2\pi_u^{-1}3\pi_u5\sigma_u^{-1})+0.39(5\sigma_u^{-1}3\pi_u2\pi_u^{-1})-0.30(2\pi_g^{-2}3\pi_u^2 5\sigma_u^{-1})$ |
| 6 | 21.35 | 21.25 | 21.34 | 21.35 | 21.3 | $^2\Sigma_u^+$ | 21.23 | 0.170 | $0.39(4\sigma_u^{-1})+0.56(2\pi_g^{-2}7\sigma_u)-0.39(2\pi_g^{-1}8\sigma_g2\pi_u^{-1})$ |
| | | | | | | $^2\Sigma_u^+$ | 21.27 | 0.039 | $0.61(2\pi_g^{-2}7\sigma_u)-0.37(2\pi_g^{-1}8\sigma_g2\pi_u^{-1})$ |
| | | | | | | $^2\Pi_g$ | 21.35 | 0.004 | $0.38(2\pi_u^{-1}3\pi_u2\pi_g^{-1})+0.37(2\pi_g^{-1}3\pi_u2\pi_u^{-1})+0.48(2\pi_g^{-3}3\pi_u^2)+0.38(2\pi_g^{-3}3\pi_u^2)$ |
| | | | | | | $^2\Pi_g$ | 21.93 | 0.002 | $0.44(2\pi_g^{-1}3\pi_u2\pi_u^{-1})+0.36(2\pi_u^{-1}3\pi_u2\pi_g^{-1})+0.66(2\pi_g^{-3}3\pi_u^2)+0.22(2\pi_g^{-3}3\pi_u^2)$ |
| 7 | 21.6 | 21.6 | 21.76 | 21.56 | ... | $^2\Sigma_u^+$ | 22.27 | 0.052 | $0.21(4\sigma_u^{-1})-0.50(2\pi_g^{-1}8\sigma_g2\pi_u^{-1})$ |
| 8 | 22.4 | 22.4 | 22.69 | ... | ... | $^2\Sigma_u^+$ | 22.77 | 0.180 | $0.40(4\sigma_u^{-1})-0.34(2\pi_g^{-2}7\sigma_u)-0.33(5\sigma_u^{-1}3\pi_u2\pi_u^{-1})-0.32(2\pi_g^{-2}7\sigma_u)-0.21(2\pi_g^{-2}3\pi_u^2 5\sigma_u^{-1})$ |
| | | | | | | $^2\Sigma_g^+$ | 23.33 | 0.010 | $0.60(2\pi_g^{-2}9\sigma_g)+0.60(2\pi_g^{-2}9\sigma_g)$ |
| 9 | 23.3 | 23.0 | 23.05 | ... | ... | $^2\Sigma_g^+$ | 23.60 | 0.077 | $0.53(2\pi_g^{-1}3\pi_u5\sigma_u^{-1})+0.53(2\pi_g^{-1}3\pi_u5\sigma_u^{-1})$ |
| | | | | | | $^2\Pi_g$ | 23.72 | 0.010 | $0.39(2\pi_g^{-1}3\pi_u2\pi_u^{-1})+0.45(2\pi_g^{-3}3\pi_u^2)+0.43(2\pi_g^{-3}3\pi_u^2)$ |
| | | | | | | $^2\Sigma_u^+$ | 23.72 | 0.035 | $0.30(5\sigma_u^{-1}3\pi_u2\pi_u^{-1})+1.00(2\pi_g^{-2}3\pi_u^2 5\sigma_u^{-1})+0.33(2\pi_g^{-2}3\pi_u^2 5\sigma_u^{-1})+0.32(2\pi_g^{-2}3\pi_u^2 5\sigma_u^{-1})+0.30(2\pi_g^{-2}3\pi_u^2 5\sigma_u^{-1})$ |
| | | | | | | $^2\Pi_u$ | 24.17 | 0.008 | $0.69(2\pi_g^{-2}3\pi_u)+0.34(2\pi_u^{-2}3\pi_u)+0.25(2\pi_g^{-2}3\pi_u^2 2\pi_u^{-1})-0.23(2\pi_g^{-2}3\pi_u^2 2\pi_u^{-1})$ |
| 10 | 24.1 | 24.0 | 23.91 | 23.96 | 23.9 | $^2\Sigma_g^+$ | 24.19 | 0.270 | $0.49(6\sigma_g^{-1})+0.47(7\sigma_g^{-1}3\pi_u2\pi_u^{-1})+0.45(7\sigma_g^{-1}3\pi_u2\pi_u^{-1})+0.33(2\pi_u^{-1}3\pi_u7\sigma_g^{-1})+0.33(2\pi_u^{-1}3\pi_u7\sigma_g^{-1})$ |
| | | | | | | $^2\Sigma_u^+$ | 24.59 | 0.009 | $0.41(5\sigma_u^{-1}3\pi_u2\pi_u^{-1})-0.35(7\sigma_g^{-1}3\pi_u2\pi_g^{-1})-0.35(2\pi_g^{-2}6\sigma_u)-0.45(2\pi_g^{-2}3\pi_u^2 5\sigma_u^{-1})-0.30(2\pi_g^{-2}3\pi_u^2 5\sigma_u^{-1})$ |
| 11 | 24.6 | 24.3 | ... | ... | ... | $^2\Sigma_g^+$ | 24.77 | 0.025 | $0.46(2\pi_u^{-1}7\sigma_u2\pi_g^{-1})+0.34(2\pi_u^{-1}7\sigma_u2\pi_g^{-1})$ |
| | | | | | | $^2\Sigma_u^+$ | 24.81 | 0.011 | $0.40(2\pi_g^{-2}6\sigma_u)-0.35(2\pi_g^{-2}6\sigma_u)-0.32(2\pi_g^{-1}3\pi_u7\sigma_g^{-1})$ |
| 12 | 25.25 | 25.2 | ... | ... | ... | $^2\Sigma_u^+$ | 25.25 | 0.026 | $0.38(2\pi_g^{-1}3\pi_u5\sigma_u^{-1})-0.34(5\sigma_u^{-1}3\pi_u2\pi_u^{-1})$ |
| 13 | 26.35 | ... | ... | ... | 26.2 | $^2\Sigma_g^+$ | 25.83 | 0.101 | $0.30(6\sigma_g^{-1})-0.35(7\sigma_g^{-1}3\pi_u2\pi_u^{-1})-0.32(7\sigma_g^{-1}3\pi_u2\pi_u^{-1})$ |
| | | | | | | $^2\Sigma_g^+$ | 26.31 | 0.004 | $0.64(2\pi_g^{-2}1\delta_g)+0.55(2\pi_g^{-2}1\delta_g)+0.38(2\pi_g^{-2}1\delta_g)-0.30(2\pi_g^{-2}1\delta_g)$ |
| | | | | | | $^2\Sigma_g^+$ | 26.46 | 0.010 | $0.41(2\pi_u^{-2}8\sigma_g)+0.32(2\pi_u^{-2}8\sigma_g)-0.31(2\pi_g^{-1}7\sigma_u2\pi_u^{-1})+0.30(2\pi_g^{-2}1\delta_g)$ |
| | | | | | | $^2\Sigma_g^+$ | 26.62 | 0.011 | $0.61(2\pi_g^{-2}1\delta_g)+0.41(2\pi_g^{-2}1\delta_g)$ |

TABLE II. (*Continued.*)

| SRPES[a] No. | PES[b] | PES[c] | Hell[d] | $(e,2e)$[e] | State | I.P. (eV) | Intensity | Main configurations ($|C|>0.3$) |
|---|---|---|---|---|---|---|---|---|
| 14  27.4 | ... | ... | ... | 27.1 | $^2\Sigma_u^+$ | 27.02 | 0.073 | $0.25(4\sigma_u^{-1})+0.31(2\pi_u^{-1}3\pi_u5\sigma_u^{-1})+0.31(2\pi_u^{-1}3\pi_u5\sigma_u^{-1})$ $-0.34(2\pi_g^{-2}3\pi_u^25\sigma_u^{-1})+0.34(2\pi_g^{-2}3\pi_u^25\sigma_u^{-1})$ |
| | | | | | $^2\Sigma_u^+$ | 27.17 | 0.017 | $0.60(2\pi_g^{-2}1\delta_u)+0.47(2\pi_g^{-2}1\delta_u)+0.41(2\pi_g^{-2}1\delta_u)$ |
| | | | | | $^2\Sigma_g^+$ | 27.27 | 0.005 | $0.46(2\pi_u^{-1}6\sigma_u2\pi_g^{-1})-0.33(2\pi_g^{-1}6\sigma_u2\pi_u^{-1})$ |
| | | | | | $^2\Sigma_g^+$ | 27.40 | 0.013 | $0.45(2\pi_g^{-2}1\delta_g)-0.33(2\pi_g^{-2}1\delta_g)$ |
| | | | | | $^2\Sigma_g^+$ | 27.94 | 0.021 | $0.62(5\sigma_u^{-2}8\sigma_g)$ |
| | | | | | $^2\Sigma_u^+$ | 28.15 | 0.007 | $0.60(2\pi_g^{-2}3\pi_u^25\sigma_u^{-1})-0.32(2\pi_g^{-1}9\sigma_g2\pi_u^{-1})$ $-0.31(2\pi_g^{-1}9\sigma_g2\pi_u^{-1})+0.30(2\pi_g^{-2}3\pi_u^25\sigma_u^{-1})$ |
| 15  28.7 | ... | ... | ... | 28.8 | $^2\Sigma_g^+$ | 28.22 | 0.089 | $0.35(4\sigma_u^{-1}3\pi_u2\pi_g^{-1})+0.33(2\pi_g^{-2}1\delta_g)$ |
| | | | | | $^2\Sigma_u^+$ | 28.28 | 0.009 | $0.42(2\pi_g^{-2}1\delta_u)+0.41(2\pi_g^{-1}1\delta_g2\pi_u^{-1})$ $-0.40(2\pi_u^{-1}1\delta_g2\pi_g^{-1})-0.37(2\pi_g^{-2}1\delta_u)$ $+0.36(2\pi_u^{-1}1\delta_g2\pi_g^{-1})$ |
| | | | | | $^2\Sigma_u^+$ | 28.47 | 0.007 | $0.47(2\pi_g^{-1}1\delta_g2\pi_u^{-1})+0.45(2\pi_g^{-2}1\delta_u)$ $+0.38(2\pi_u^{-1}1\delta_g2\pi_g^{-1})-0.36(2\pi_u^{-1}1\delta_g2\pi_g^{-1})$ $-0.24(2\pi_g^{-2}3\pi_u^25\sigma_u^{-1})$ |
| | | | | | $^2\Sigma_u^+$ | 28.67 | 0.042 | $0.42(2\pi_u^{-1}9\sigma_g2\pi_g^{-1})+0.41(2\pi_u^{-1}9\sigma_g2\pi_g^{-1})$ $+0.40(2\pi_g^{-1}9\sigma_g2\pi_u^{-1})+0.35(2\pi_g^{-1}9\sigma_g2\pi_u^{-1})$ |

[a]Reference 7.
[b]Reference 8: experiment was due to the SRPES and He II PES.
[c]Reference 6.
[d]Reference 2.
[e]Reference 5.

citation, therefore the EGCI including up to triples was performed for the reference-CI. The calculational dimensions for the reference-EGCI and resultant SAC-CI general-$R$ were summarized in Table I. The former dimensions were around 5600 and the latter's after perturbation selection were almost 85 000 for each symmetry of $D_{\infty h}$. In Fig. 1, the SAC-CI general-$R$ spectrum convoluting with Gaussian envelope for describing the Frank–Condon width and the resolution of spectrometer was compared with the experimental PES;[8] the FWHM of Gaussian was adopted as $0.05^*\Delta E$ (in eV). In Table II, the results of IPs, monopole intensities, and detailed ionization characters for the valence ionized states, which have large intensity greater than 0.005, were presented with several experimental IPs.[2,5–8]

Four main peaks in the outer-valence region were dominantly described by the single electron process and the previous SAC-CI SD-$R$[9] calculation has already given accurate results. In the present work, their IPs were calculated as 9.70, 12.76, 14.38, and 16.19 eV for $X^2\Pi_g$, $A^2\Pi_u$, $B^2\Sigma_u^+$, and $C^2\Sigma_g^+$ states, respectively, which were compared with the experimental vertical IPs 10.080, 12.698, 14.477, and 16.190 eV by the high-resolution He I PES.[10] The intensities of the $A^2\Pi_u$ and $C^2\Sigma_g^+$ states were considerably distributed to the shake-up states: the monopole intensities were calculated as 0.693 and 0.705 for these states. The relative intensities of the main peaks are almost the same as those of other theoretical calculations by the CIPSI[7] and simplified ADC(4).[8]

Next, we discuss the spectrum of the shake-up states comparing with the high-resolution spectrum by the SRPES[7,8] and He II PES.[8] So far, three satellite peaks were experimentally identified in the outer-valence region of $CS_2$. These peaks were assigned to $^2\Pi_u$ states[7,8] and, especially,

the second one $(1')$ was recently observed at the foot of the main peak $B$.[8] Accordingly, the present calculation gave four $^2\Pi_u$ states in this energy region at 14.75(1), 15.19, 15.69(1'), and 18.24(2) eV. These outer-valence satellites were calculated in the higher energy region in the previous SAC-CI SD-$R$ study.[9] They are characterized as $(2\pi_g^{-2}3\pi_u)$ and have the intensity mainly through the final-state correlation interaction with $(2\pi_u^{-1})$ state. The shake-up states at 15.19 and 15.69 eV split when including an extensive basis set. The
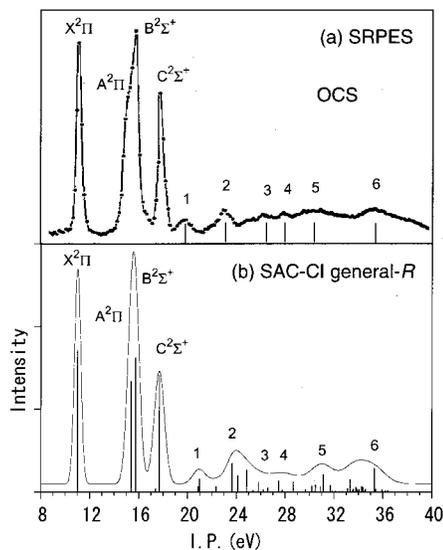


FIG. 2. Valence ionization spectra of OCS by (a) SRPES (Ref. 15) and (b) SAC-CI general-$R$ method.

TABLE III. Ionization potential (I.P.) (in eV), monopole intensity and main configuration of the valence ionized states of OCS.

| Experimental I.P. | | | | | | SAC-CI general-$R$ | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| HeI[a] PES | X-ray[b] PES | $(e,2e)$[c] | $(e,2e)$[d] | SRPES[e] No. | | State | I.P. (eV) | Intensity | Main configurations ($|C|>0.3$) |
| 11.19 | ... | ... | ... | | ... | $X^2\Pi$ | 11.02 | 0.857 | $0.90(3\pi^{-1})$ |
| 15.08 | ... | ... | ... | | ... | $A^2\Pi$ | 15.39 | 0.669 | $0.79(2\pi^{-1})-0.33(3\pi^{-1}4\pi2\pi^{-1})$ |
| 16.04 | ... | ... | ... | | ... | $B^2\Sigma^+$ | 15.75 | 0.809 | $0.86(9\sigma^{-1})$ |
| ... | ... | ... | ... | | ... | $^2\Pi$ | 17.40 | 0.019 | $0.79(3\pi^{-2}4\pi)+0.40(3\pi^{-2}4\pi)$ |
| 17.96 | ... | ... | ... | | ... | $C^2\Sigma^+$ | 17.70 | 0.708 | $0.81(8\sigma^{-1})$ |
| ... | ... | 20.5 | 20.2 | 1 | 19.9 | $^2\Sigma^+$ | 20.89 | 0.033 | $0.54(3\pi^{-2}10\sigma)+0.54(3\pi^{-2}10\sigma)$ |
| | | | | | | $^2\Pi$ | 20.99 | 0.079 | $0.26(2\pi^{-1})+0.67(3\pi^{-2}4\pi)+0.50(3\pi^{-2}4\pi)$ |
| ... | ... | ... | 21.7 | ... | ... | $^2\Pi$ | 22.07 | 0.005 | $0.61(2\pi^{-1}4\pi3\pi^{-1})+0.47(2\pi^{-1}4\pi3\pi^{-1})$ $+0.43(3\pi^{-1}4\pi2\pi^{-1})+0.40(3\pi^{-1}4\pi2\pi^{-1})$ |
| | | | | | | $^2\Sigma^+$ | 22.35 | 0.033 | $0.55(9\sigma^{-1}4\pi3\pi^{-1})+0.55(9\sigma^{-1}4\pi3\pi^{-1})$ $+0.48(9\sigma^{-1}4\pi3\pi^{-1})+0.48(9\sigma^{-1}4\pi3\pi^{-1})$ |
| ... | 23.0 | 23.5 | 22.8 | 2 | 23.0 | $^2\Sigma^+$ | 23.69 | 0.174 | $0.38(7\sigma^{-1})+0.45(8\sigma^{-1}4\pi3\pi^{-1})+0.45(8\sigma^{-1}4\pi3\pi^{-1})$ $-0.32(8\sigma^{-1}4\pi3\pi^{-1})-0.31(3\pi^{-1}4\pi8\sigma^{-1})$ $+0.31(3\pi^{-1}4\pi8\sigma^{-1})$ |
| | | | | | | $^2\Sigma^+$ | 24.13 | 0.098 | $0.33(3\pi^{-2}11\sigma)+0.33(3\pi^{-2}11\sigma)$ |
| ... | 25.0 | ... | 24.1 | ... | ... | $^2\Sigma^+$ | 24.85 | 0.132 | $0.35(7\sigma^{-1})-0.38(9\sigma^{-1}4\pi2\pi^{-1})-0.38(9\sigma^{-1}4\pi2\pi^{-1})$ $+0.31(3\pi^{-2}11\sigma)+0.31(3\pi^{-2}11\sigma)$ |
| | | | | | | $^2\Pi$ | 25.41 | 0.009 | $0.59(2\pi^{-1}4\pi3\pi^{-1})+0.55(2\pi^{-1}4\pi3\pi^{-1})$ |
| ... | ... | ... | 26.0 | 3 | 26.3 | $^2\Pi$ | 25.83 | 0.061 | $0.25(2\pi^{-1})-0.56(3\pi^{-1}4\pi2\pi^{-1})$ $-0.49(3\pi^{-1}4\pi2\pi^{-1})-0.32(9\sigma^{-1}10\sigma2\pi^{-1})$ |
| | | | | | | $^2\Sigma^+$ | 26.24 | 0.014 | $0.40(3\pi^{-1}10\sigma2\pi^{-1})+0.40(3\pi^{-1}10\sigma2\pi^{-1})$ $+0.33(2\pi^{-1}10\sigma3\pi^{-1})+0.33(2\pi^{-1}10\sigma3\pi^{-1})$ |
| | | | | | | $^2\Sigma^+$ | 26.60 | 0.026 | $0.35(2\pi^{-1}10\sigma3\pi^{-1})+0.35(2\pi^{-1}10\sigma3\pi^{-1})$ |
| ... | 27.4 | 27.1 | 27.9 | 4 | 27.8 | $^2\Sigma^+$ | 27.48 | 0.068 | $0.34(3\pi^{-1}4\pi9\sigma^{-1})+0.34(3\pi^{-1}4\pi9\sigma^{-1})$ |
| | | | | | | $^2\Pi$ | 27.73 | 0.005 | $0.65(3\pi^{-2}5\pi)+0.45(3\pi^{-2}5\pi)-0.34(3\pi^{-2}10\sigma)$ |
| | | | | | | $^2\Sigma^+$ | 27.78 | 0.012 | $0.43(3\pi^{-2}12\sigma)+0.43(3\pi^{-2}12\sigma)$ $-0.34(3\pi^{-2}11\sigma)-0.34(3\pi^{-2}11\sigma)$ |
| | | | | | | $^2\Sigma^+$ | 28.06 | 0.004 | $0.35(2\pi^{-1}11\sigma3\pi^{-1})+0.35(2\pi^{-1}11\sigma3\pi^{-1})$ |
| ... | ... | ... | 29.0 | ... | ... | $^2\Sigma^+$ | 28.67 | 0.062 | $0.33(3\pi^{-1}4\pi8\sigma^{-1})+0.33(3\pi^{-1}4\pi8\sigma^{-1})$ |
| | | | | | | $^2\Sigma^+$ | 29.68 | 0.014 | $0.46(3\pi^{-1}11\sigma2\pi^{-1})+0.46(3\pi^{-1}11\sigma2\pi^{-1})$ $+0.33(2\pi^{-1}11\sigma3\pi^{-1})$ |
| | | | | | | $^2\Sigma^+$ | 30.20 | 0.035 | $0.30(3\pi^{-2}1\delta)+0.30(3\pi^{-2}1\delta)$ |
| ... | 31.0 | 30.0 | 30.9 | 5 | 30.4 | $^2\Sigma^+$ | 30.49 | 0.041 | $0.38(2\pi^{-1}4\pi9\sigma^{-1})+0.38(2\pi^{-1}4\pi9\sigma^{-1})$ $+0.37(9\sigma^{-2}10\sigma)$ |
| | | | | | | $^2\Sigma^+$ | 30.89 | 0.031 | $0.45(3\pi^{-2}13\sigma)+0.45(3\pi^{-2}13\sigma)$ $-0.37(8\sigma^{-1}4\pi9\sigma^{-1})$ |
| | | | | | | $^2\Pi$ | 31.14 | 0.005 | $0.46(9\sigma^{-2}4\pi)-0.38(8\sigma^{-1}4\pi9\sigma^{-1})$ $-0.38(9\sigma^{-1}4\pi8\sigma^{-1})-0.32(2\pi^{-2}4\pi)$ |
| | | | | | | $^2\Sigma^+$ | 31.15 | 0.104 | $0.30(7\sigma^{-1})-0.45(8\sigma^{-1}10\sigma9\sigma^-)$ |
| | | | | | | $^2\Sigma^+$ | 31.72 | 0.042 | $0.49(8\sigma^{-1}4\pi2\pi^{-1})+0.49(8\sigma^{-1}4\pi2\pi^{-1})$ |
| | | | | | | $^2\Pi$ | 31.89 | 0.007 | $0.31(3\pi^{-2}6\pi)-0.31(3\pi^{-1}5\pi2\pi^{-1})$ |
| | | | | | | $^2\Sigma^+$ | 32.13 | 0.007 | $0.53(9\sigma^{-1}5\pi3\pi^{-1})+0.53(9\sigma^{-1}5\pi3\pi^{-1})$ |
| | | | | | | $^2\Pi$ | 32.41 | 0.005 | $0.45(9\sigma^{-1}11\sigma3\pi^{-1})-0.39(9\sigma^{-1}12\sigma3\pi^{-1})$ $-0.32(9\sigma^{-1}10\sigma2\pi^{-1})-0.32(8\sigma^{-1}12\sigma3\pi^{-1})$ |
| | | | | | | $^2\Sigma^+$ | 32.71 | 0.004 | $0.51(3\pi^{-1}5\pi9\sigma^{-1})+0.51(3\pi^{-1}5\pi9\sigma^{-1})$ $+0.40(3\pi^{-1}5\pi8\sigma^{-1})+0.40(3\pi^{-1}5\pi8\sigma^{-1})$ |
| ... | ... | ... | 32.6 | ... | ... | $^2\Sigma^+$ | 33.11 | 0.019 | $0.35(9\sigma^{-2}10\sigma)-0.33(8\sigma^{-1}5\pi3\pi^{-1})$ $-0.33(8\sigma^{-1}5\pi3\pi^{-1})-0.32(8\sigma^{-1}10\sigma9\sigma^{-1})$ |
| | | | | | | $^2\Sigma^+$ | 33.33 | 0.076 | $0.26(6\sigma)-0.28(7\sigma^{-1}4\pi3\pi^{-1})-0.28(7\sigma^{-1}4\pi3\pi^{-1})$ |
| | | | | | | $^2\Sigma^+$ | 33.54 | 0.006 | $0.34(9\sigma^{-1}10\sigma8\sigma^{-1})$ |
| | | | | | | $^2\Sigma^+$ | 33.58 | 0.016 | $0.39(9\sigma^{-1}10\sigma8\sigma^{-1})+0.31(3\pi^{-1}12\sigma2\pi^{-1})$ $+0.31(3\pi^{-1}12\sigma2\pi^{-1})$ |
| | | | | | | $^2\Sigma^+$ | 33.81 | 0.029 | $0.28(7\sigma^{-1}4\pi3\pi^{-1})$ |
| | | | | | | $^2\Sigma^+$ | 33.82 | 0.012 | $0.27(2\pi^{-1}1\delta3\pi^{-1})$ |
| | | | | | | $^2\Sigma^+$ | 33.93 | 0.018 | $0.38(2\pi^{-1}1\delta3\pi^{-1})-0.32(2\pi^{-1}1\delta3\pi^{-1})$ |
| | | | | | | $^2\Sigma^+$ | 34.08 | 0.014 | $0.30(2\pi^{-1}1\delta3\pi^{-1})$ |
| | | | | | | $^2\Sigma^+$ | 34.08 | 0.009 | $0.33(3\pi^{-2}14\sigma)+0.30(2\pi^{-1}1\delta3\pi^{-1})$ |
| ... | ... | ... | 34.2 | ... | ... | $^2\Sigma^+$ | 34.27 | 0.033 | $0.38(9\sigma^{-2}11\sigma)+0.33(8\sigma^{-1}10\sigma9\sigma^{-1})$ |
| | | | | | | $^2\Sigma^+$ | 34.40 | 0.029 | $0.45(9\sigma^{-1}6\pi3\pi^{-1})+0.45(9\sigma^{-1}6\pi3\pi^{-1})$ |
| | | | | | | $^2\Sigma^+$ | 34.53 | 0.010 | $0.37(3\pi^{-2}14\sigma)+0.37(3\pi^{-2}14\sigma)$ |
| | | | | | | $^2\Sigma^+$ | 34.58 | 0.018 | $0.46(8\sigma^{-1}11\sigma9\sigma^{-1})-0.32(9\sigma^{-2}10\sigma)$ |

TABLE III. (*Continued.*)

| HeI[a] PES | X-ray[b] PES | $(e,2e)$[c] | $(e,2e)$[d] | SRPES[e] No. | | State | I.P. (eV) | Intensity | Main configurations ($|C|>0.3$) |
|---|---|---|---|---|---|---|---|---|---|
| ... | 35.7 | 35.8 | 35.8 | 6 | 35.7 | $^2\Sigma^+$ | 35.30 | 0.141 | $0.36(6\sigma^{-1})$ |
| | | | | | | $^2\Sigma^+$ | 35.42 | 0.018 | $0.42(2\pi^{-2}10\sigma)+0.42(2\pi^{-2}10\sigma)$ |
| | | | | | | $^2\Sigma^+$ | 35.94 | 0.015 | $0.50(9\sigma^{-1}11\sigma8\sigma^{-1})$ |
| | | | | | | $^2\Sigma^+$ | 36.21 | 0.007 | $0.41(2\pi^{-1}13\sigma3\pi^{-1})+0.41(2\pi^{-1}13\sigma3\pi^{-1})$ |
| | | | | | | $^2\Sigma^+$ | 36.41 | 0.009 | $0.32(9\sigma^{-2}12\sigma)-0.31(8\sigma^{-1}11\sigma9\sigma^{-1})$ $-0.31(9\sigma^{-1}11\sigma8\sigma^{-1})$ |

[a]Reference 10.
[b]Reference 1.
[c]Reference 12.
[d]Reference 13.
[e]Reference 15.

present calculation still overestimated the IPs of these correlation peaks, especially for peak (2).

Third to fifth correlation peaks were observed at 19.15 (3), 20.4 (4), and 20.8 (5) eV in SRPES.[7] The peak (3) was assigned to $^2\Sigma_g^+$ state in the recent two SRPES works;[7,8] however, the assignment of the peak (4) was contradictory as $^2\Pi_g$ (Ref. 7) or $^2\Sigma_u^+$ (Ref. 8). The former assignment was based on the angular distribution and the latter was due to the angle dependence of the cross section relative to the incident radiation with the help of ADC calculation. In Ref. 8, it was also proposed that the peak (4) is composed by more-than-one shake-up states since it has unusual vibrational progression and the peak (5) was not observed. In the present calculation, two $^2\Sigma_g^+$ states were calculated at 19.20 and 19.74 eV, which were attributed to the peak (3), two $^2\Pi_g$ states were obtained at 20.15 and 20.23 eV for the peak (4), and one $^2\Sigma_u^+$ state at 20.88 eV for the peak (5). Therefore, for the peak (4), we support the assignment of Roy *et al.*[7] and proposed that the overlapping states, which were observed as two components at least by Baltzer *et al.*,[8] were interpreted as the $^2\Pi_g$ and $^2\Sigma_u^+$ states. Note that the contribution of triples was found to be considerably large for the $^2\Pi_g$ states of the peak (4).

The prominent peak (6) was observed at 21.35 eV and assigned to $^2\Sigma_u^+$ state.[7] Correspondingly, the general-$R$ calculation gave $^2\Sigma_u^+$ states with considerable intensity at 21.23 and 21.27 eV and these states were characterized as $(2\pi_g^{-2}7\sigma_u)$ interacting with $(4\sigma_u^{-1})$ state. We also found two $^2\Pi_g$ states in this region. In the energy region from peak (7) observed at 21.6 eV to peak (9) at 23.3 eV,[7] many $^2\Sigma_u^+$ and $^2\Sigma_g^+$ states were predicted: $^2\Sigma_u^+$ states were calculated at 22.27, 22.77, and 23.72 eV and $^2\Sigma_g^+$ states were also obtained at 23.33 and 23.60 eV. We attribute these states to the peaks from (7) to (9). It should be noted that the spectrum in this energy region was calculated very differently between the SDT-$R$ and SDTQ-$R$ methods. This is because the triples have large weights for some shake-up states and the quadruple $R$-operators become important in such case.

The peak (10) observed at 24.1 eV again has large intensity in SRPES.[7] This peak was clearly attributed to the $^2\Sigma_g^+$ state calculated at 24.19 eV with large intensity of 0.27 origi-

nating in $(6\sigma_g)^{-1}$. The previous SAC-CI SD-$R$ calculation[9] also reproduced the positions of the prominent peaks (6) and (10) and, hence, the qualitative picture of the spectrum. As the shoulder of the peak (10), peak (11) was observed at 24.6 eV.[7] For this shoulder, we obtained three shake-up states; one $^2\Sigma_g^+$ state at 24.77 eV and two $^2\Sigma_u^+$ states at 24.59 and 24.81 eV.

Above the peak (11), $^2\Sigma_u^+$ and $^2\Sigma_g^+$ states were calculated at 25.25 and 25.83 eV, which are the candidates of the peaks (12) and (13) observed at 25.25 and 26.35 eV, respectively.[7] The intensity of the former state was calculated smaller than the latter, which accords with the feature of the experimental spectrum. Around and above the double ionization threshold determined at 27.3 eV,[11] many shake-up states were calculated and some of them were characterized as triple electron processes. The prominent states with relatively large intensity are $^2\Sigma_u^+$ and $^2\Sigma_g^+$ states calculated at 27.02, 28.22, and 28.67 eV. They are assigned to the peaks (14) and (15), which were observed at 27.4 and 28.7 eV.[7] Many continuous shake-up states around this energy region were also attributed to these peaks. Above this energy, no significant peaks which have considerable intensity were calculated and the peaks above 30 eV observed in SRPES[7] may be attributed to the doubly ionized states.

## B. OCS

The ground state electronic configuration of OCS is written as

$$(\text{core})^{14}(6\sigma)^2(7\sigma)^2(8\sigma)^2(2\pi)^4(9\sigma)^2(3\pi)^4.$$

The valence-ionization spectrum up to ~36 eV, whose energy region has been measured by the SRPES,[15] was examined by the SAC-CI general-$R$ method; 80 $^2\Sigma^+$ states and 40 $^2\Pi$ states were solved for calculating the spectrum. The photoion-photoion coincidence (PIPICO) and double charge transfer experiments with the CIPSI calculation showed that several double-ionized states exist in the energy region of 31.8–40.4 eV.[11] From the preliminary calculation, the shape of the theoretical spectrum was found to be less dependent on the inclusion of higher-than-triple $R$-operators and, there-

TABLE IV. Ionization potential (I.P.) (in eV) and monopole intensity for the low-lying valence ionized states of OCS calculated with the augmented basis sets.

| State | VTZ+2d (present) | | VTZ+2d+diffuse[a] | | VTZ+3d[b] | |
|---|---|---|---|---|---|---|
| | I.P. | Intensity | I.P. | Intensity | I.P. | Intensity |
| $^2\Sigma^+$ | 15.75 | 0.809 | 15.85 | 0.808 | 15.89 | 0.808 |
| | 17.70 | 0.708 | 17.87 | 0.706 | 17.89 | 0.703 |
| | 20.89 | 0.033 | 21.04 | 0.031 | 20.97 | 0.030 |
| | 22.35 | 0.033 | 22.44 | 0.031 | 22.47 | 0.030 |
| $^2\Pi$ | 11.02 | 0.857 | 11.08 | 0.859 | 11.21 | 0.857 |
| | 15.39 | 0.669 | 15.54 | 0.662 | 15.56 | 0.662 |
| | 17.40 | 0.019 | 17.45 | 0.020 | 17.44 | 0.019 |
| | 20.99 | 0.079 | 21.00 | 0.082 | 21.07 | 0.074 |

[a]Diffuse function of $[1s1p1d]$ are added on each atom.
[b]One polarization function with $\zeta_d = 1.25$ is added on S atom.

fore, we exploited the general-$R$ calculations up to triple $R$-operators with the SD-CI reference states. The resultant SAC-CI dimensions were 97 117 and 83 562 for $^2\Sigma^+$ and $^2\Pi$ states, respectively, as shown in Table I. In Fig. 2, the theoretical spectrum was presented with the latest SRPES[15] measured at a photon energy of 60 eV. The peaks of the theoretical spectrum were convoluted by Gaussians with FWHM of $0.08*\Delta E$ (in eV). The calculated IPs, intensities, and the characterization of the ionized states were summarized in Table III in comparison with the IPs determined by the He I PES,[10] x-ray PES,[1] dipole $(e,2e)$,[12,13] and SRPES.[15]

High-resolution He I PES[10] reported the outermost four main peaks at 11.185, 15.078, 16.042, and 17.957 eV, for $X^2\Pi$, $A^2\Pi$, $B^2\Sigma^+$, and $C^2\Sigma^+$ states, respectively. The $A^2\Pi$ and $B^2\Sigma^+$ states exist very close in energy and the ordering of these states was not reproduced in the previous SAC-CI SD-$R$ calculation.[9] In the present work, the general-$R$ method gave the correct ordering of the main peaks: four peaks were calculated at $11.02(X)$, $15.39(A)$, $15.75(B)$, and $17.70(C)$ eV, In parallel, we also executed the SD-$R$ calculation with the same basis set and found that the inclusion of the higher-order $R$-operators was important for the ordering of $A$ and $B$ states. Comparing the SAC-CI coefficients between the general-$R$ and SD-$R$ methods, weights of doubles for $A$ state by the former method were found to be larger than those by the latter. The monopole intensities of the $A$ and $C$ states were considerably distributed to the satellite peaks as found in their intensities, 0.669 and 0.708, respectively, which also shows the contribution of doubles is significant for these two states.

The characterization of the inner-valence spectrum of OCS is still not definitive as pointed out in the SRPES study.[15] Though there are extensive experimental works,[1,2,12–15] only two theoretical works, namely SAC-CI SD-$R$ method[9] and the 2ph-TDA method,[12] have examined the inner-valence region. First two correlation peaks were clearly observed in the SRPES at 19.9 and 23.0 eV.[15] In the present results, both the $^2\Sigma^+$ and $^2\Pi$ states were calculated at 20.89 and 20.99 eV, respectively. They are the candidates for the first peak and are characterized as $(3\pi^{-2}10\sigma)$ and $(3\pi^{-2}4\pi)$. We also obtained the $^2\Pi$ state (17.40 eV) with considerable intensity at the foot of main peak $C$, which has never been reported in the experimental work. For the sec-

ond peak at 23.0 eV, four $^2\Sigma^+$ states calculated at 22.35, 23.69, 24.13, and 24.85 eV and one $^2\Pi$ state at 22.07 eV are attributed. White et al.[13] observed detailed spectrum in this energy region using the dipole $(e,2e)$; three peaks at 21.7, 22.8, and 24.1 eV. We assign $^2\Pi$ state calculated at 22.07 eV to the peak 21.7 eV, three $^2\Sigma^+$ states obtained at 22.35, 23.69, and 24.13 eV to the peak at 22.8 eV, and $^2\Sigma^+$ state at 24.85 eV to the peak at 24.1 eV.

The complex and continuous spectrum was observed in the energy region of 25–40 eV.[15] In the theoretical works,[9,12] many shake-up states associated with the ionization of $6\sigma$ and $7\sigma$ MOs were predicted, however, it was criticized that these calculated states were separately clustered at around 25 and 36 eV against the experimental observation.[15] The present calculation gave continuous band of the satellite spectrum as seen in Fig. 2. Since numerous states were calculated, one-to-one assignment of the observed peaks would be difficult; however, we proposed our assignment with the shake-up states whose intensity was calculated to be larger than 0.01. For the peak (3) observed at 26.3 eV,[15] two $^2\Pi$ states at 25.41 and 25.83 eV and two $^2\Sigma^+$ states at 26.24 and 26.60 eV are attributed. Next peak (4) observed at around 27.8 eV[15] is assigned to the $^2\Sigma^+$ states calculated at 27.48 and 27.78 eV. For the peak observed by dipole $(e,2e)$[13] at 29.0 eV, two $^2\Sigma^+$ states calculated at 28.67 and 29.68 eV are candidates. Numerous states were calculated from 30 to 32 eV, which were attributed to the band (5) measured around 30.4 eV.

Dipole $(e,2e)$[13] observed two bands at 32.6 and 34.2 eV, for which the SAC-CI general-$R$ method gave 15 $^2\Sigma^+$ states from 32.13 to 34.58 eV. This energy region is above the double ionization threshold[11] and, therefore, these states may be observed as the auto-ionizing states with the continuum background. Finally, for the peak at 35.7 eV,[15] $^2\Sigma^+$ state with large intensity of 0.141 was calculated at 35.30 eV. In the previous SAC-CI study,[9] many shake-up states associated with $(6\sigma)^{-1}$ were calculated at around this energy region.

## IV. CONCLUSION

The valence ionization spectra of $CS_2$ and OCS were studied by the SAC-CI general-$R$ method in both outer- and inner-valence regions. The present calculation finely simu-

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lated the shapes of the experimental spectra and gave the detailed and quantitative assignments of the satellite peaks.

For CS$_2$, the present results presented the assignments of the satellites up to peak (15) measured by the SRPES.[7,8] Four $^2\Pi_u$ states were calculated in the outer-valence region and were attributed to the observed peaks (1), (1)′ and (2).[7,8] Three peaks, (3), (4), and (5), were assigned to the $^2\Sigma_g^+$, $^2\Pi_g$, and $^2\Sigma_u^+$ states, respectively. The peak (4) observed with two components at least by recent SRPES[8] was interpreted as the $^2\Pi_g$ and $^2\Sigma_u^+$ states. The prominent peaks (6) and (10) were assigned as the $^2\Sigma_u^+$ and $^2\Sigma_g^+$ states, respectively, and, for the satellites between these states, contributions of triples were remarkable: quadruple $R$-operators were important for reproducing the shape of the spectrum, especially for the peaks (8) and (9). Numerous $^2\Sigma_u^+$ and $^2\Sigma_g^+$ states, some of which were described by triples, continued up to double ionization threshold. Above 28 eV, no significant peaks were calculated.

The present calculation has also given detailed theoretical information on the valence-ionization spectrum of OCS. The position of the main peaks was correctly reproduced, especially for the ordering of $A$ and $B$ states, which was not obtained in the previous SAC-CI SD-$R$ study:[9] the higher $R$-operators were found to be significant for this ordering. For the first outer-valence satellite observed by the SRPES[15] and ($e$,2$e$),[12,13] both $^2\Sigma^+$ and $^2\Pi$ states were calculated. The second satellite of the SRPES[15] was attributed to four $^2\Sigma^+$ states and one $^2\Pi$ state, and these five shake-up states were also assigned to the three satellites measured by dipole ($e$,2$e$).[13] Below the $C^2\Sigma^+$ state, one satellite peak of $^2\Pi$ state, which has not been observed by experiment, was predicted. For the energy region of 24–36 eV, continuous band of the satellite spectrum was calculated, which reproduced the feature of SRPES.[15] Above the double ionization threshold, some satellite peaks were also obtained.

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## APPENDIX: EXAMINATION OF THE BASIS SETS

The present basis set was examined for the low-lying valence-ionized states of OCS with the additional polarization function and diffuse functions. The SAC-CI general-$R$ calculations with the augmented basis sets were performed for the first ten states of each symmetry and the results were compared in Table IV. Since the results with the VTZ plus double polarization function (VTZ2P) were obtained by the calculations with the selection of the large number of solutions, the IPs with the better basis sets were calculated slightly higher than the results with VTZ2P. Nevertheless, there was no remarkable difference for the calculated IPs and intensities. From this examination, the present basis set of VTZ2P was found to be sufficient for describing the electron correlations of the shake-up states and suitable for calculat-

ing entire valence ionization spectra with the moderate computational cost.

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