

CLUSTER EXPANSION OF THE WAVEFUNCTION. OUTER- AND INNER-VALENCE IONIZATION SPECTRA OF CS₂ AND COS

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The ionization spectra of CS₂ and COS are calculated by the SAC CI theory for both the outer- and the inner-valence region. The theoretical spectra compare well with the Mg K α and He II photoelectron spectra, as well as the previous results for CO₂. In the inner-valence region, the theoretical spectra consist of a large number of peaks due to a mixing between single ionizations and simultaneous ionization–excitation (shake-up) configurations. Assignments of the observed spectra and explanations of the origins of the similarities and differences in the photoelectron spectra of CO₂, CS₂ and COS are given. The important role of four-electron excited configurations in addition to three-electron ones, which are included as unlinked terms in the SAC CI theory, is indicated.

1. Introduction

It is generally recognized that electron correlations are very important for adequate descriptions of excited states. In this series of papers [1–4], we study electron correlations of molecules in various electronic states by the cluster-expansion approach. We have applied the SAC (symmetry-adapted-cluster) [1] and SAC CI [2] theories to the ground state, singlet and triplet excited states, and ionized and electron-attached states of molecules such as H₂O, CH₂, H₂CO, CO₂ and N₂O [3,4]. We have also studied the spin- and electron-correlation effects in several open-shell doublet radicals [3,4].

In this paper, we study theoretically the ionization spectra of CS₂ and COS by the SAC and SAC CI theories. We give theoretical ionization spectra in outer- and inner-valence regions for the isoelectronic molecules CO₂, CS₂, and COS; for CO₂ we refer to the previous results for comparison [4]. Allan et al. [5] observed the ionization spectra of CO₂, CS₂ and COS over the whole valence-energy region by Mg K α photoelectron spectroscopy. Potts and Williams [6] reported He II photoelectron spectra of these molecules. In addition to the sharp peaks for ionizations from the outer-valence orbitals [5–8], they observed many broad and overlapping peaks which might be assigned

to ionizations of inner-valence electrons and satellites of the outer- and inner-valence ionizations. Brion and co-workers also reported the ionization spectra of CO₂ [9,10] and COS [11] from outer- to inner-valence regions by (e, 2e) electron impact spectroscopy. Fig. 1 reproduces the photoelectron spectra observed by Allan et al. [5]. The spectra of the inner-valence regions are complex but show a beautiful change of patterns upon replacing oxygen by sulfur atoms. They seem to give a challenge to theoretical chemists to reproduce and assign the spectra. Here, we try to do that by the SAC CI theory.

The first systematic theoretical studies of the ionization spectra of CO₂, CS₂, and COS over the complete valence-electron energy region were reported by Cederbaum, Domcke, Schirmer, von Niessen and co-workers [10–13]. They developed and used two different Green's function techniques [14,15]; one for the outer-valence-type calculations and the other for the inner-valence-type calculations (2ph TDA approximation). The former calculations seem to give accurate results [16], but give no information on accompanying satellites and cannot be applied to the region of the inner-valence orbitals [13]. The latter 2ph TDA approximation seems to include electron correlations only insufficiently for both ground and ionized states, but has been applied successfully to reveal several im-

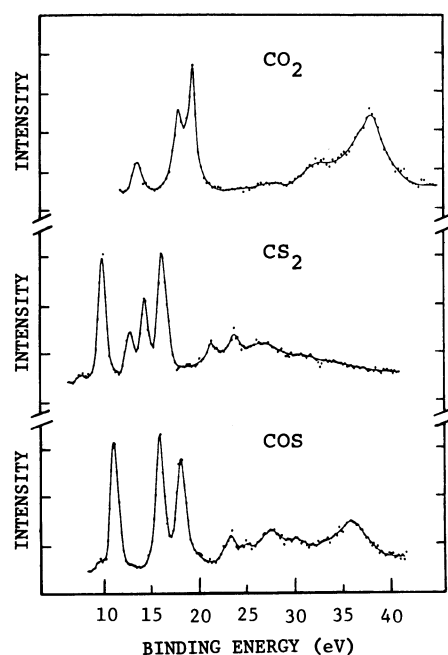


Fig. 1. Experimental photoelectron spectra of CO₂, CS₂ and COS observed by Allan et al. [5].

portant features of the inner-valence ionizations, especially a strong final-state correlation effect.

To describe adequately electron correlations in the excited states, it is necessary to include single and double excitations from the main reference configurations of the states. For a description of outer-valence ionizations, which are normally one-electron processes, up to three-electron excited configurations are necessary (one-electron ionizations plus two-electron excitations from them). However, for the inner-valence ionizations, the final states are strong mixtures of single ionizations and simultaneous ionization–excitation (shake-up) configurations. Then, to describe adequately correlation effects in the inner-valence ionizations, it is necessary to include also double excitations from the simultaneous ionization–excitation (shake-up) configurations. This results in four-electron excited configurations (one-electron ionization plus three-electron excitation). In the SAC CI theory, we describe these correlation effects on the basis of the ground-state correlations, because most of the correlations should be similar between the ground and ionized states. It was shown previously that this view-

point is justified theoretically in the cluster-expansion approach and results in the SAC CI theory [2]. In an ordinary multi-reference (MR) CI approach [17], calculations of the inner-valence ionizations are difficult because they involve the solution of a large number of eigenvalues and eigenvectors of a matrix of a very large dimension.

Previously, we have applied the SAC CI theory to the outer- and inner-valence ionizations of H₂O [18], CO₂ and N₂O [4]. The ground state was calculated by the SAC theory, including single and double excitations (linked) and quadrupole excitations (unlinked), so that the result includes a sufficient amount of correlation effects. The ionized states were calculated by the SAC CI theory, including ionization and ionization–excitation configurations (linked) and two-electron excitations from important ones of these linked configurations (i.e. three- and four-electron excitations) in the unlinked terms. Then, the calculated ionized states also include a large amount of correlation effects. Theoretically, we need not distinguish outer-valence and inner-valence ionizations. We have clarified the theoretical origins of the similarities and differences in the photoelectron spectra of the isoelectronic compounds CO₂ and N₂O [4]. Here, we report the results of applications of this theory to the ionization spectra of CS₂ and COS and compare them with the previous results for CO₂ [4]. We are especially interested in a beautiful change of the spectral patterns shown in fig. 1.

2. Computational method

Calculations were carried out for CS₂ and COS at their experimental geometry. Both are linear molecules and the bond lengths are C–S = 1.5545 Å for CS₂, and C–O = 1.160 Å, C–S = 1.560 Å for COS [19]. We have used two kinds of basis set. Basis I consists of (9s6p) GTOs of Huzinaga [20] contracted to a [4s2p] set by Dunning [21] [short nomenclature (9s6p/4s2p)] for C and O and an (11s7p/6s4p) set for S [22]. A set of diffuse sp functions was placed on the central carbon to represent the Rydberg orbitals ($\zeta(s) = 0.023$, $\zeta(p) = 0.021$) [22]. This set consists of 50 and 42 CGTOs for CS₂ and COS, respectively. Basis II consists of basis I plus a set of d-polarization functions on each atom. The exponents are 0.75, 0.85

Table 1
Dimensions of the linked operators and the computer times for the SAC and SAC CI calculations of CS₂ and COS ^{a)}

Molecule	State ^{b)}	Basis I			Computer time ^{c)} (min)	Basis II			Computer time ^{c)} (min.)
		SE	DE	total		SE	DE	total	
CS ₂	ground	116	600	717	1.8	176	1346	1523	6.4
	ionized								
	s	4	292	296	9.3(6.8)	4	400	404	25.5(18.7)
COS	a	4	287	291		4	384	388	
	ground	184	668	853	2.5	328	1418	1746	5.3
	ionized	8	591	599	19.7(11.7)	8	803	811	36.3(21.0)

^{a)} SE: single excitation, DE: double excitation.

^{b)} s and a are abbreviations for symmetric and antisymmetric with respect to the C₂ operation.

^{c)} For the ionized states, the computer time is for 3,4-excited calculations. Values in parentheses are the CPU time used for including 4-excited configurations.

and 0.6 for C, O and S, respectively. This set consists of 68 and 60 CGTOs for CS₂ and COS, respectively.

We have calculated the correlated ground state by the SAC theory and the correlated ionized states by the SAC CI theory. The calculational details [23] are the same as those summarized in ref. [4]. The values of the thresholds λ_g and λ_e for selections of the linked operators are 5.0×10^{-5} and 1.0×10^{-4} au, respectively. These values are larger than those used previously for CO₂ ($\lambda_g = 1.0 \times 10^{-5}$, $\lambda_e = 5.0 \times 10^{-5}$). The other parameters are the same as in ref. [4]. We have fixed the occupation numbers of the core orbitals at 2.0 and excluded the five highest and two highest virtual orbitals of CS₂ and COS, respectively, from the SAC and SAC CI calculations. We have carried out two types of SAC CI calculations. One includes up to three-electron excited configurations and the other up to four-electron excited configurations. These are referred to hereafter as 3-excited and 3,4-excited calculations, respectively. We have used Hartree–Fock configurations and orbitals of the neutral ground state of CS₂ and COS as reference orbitals throughout the present calculations of the ground and ionized states. This is an important feature because several necessary requirements between states are satisfied automatically [2].

Table 1 shows the dimensions of the linked operators in the SAC and SAC CI calculations. The dimensions are small though the calculations include large amounts of correlation effects as shown below. This is an important feature of the SAC and SAC CI theories [2]. Table 1 also includes the computer times.

For the ionized states, most of the time was used for the calculations of integrals for the 4-excited configurations as shown in parentheses in table 1. For the 3-excited calculations, only the difference was necessary.

3. Results

3.1. Main ionization peaks

The energy of the Hartree–Fock wavefunction used as a reference configuration and the correlation energy calculated by the CI and SAC methods are shown in table 2. (1 + 2) CI denotes a CI including single and double excitations used as linked operators in the SAC calculation. The SAC calculation is due to the non-variational (NV) method [2]. The d-orbitals are important for both Hartree–Fock and correlation energies. The effects on the SCF energy are -0.09 and -0.11 au for CS₂ and COS, respectively, and those on the correlation energy are -0.12 and -0.09 au, respectively. The total effects are as large as -0.21 and -0.19 au for CS₂ and COS, respectively.

Tables 3 and 4 show the ionization potentials of CS₂ and COS, respectively. The first four are outer-valence ionizations and the last two inner-valence ionizations. For the latter, we have given only the main peaks, though there are many peaks of similar intensities in the same energy regions of the theoretical spectra as shown below.

The orbital sequence of the Hartree–Fock configuration is

Table 2
Hartree–Fock energy and correlation energy of the ground state of CS₂ and COS (au)^{a)}

Method	CS ₂		COS	
	basis I	basis II	basis I	basis II
Hartree–Fock	–832.79005	–832.88274	–510.17508	–510.28024
(1 + 2)CI	–0.17816	–0.29627	–0.22199	–0.31159
SAC NV	–0.18892	–0.31119	–0.23507	–0.32408

^{a)} Basis I; [4s2p] set for C and O, [6s4p] set for S plus Rydberg sp set on C. Basis II; basis I plus d-polarization function on each atom.

$$(\text{core})^{22}(5\sigma_g)^2(4\sigma_u)^2(6\sigma_g)^2(5\sigma_u)^2(2\pi_u)^4(2\pi_g)^4 \quad (1)$$

for CS₂ and

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

for COS. This sequence was not affected by the inclusion of d-orbitals, as seen from tables 3 and 4. This is different from the case of CO₂ [4,16]. The ordering of the 2 π and 9 σ levels of COS is different from those in CS₂ and CO₂, but the same as that in N₂O [4], all isoelectronic molecules. McLean and Yoshimine [24] reported the same sequence for COS by calculations of accuracy near the Hartree–Fock limit.

We first discuss the ionization potentials of CS₂ shown in table 3. Except for the first ionization potential from the 2 π_g orbital, the Koopmans values are larger than the experimental values. The SAC CI results shown in table 3 are due to an approximate variational solution [2]. It is seen that within the SAC CI calculations, the results from 3,4-excited calculations with basis II (actually the most elaborate calculations) show the best overall agreement with experiments. The effects of d-orbitals are 0.05 to –0.4 eV for the outer-valence ionization but as large as \approx –1 eV for the inner-valence ionization. The effect of the four-electron excited configurations in the unlinked term is larger than the effect of d-orbitals. They affect only the ionized state and work to lower it. The effect is –0.3 to –0.8 eV for outer-valence ionizations and –1.0 to –1.7 eV for inner-valence ionizations. We note that the effect of the four-electron excited configurations is larger, as expected, for ionizations which have larger mixing with the simultaneous ionization–excitation processes. This is seen from the intensity P shown later in table 5. The smaller the P values, the larger the effect of the four-electron excited configurations.

We will show later that larger effects of the 4-excited configurations are seen for the intensities of the main peaks and the intensities and positions of the satellite peaks.

Table 4 shows a summary of the ionization potentials of COS. The present calculations failed to give a correct ordering for the ionizations from the 2 π and 9 σ orbitals. The results of the 3,4-excited calculations for these states are almost degenerate (the spacing is –0.13 and –0.05 eV in comparison with the experimental spacing, 0.52 eV). Taking into account the previous results for CO₂ [4,16] we think that a further improvement in the basis set would resolve this discrepancy. Further, considering the complexity of the photoelectron spectra of the second and third peaks [7], an experimental study seems also to be necessary.

The SAC CI results of 3,4-excited calculations show satisfactory overall agreement with experiments. The effects of d-orbitals are 0.1 to 0.4 eV for the outer-valence ionization and –0.6 to –0.8 eV for the inner-valence ionization. For the outer-valence ionizations, the d-orbitals tend to lower the ground state more than the ionized states. The effects of four-electron excited configurations are –0.3 to –0.7 eV, again a bit larger than the effects of d-orbitals. This effect works to lower the ionized state. For ionization from the 6 σ orbital, the effect of 4-excited configurations apparently increases the ionization energy. This is due to a large change in the configurational mixing in the corresponding ionized states. (Note that the intensity of the main peak for ionization from the 6 σ orbital is as small as 0.20 as seen from table 6 given below.)

Table 3
Ionization energy for the main peaks of CS₂ (eV)

State	Orbital picture	Koopmans		SAC CI (basis I) a)		SAC CI (basis II) a)		Exp. b)	CI d)	Green function e)	
		basis I	basis II	3-excited	3,4-excited	3-excited	3,4-excited			OVT	TDA
2Π _g	2π _g → ∞	10.25	10.12	9.71	9.45	10.02	9.68	10.06	9.23	9.83	9.39
2Π _u	2π _u → ∞	14.79	14.36	13.50	12.79	13.63	12.84	12.83	12.67	12.89	12.05
2Σ _u	5σ _u → ∞	15.78	15.87	14.29	13.87	14.77	14.18	14.47	14.01	14.37	13.61
2Σ _g	6σ _g → ∞	18.39	18.49	15.85	16.45	16.88	16.06	16.19	16.22	16.39	15.40
2Σ _u	4σ _u → ∞	28.71	27.91	25.37	23.95	24.51	22.85	(~24) c)	—	—	22.83
2Σ _g	5σ _g → ∞	32.05	31.30	27.80	26.81	26.67	25.71	(26~27) c)	—	—	28.04

a) The energy is relative to the neutral ground-state energy given in table 2. The notation 3-excited and 3,4-excited stands for calculations including up to three-electron excited configurations and up to four-electron excited configurations, respectively.

b) Ref. [7].

c) Read from the spectra shown in fig. 1 considering the present theoretical spectra shown in figs. 2 and 3.

d) Ref. [8]. e) Ref. [13].

Table 4
Ionization energy for the main peaks of COS (eV)

State	Orbital picture	Koopmans		SAC CI (basis I) a)		SAC CI (basis II) a)		Exp. b)	Green function c)	
		basis I	basis II	3-excited	3,4-excited	3-excited	3,4-excited		TDA	
2Π	3π → ∞	11.53	11.44	10.90	10.64	11.14	10.83	11.18	10.53	
2Π	2π → ∞	18.47	18.01	16.43	15.55	16.43	15.69	15.52	14.89	
2Σ	9σ → ∞	17.27	17.35	15.81	15.42	16.12	15.64	16.04	15.31	
2Σ	8σ → ∞	21.18	21.20	18.16	17.51	18.56	17.87	17.90	17.29	
2Σ	7σ → ∞	30.73	29.90	27.27	26.94	26.40	26.13	27.4	25.24	
2Σ	6σ → ∞	42.04	41.07	37.48	36.44	35.60	35.80	35.8	35.30	

a) See footnote a of table 3. b) Refs. [5,7]. c) Ref. [11].

3.2. Inner-valence ionizations and satellite peaks

Fig. 1 shows many broad and overlapping ionization peaks in the energy region above 20 eV. This suggests that in this region of ionizations, the main peaks have only low intensities and there are many satellite peaks of comparable intensities. In tables 5 and 6 are shown the calculated ionization potentials, orbital assignments, intensities, and the main configurations of the ionized states for CS₂ and COS, respectively. The intensities were approximated to be proportional to the transition monopole

$$P_K = \sum_i |\langle \Psi_K^\dagger | a_i \Psi_g \rangle|^2 \approx \sum_i |\langle \Psi_K | a_i \Phi_0 \rangle|^2, \quad (3)$$

where Ψ_K is the K th excited ionized state, a_i annihilates an electron in the orbital ϕ_i , and Φ_0 is the Hartree–Fock configuration. Because of this approximation, the present theoretical spectra should be compared with photoelectron spectra obtained with high photon energy. The Mg K α spectra observed by Allan et al. [5] are then most suitable for comparison. The results of tables 5 and 6 are from the 3,4-excited calculations with basis II. Calculated peaks with intensities larger than ≈ 0.02 are shown, though there were many peaks with smaller intensities. Figs. 2 and 3 present theoretical ionization spectra of CO₂, CS₂, and COS calculated by the SAC CI theory. Only peaks with intensities larger than 0.01 are shown. Fig. 2 is obtained with basis I and fig. 3 with basis II. Both are

Table 5

Ionization energies, orbital assignments, intensities, and the main configurations for the valence ionizations and satellite peaks of CS₂ calculated by the SAC CI theory ^{a, b)}

Ionization energy (eV)		Main orbital	Intensity P	Main configuration ^{d, e)}
calc.	exp. ^{c)}			
9.68	10.06	$2\pi_g$	0.93	$0.97(2\pi_g)^{-1}$
12.84	12.83	$2\pi_u$	0.82	$0.90(2\pi_u)^{-1}$
14.18	14.47	$5\sigma_u$	0.89	$0.94(5\sigma_u)^{-1}$
16.06	16.19	$6\sigma_g$	0.82	$0.91(6\sigma_g)^{-1}$
17.00	17.1	$2\pi_u$	0.02	$0.51(2\pi_g)^{-2}(3\pi_u)^1$
21.16	21.35	$2\pi_u$	0.10	$0.62(2\pi_g)^{-2}(3\pi_u)^1 + 0.31(2\pi_u)^{-1}$
21.67	21.56	$5\sigma_g$	0.02	$0.78(2\pi_g)^{-2}(8\sigma_g)^1$
22.24		$6\sigma_g(5\sigma_g)$	0.03	$0.50(2\pi_g)^{-2}(8\sigma_g)^1$
22.85		$4\sigma_u$	0.53	$0.72(4\sigma_u)^{-1} + 0.28(2\pi_g)^{-2}(7\sigma_u)^1$
23.15		$4\sigma_u$	0.07	$0.44(2\pi_u)^{-1}(5\sigma_u)^{-1}(3\pi_u)^1$
24.76		$4\sigma_u$	0.06	$0.40(2\pi_u)^{-1}(2\pi_g)^{-1}(8\sigma_g)^1$
25.47		$4\sigma_u$	0.06	$0.75(2\pi_g)^{-2}(7\sigma_u)^1$
25.71		$5\sigma_g$	0.46	$0.67(5\sigma_g)^{-1} + 0.27(6\sigma_g)^{-1}(2\pi_u)^{-1}(3\pi_u)^1$
26.67		$5\sigma_g(6\sigma_g)$	0.19	$0.50(5\sigma_u)^{-1}(2\pi_g)^{-1}(3\pi_u)^1 + 0.37(5\sigma_g)^{-1} - 0.24(6\sigma_g)^{-1}$
27.63		$5\sigma_u$	0.03	$0.37(6\sigma_g)^{-1}(2\pi_g)^{-1}(3\pi_u)^1$
29.26		$5\sigma_g$	0.05	$0.59(2\pi_u)^{-2}(8\sigma_g)^1$
29.37		$4\sigma_u$	0.04	$0.40(2\pi_u)^{-1}(2\pi_g)^{-1}(8\sigma_g)^1$
30.04		$5\sigma_g$	0.04	$0.40(2\pi_u)^{-2}(8\sigma_g)^1$
37.96		$5\sigma_g$	0.04	$0.37(2\pi_g)^{-2}(1\delta_g)^1$
39.47		$5\sigma_g$	0.03	$0.50(6\sigma_g)^{-2}(8\sigma_g)^1$
40.05		$4\sigma_u$	0.03	$0.28(2\pi_u)^{-1}(5\sigma_u)^{-1}(5\pi_u)^1$

^{a)} The results of 3,4-excited calculations with basis II. The calculated energy is relative to the neutral ground-state energy, -832.88274 au.

^{b)} Only peaks with intensity P larger than 0.02 are given, except for the peaks at 17.00 and 21.67 eV.

^{c)} Refs. [5–7].

^{d)} The notation $(i)^{-1}$ and $(i)^{-1}(j)^{-1}(a)^1$ stands for the configurations $I_i|0\rangle$ and $I_i S_j^a|0\rangle$, respectively, where I_i and S_j^a denote the ionization and excitation operators, respectively.

^{e)} The orbital sequence is $(\text{core})^{22}(5\sigma_g)^2(4\sigma_u)^2(6\sigma_g)^2(5\sigma_u)^2(2\pi_u)^4(2\pi_g)^4(3\pi_u)^0(7\sigma_g)^0(6\sigma_u)^0(4\pi_u)^0(8\sigma_g)^0(7\sigma_u)^0(8\sigma_u)^0 \dots$

Table 6

Ionization energies, orbital assignments, intensities, and the main configurations for the valence ionizations and satellite peaks of COS calculated by the SAC CI theory ^{a, b)}

Ionization energy (eV)		Main orbital	Intensity <i>P</i>	Main configuration ^{d, e)}
calc.	exp. ^{c)}			
10.83	11.18	3 π	0.94	0.96(3 π) ⁻¹
15.64	16.04	9 σ	0.90	0.94(9 σ) ⁻¹ - 0.11(8 σ) ⁻¹ (3 π) ⁻¹ (5 π) ¹
15.69	15.52	2 π	0.83	0.90(2 π) ⁻¹ - 0.26(2 π) ⁻¹ (3 π) ⁻¹ (5 π) ¹
17.87	17.90	8 σ	0.84	0.91(8 σ) ⁻¹ - 0.19(8 σ) ⁻¹ (3 π) ⁻¹ (5 π) ¹
21.06	20.14	2 π	0.01	0.84(3 π) ⁻² (5 π) ¹
24.23	23.56	7 σ	0.24	0.81(3 π) ⁻² (12 σ) ¹ - 0.48(7 σ) ⁻¹
24.97		2 π	0.05	0.67(3 π) ⁻² (5 π) ¹
25.68		7 σ	0.19	0.54(3 π) ⁻¹ (9 σ) ⁻¹ (5 π) ¹ - 0.43(7 σ) ⁻¹
26.13	27.4	7 σ	0.27	0.52(7 σ) ⁻¹ + 0.52(3 π) ⁻¹ (8 σ) ⁻¹ (5 π) ¹
27.50		7 σ	0.05	0.61(2 π) ⁻¹ (9 σ) ⁻¹ (5 π) ¹
30.44		8 σ	0.06	0.35(8 σ) ⁻¹ (3 π) ⁻¹ (5 π) ¹
32.30		7 σ	0.08	0.36(9 σ) ⁻¹ (3 π) ⁻¹ (5 π) ¹
35.35		6 σ	0.07	0.44(3 π) ⁻¹ (9 σ) ⁻¹ (4 π) ¹
35.48		6 σ	0.04	0.35(3 π) ⁻¹ (8 σ) ⁻¹ (4 π) ¹
35.69		6 σ	0.17	0.48(3 π) ⁻² (13 σ) ¹ + 0.41(3 π) ⁻² (14 σ) ¹ + 0.40(6 σ) ⁻¹
35.80	35.8	6 σ	0.20	0.45(6 σ) ⁻¹ + 0.37(3 π) ⁻¹ (8 σ) ⁻¹ (4 π) ¹
36.06		6 σ	0.11	0.36(9 σ) ⁻² (12 σ) ¹ - 0.33(8 σ) ⁻¹ (3 π) ⁻¹ (4 π) ¹ + 0.33(6 σ) ⁻¹
36.68		6 σ (7 σ)	0.05	0.56(9 σ) ⁻² (12 σ) ¹ + 0.56(9 σ) ⁻¹ (8 σ) ⁻¹ (12 σ) ¹
38.17		6 σ	0.03	0.36(2 π) ⁻¹ (8 σ) ⁻¹ (5 π) ¹

^{a)} The results of 3,4-excited calculations with basis II. The calculated energy is relative to the neutral ground-state energy, -510.28024 au.

^{b)} Only peaks with intensity larger than 0.02 are given, except for the peak at 21.06 eV.

^{c)} Refs. [5-7].

^{d)} The orbital sequence is (core)¹⁴(6 σ)²(7 σ)²(8 σ)²(2 π)⁴(9 σ)²(3 π)⁴(10 σ)⁰(4 π)⁰(11 σ)⁰(5 π)⁰(12 σ)⁰(13 σ)⁰(14 σ)⁰(6 π)⁰ ...

^{e)} See footnote d of table 5.

from the 3,4-excited calculations. The spectra of CO₂ were redrawn from the results given in ref. [4].

The theoretical ionization spectra shown in figs. 2 and 3 reproduce the general features of the experimental spectra shown in fig. 1. Especially, the beautiful changes of patterns among the spectra of CO₂, CS₂, and COS are well reproduced. Of the two theoretical spectra, fig. 3 obtained with basis II including d-orbitals compares better with experiments than fig. 2 obtained with basis I, as is evident from tables 3 and 4 for the outer-valence ionizations.

In the inner-valence region, 22-45 eV, the observed spectra of CO₂ are composed of a single broad peak in the 30-43 eV region with a flat shoulder in the 30-35 eV region. We see such a feature in the theoretical spectra, which are composed of two main and many satellite peaks.

In the observed spectra of CS₂, the peaks are shifted much to the lower-energy region. Three relatively

broad peaks are observed in the 20-22.5, 22.5-25, and 25-27.5 eV regions. At higher energies, the spectra show a flat envelope, monotonously decreasing in intensity but indicating the existence of several peaks. In the theoretical spectra, two strong peaks are calculated at 22.9 and 25.7 eV (basis II) due mainly to ionizations from the 4 σ_u and 5 σ_g orbitals, respectively. We assign these peaks to the peaks observed at 22.5-25 and 25-27.5 eV. The peak observed at 20-22.5 eV is assigned mainly to a satellite of the ionization from the 2 π_u orbital. From the He II spectra [6,13], this peak seems to consist of two or three peaks as will be discussed below. Allan et al. [5] assigned the peaks at 20-22.5 and 22.5-25 eV to satellite peaks and the peak at 25-27.5 eV as a composite of the main peaks of the ionizations from the 4 σ_u and 5 σ_g orbitals. The present assignments are different from theirs. The envelope starting at \approx 27.5 eV is assigned from the theoretical spectrum as being due to a number of peaks with

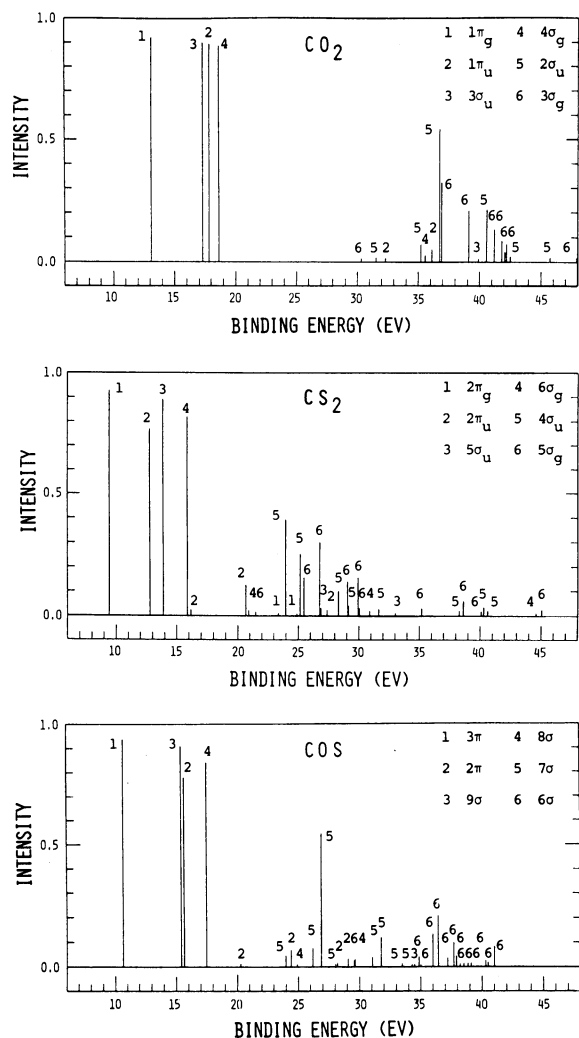


Fig. 2. Theoretical ionization spectra of CO₂, CS₂ and COS calculated by the SAC CI theory with basis I. The calculations include 3,4-excited configurations.

small intensities which are satellites of the ionizations from the $4\sigma_u$ and $5\sigma_g$ orbitals.

The spectrum of COS in the inner-valence region is somehow a synthesis of the spectra of CO₂ and CS₂. Peaks are seen at about 23, 25, 27.4, 30 and 35.7 eV [6]. From the theoretical spectra shown in figs. 2 and 3, we assign the peaks at 27.4 and 35.7 eV to ionizations from the 7σ and 6σ orbitals, respectively. These peaks are not single peaks, but each is composed of a

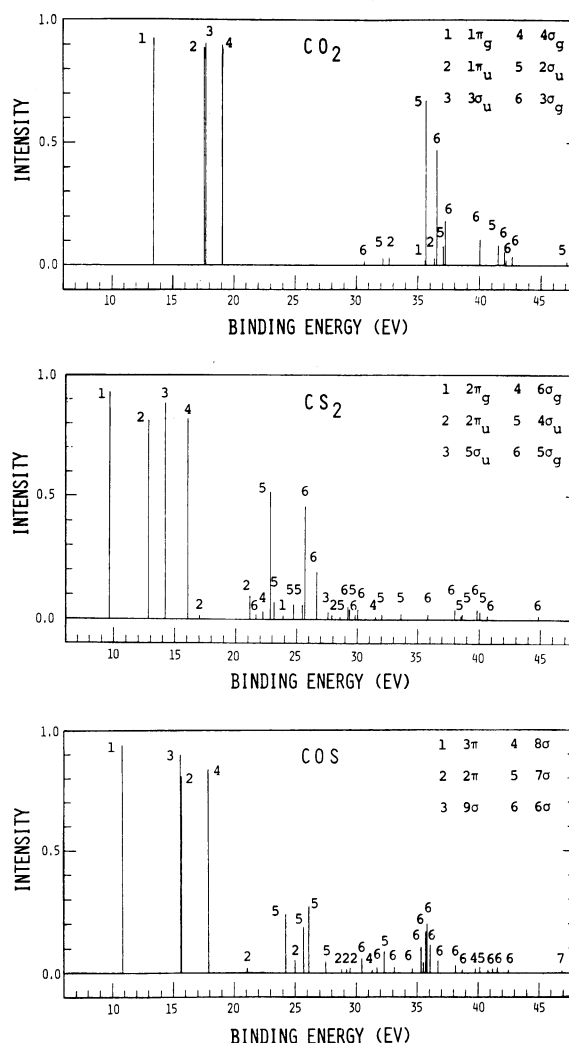


Fig. 3. Theoretical ionization spectra of CO₂, CS₂ and COS calculated by the SAC CI theory with basis II. The calculations include 3,4-excited configurations.

main peak and its satellites. The peaks observed at 23 and 25 eV may probably be assigned to the satellites of the ionizations from the 7σ and 2π MOs, respectively. The peak observed at 30 eV will be a composite of the satellites of 2π , 6σ and 8σ ionizations. However, for these satellite peaks of low intensities, the assignments to the main orbitals are almost meaningless. It is better to assign it to ionization–excitation (shake-up) configurations as shown in tables 5 and 6.

Potts and Williams [6] and Schirmer et al. [13] ob-

served the He II photoelectron spectra of CS₂ and reported peaks at 14.06, 17.06, 18.97, 20.22, 21.35, 21.56 and 23.96 eV. Our theoretical results explain some of these. The peak at 17.06 eV would correspond to the theoretical peak at 17.0 eV (basis II). It is assigned to a satellite of the $2\pi_u$ ionization and as seen from table 5, the main configuration is $(2\pi_g)^{-2}(3\pi_u)^1$, i.e. an ionization from the $2\pi_g$ orbital accompanied by a simultaneous excitation from the $2\pi_g$ to $3\pi_u$ orbital, the lowest π^* MO with some Rydberg character. This assignment is the same as that of Schirmer et al. [13] by the 2ph TDA method. The peak observed at 21.35 eV would correspond to the theoretical peak calculated at 21.16 eV (basis II). It is again a satellite of the $2\pi_u$ ionization with the same main configuration $(2\pi_g)^{-2}(3\pi_u)^1$. The peak observed at 21.56 eV is assigned to a satellite of either an outer-valence ionization from the $6\sigma_g$ MO or an inner-valence ionization from the $5\sigma_g$ MO or the mixture thereof. As seen from table 5, these peaks are calculated at 21.67 and 22.24 eV (basis II) and the main configuration is $(2\pi_g)^{-2}(8\sigma_g)^1$ for both peaks. The $8\sigma_g$ MO is an s_C-s_S antibonding MO. The peak observed at 23.96 eV would be the same peak as that observed at 22.5–25 eV by Allan et al. [5]. It is assigned to ionization from the $4\sigma_u$ MO. For the peaks observed at 14.06, 18.97 and 20.22 eV, however, we have no theoretical counterparts.

For COS, Potts and Williams [6] observed peaks at 20.14 and 23.56 eV. The former would correspond to the peak calculated at 20.27 eV (basis I) or 21.06 eV (basis II) which is a satellite of the ionization from the 2π orbital. The main configuration is $(3\pi)^{-2}(5\pi)^1$. 5π is an antibonding π^* orbital of valence character. (The Rydberg π -type orbital appears as 4π .) The relatively strong peak observed at 23.56 eV would be assigned to a satellite of the ionization from the 7σ MO, as discussed above.

The main configurations of the satellite peaks are generated by simultaneous ionization–excitations from the Hartree–Fock configuration of the neutral ground state. As seen from tables 5 and 6, the unoccupied orbitals used for the simultaneous excitations are predominantly $3\pi_u$, $8\sigma_g$ and $7\sigma_u$ MOs for CS₂ and 5π , 4π , 12σ , 13σ and 14σ MOs for COS. For CS₂, the $3\pi_u$ MO is an antibonding π^* orbital mixed with the Rydberg orbital. The $8\sigma_g$ and $7\sigma_u$ MOs are the valence s_C-s_S and $p_{\sigma C}-p_{\sigma S}$ antibonding orbitals, re-

spectively. The lower $7\sigma_g$ and $6\sigma_u$ MOs are Rydberg-type MOs, so that they do not participate strongly in the shake-up processes. For COS, the 5π MO is a valence π^* antibonding orbital and the 4π MO a Rydberg p_π MO. The 12σ , 13σ and 14σ MOs are σ -type valence antibonding orbitals. The lower 10σ and 11σ MOs are Rydberg-type orbitals. Thus, the main configurations of the shake-up states are generated by the two-electron loss from the bonding orbitals and the one-electron addition to the strongly antibonding orbitals. Therefore, it is quite possible that the geometries of molecules in the shake-up ionized states are very different from that of the neutral ground state. This effect should also be a reason for the broadness of the observed spectra in the inner-valence region, though the existence of a large number of shake-up states as shown in figs. 2 and 3 should be the primary origin of the broad and overlapping nature of the spectra.

The differences between figs. 2 and 3 constitute the effects of d-polarization functions on the ionization spectra. The d-orbitals are very important for the orderings between the second two peaks (peaks 2 and 3) of CO₂ and COS. For CO₂, a correct ordering is obtained only with the basis which includes the d-orbitals [4]. For COS, the two peaks become almost degenerate when d-orbitals are added (see table 4). For the inner-valence region, we have no definite criteria, but the spectra are affected considerably. The inclusion of d-orbitals tends to shift the main peaks to lower energy by ≈ 1 eV and to make the intensity of the main peaks stronger. Though the intensity of the main peaks of COS apparently becomes weaker by the inclusion of d-orbitals, the intensities of close-lying satellites are strengthened, so that the resultant composite peak will become stronger.

3.3. Importance of 4-excited configurations

To describe the correlations in the shake-up states adequately, it is necessary to include double excitations from the simultaneous ionization–excitation (shake-up) configurations. This results in the 4-excited configurations (one-electron ionization plus three-electron excitation from the Hartree–Fock configuration of the neutral ground state). In the present SAC CI theory, they are included in the unlinked terms [2]. To demonstrate the importance of 4-excited configurations, the spectra calculated without these configu-

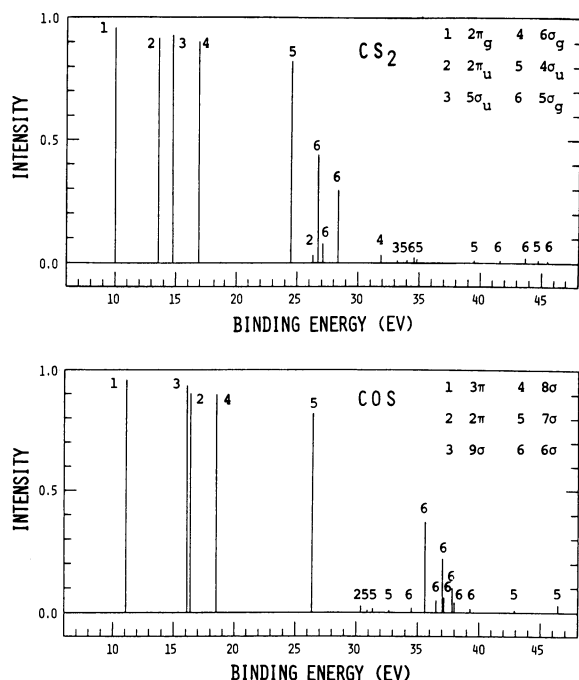


Fig. 4. Theoretical ionization spectra of CS₂ and COS obtained without including 4-excited configurations in the SAC CI calculations with basis II.

rations are shown in fig. 4, which gives the results of 3-excited calculations with basis II.

Comparing fig. 4 with fig. 3, we note that the outer-valence ionizations are little affected by the 4-excitations, except for their intensities. For the inner-valence ionizations, the positions of the main peaks are relatively unaffected. These results are reasonable because for these the main effects are represented by the 3-excited configurations included in both calculations. However, the 4-excited configurations are very important for the intensities of the main peaks of the inner-valence ionizations. These peaks in fig. 4 are too strong compared to the experimental spectra shown in fig. 1. Further, the 4-excited configurations are very important for the positions and intensities of the satellite peaks. A large number of satellite peaks disappears when we neglect the 4-excitations. The broad and overlapping features of the spectra of the inner-valence ionizations are not explained without the existence of a large number of satellites shown in fig. 3. The 4-excitations work to stabilize the shake-up con-

figurations and make them easier to mix with the single-ionization configurations.

4. Conclusion

We have studied the ionization spectra of CO₂, CS₂ and COS from outer- to inner-valence regions by the SAC CI theory. The calculations with basis II including 3,4-excited configurations show the best overall agreement with experiment in both outer- and inner-valence regions. For COS, however, we failed to reproduce the ordering of the ionizations from the 2π and 9σ orbitals. For the outer-valence ionizations, the relative intensities are calculated to be larger than 0.8, so that one-particle picture of ionization is essentially correct. For the inner-valence ionizations, however, the mixing between single ionizations and simultaneous ionization–excitation (shake-up) configurations is so large that a distinction between parent and satellite peaks becomes almost meaningless. This is especially so for the innermost valence ionizations.

We have given systematic assignments of the spectra and clarified the origins of the similarities and differences in the photoelectron spectra of CO₂, CS₂ and COS. The broad and overlapping features of the spectra of the inner-valence ionizations are primarily due to the existence of a large number of peaks (main and satellites). The idea of the Koopmans model of ionization breaks down completely in this region of the spectra. Further, since the shake-up process involves excitation of an electron to a strongly antibonding orbital, the geometry of such state should be considerably different from that of the neutral ground state. This should also be a reason for the broadness of the spectra in this region. The important roles of the d-orbitals involved in basis II and of the 4-excited configurations were also discussed.

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