

# Ionization spectrum of CO<sub>2</sub> studied by the SAC-CI general-*R* method

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## Abstract

The SAC-CI (symmetry-adapted-cluster configuration-interaction) general-*R* method was used to assign the satellite peaks of the ionization spectrum of CO<sub>2</sub>. Outer-valence satellite peaks were assigned to the <sup>2</sup>Π<sub>u</sub> and <sup>2</sup>Π<sub>g</sub> states and inner-valence satellite peaks were assigned to the <sup>2</sup>Σ<sub>u</sub><sup>+</sup> and <sup>2</sup>Σ<sub>g</sub><sup>+</sup> states. The SAC-CI general-*R* method reproduces well the experimental spectrum in both the outer and inner-valence regions. On the other hand, while the SAC-CI SD-*R* method calculates the main peaks quite well, the shake-up states are by about 3 eV higher than those of the general-*R* method. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Ionization spectrum; Outer and inner-valence regions; SAC-CI general-*R* method

## 1. Introduction

The inner-valence region of the ionization spectrum contains many satellite peaks which directly reflect the correlation effects of the molecule. Experimentally, inner-valence ionization peaks have been studied by high-resolution synchrotron radiation photoelectron spectroscopy (PES), X-ray PES (ESCA), and electron momentum spectroscopy (EMS). For the CO<sub>2</sub> molecule, the satellite peaks in the outer and inner-valence regions have been reported using several experimental techniques [1–5]. In particular, Roy et al. [5] performed high-res-

olution angle-resolved PES and gave detailed assignments of the peaks using the photon energy-dependent relative intensities and asymmetry parameters. These satellite peaks in the CO<sub>2</sub> ionization spectrum have also been investigated theoretically in some detail by the Green's function method [3,6], by the SAC (symmetry-adapted-cluster)-CI (configuration interaction) method [7], and by the CIPSI method [5]. However, since these shake-up peaks are numerous and congested, their assignments are still difficult, especially in the inner-valence region. The satellite peaks of CO<sub>2</sub> are of particular interest since some have a considerable amount of 3h2p character, i.e. simultaneous ionization and two-electron excitation (three-electron) processes, as pointed out by Roy et al. [5].

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In this study, we applied the SAC-CI general- $R$  method to the ionization spectrum of  $\text{CO}_2$  and assigned the satellite peaks in the outer- and inner-valence regions. The SAC-CI method [8–13] has been successfully applied to several molecular spectroscopic problems including ionization spectroscopy [7,14–19]. There are two standards in the SAC-CI method with respect to choice of the linked operators ( $R$ ): in the SAC-CI SD(single double)- $R$  method, single and double excitation operators are adopted for  $R$  operators, while the SAC-CI general- $R$  method [20–23] further involves triple and higher excitation operators. The SAC-CI general- $R$  method [20–23] was proposed to describe multiple-electron processes with high accuracy. This method has been shown to be useful for studying large numbers of states in the ionization spectrum [24,25]. We also performed a SAC-CI SD- $R$  calculation for comparison and to examine the effect of including the higher excitation operators in the linked excitation operators.

## 2. Computational details

The basis set should be flexible to describe the shake-up states. We used the [6s4p] GTOs of Huzinaga and Dunning [26,27] augmented with two polarization d-functions of  $\zeta_d = 2.314$  and 0.645 for O and  $\zeta_d = 1.097$  and 0.318 for C [28]; at least VQZ2P quality. The geometry is fixed to that of the experimental ground state and the vertical ionization is studied.

Both the SAC-CI general- $R$  and SD- $R$  calculations are performed for the outer and inner-valence regions. In the SAC-CI SD- $R$  method, unlinked terms of the forms  $R_r S_{jk}^{ab}|0\rangle$  and  $R_{ij}^a S_{kl}^{bc}|0\rangle$ , where  $R$  and  $S$  are the ionization and singlet-type excitation operators, respectively, are included; namely the ‘3,4-excited’ calculation [7] is performed. The active space consists of eight occupied MOs and 79 unoccupied MOs, and only the 1s orbitals of C and O are frozen as cores.

To reduce the computational effort, perturbation selection is carried out for the linked operators higher than double excitations [7,18]. For the ground state, the threshold for the linked double is  $\lambda_g = 3 \times 10^{-5}$  au and the unlinked terms are writ-

ten as the products of the important linked terms whose SDCI coefficients are larger than 0.005. For ionized states, the threshold for the linked doubles is  $\lambda_e = 1 \times 10^{-5}$  au. In the SAC-CI general- $R$  calculation, higher-order excitation operators up to sextuples are generated by the exponential-generation (EG) algorithm [20–23]. The thresholds in the exponential generation are set to  $(\lambda_{AA}, \lambda_{AAA}) = (0.01, 0.4)$  [20] and the generated higher-order excitation operators are further selected by the perturbation selection scheme: the operators whose perturbation energy contribution to the primary states is larger than  $\lambda_e = 5 \times 10^{-5}$  are adopted. The primary states are determined by a preliminary EGCI calculation using a small active space. The thresholds for this preliminary EGCI are  $(\lambda_{AA}, \lambda_{AAA}) = (0.01, 1.0)$ , and up to quadruple excitation operators are included.

The HONDO8 program [29] is used for HF SCF calculations and the SAC-CI96 program [30] is used for SAC-CI calculations.

## 3. Results and discussion

The outer and inner-valence regions up to 42 eV were studied by the SAC-CI general- $R$  and SD- $R$  methods. With SAC-CI SD- $R$ , about 90 electronic states were calculated, while about 130 ones were solved with the general- $R$  calculation. Table 1 summarizes the number of primary configurations for the selection and the dimensions of linked operators in the SAC-CI general- $R$  calculations. About 300 primary configurations were selected for each symmetry of the  $D_{2h}$  point group. Since three-electron processes exist in the primary states, up to quintuple excitation operators were included in the linked operators of the general- $R$  calculations.

In a previous SAC-CI SD- $R$  study of the ionization spectrum of  $\text{CO}_2$  [7], polarization functions were important, and including the unlinked terms of  $R_{ij}^a S_{kl}^{bc}|0\rangle$  had a large effect on the inner-valence spectrum. The resultant SAC-CI spectrum [7] reproduced the overall structure of the experimental PES. In this paper, we discuss the details of the spectrum with a refined basis set, and compare the results of the general- $R$  and SD- $R$  methods.

First, we compare the ionization spectra calculated by the SAC-CI general-*R* and SD-*R* methods with the photoelectron spectrum of CO<sub>2</sub> [1,5] in Fig. 1. We corrected the intensity according to the branching ratio of the outer valence bands of Ref. [1] for each symmetry: branching ratios are 0.13, 0.11, 0.40, 0.58, 0.78, and 1.0 for  $1\pi_g$ ,  $1\pi_u$ ,  $3\sigma_u$ ,  $4\sigma_g$ ,  $2\sigma_u$ , and  $3\sigma_g$ , respectively. For the main peaks in the outer-valence region, both the SAC-CI general-*R* and SD-*R* methods give almost the same spectrum, which agrees with the experimental spectrum. The inner-valence range of 25–45 eV contains broad bands due to many shake-up states. There are remarkable differences between the SAC-CI general-*R* and SD-*R* spectra in this energy region. The SAC-CI general-*R* method reproduces the positions and the shapes of the satellite bands, while the SAC-CI SD-*R* method does not produce acceptable results in this region. This shows the importance of including higher excitation operators in the linked excitation operators of the SAC-CI calculation to describe the inner-valence ionization spectrum, which is consistent with previous results [20,24].

Table 2 summarizes the detailed results of the SAC-CI general-*R* and SD-*R* calculations for the ionized states of CO<sub>2</sub>. The experimental values are due to synchrotron radiation PES in Refs. [4,5]. The ionization potential (IP), monopole intensity,

and excitation level are shown for states of up to 42 eV with calculated intensities greater than 0.005, except for some low-lying shake-up states.

The IPs of the main peaks are reproduced well by both the SAC-CI general-*R* and SD-*R* methods. The calculated values of 13.77, 17.72, 18.28, and 19.48 eV by the general-*R* method are consistent with the experimental values of 13.78, 17.59, 18.08, and 19.40 eV [31]. Inclusion of the higher excitation operators in the *R* operators does not greatly affect the main-peak positions as described by the one-electron process.

In the energy region of 22–30 eV, five outer-valence shake-up peaks were observed [4,5]. The three peaks observed at 22.7, 25.0, and 27.3 eV were assigned to the  $^2\Pi_u$  states. The SAC-CI general-*R* method gives four  $^2\Pi_u$  shake-up states in this energy region at 24.19, 25.63, 25.04, and 28.45 eV. The IPs calculated by the general-*R* method are about 3 eV lower than those calculated by the SD-*R* method. As a consequence, more shake-up states are calculated by the general-*R* method than by the SD-*R* method. These  $^2\Pi_u$  shake-up states correspond to the states that were assigned experimentally using the asymmetry parameter  $\beta$  [5]. The 2ph-TDA [3] and CIPSI calculations [5] also gave some  $^2\Pi_u$  states in this energy region, although their spectra were slightly different from the present one.

Table 1

Numbers of the reference configurations and the dimensions of the linked operators in the SAC-CI general-*R* calculations for the ionized states of CO<sub>2</sub>

State	Singles	Doubles	Triples	Quadruples	Quintuples	Total
<i>Numbers of reference configurations</i>						
$^2\Sigma_g^+$	2	89	217	6	–	314
$^2\Sigma_g^-$	0	32	45	2	–	79
$^2\Pi_g$	1	84	197	10	–	292
$^2\Sigma_u^-$	0	32	25	–	–	57
$^2\Sigma_u^+$	2	75	187	12	–	276
$^2\Pi_u$	1	87	231	39	–	358
<i>Dimensions of SAC-CI general-<i>R</i> calculations</i>						
$^2\Sigma_g^+$	2	772	7041	13 020	121	20 956
$^2\Sigma_g^-$	0	492	2885	3565	1	6943
$^2\Pi_g$	1	632	6746	11 204	88	18 671
$^2\Sigma_u^-$	0	492	2760	3072	–	6324
$^2\Sigma_u^+$	2	772	6742	10 770	189	18 475
$^2\Pi_u$	1	632	6697	14 329	174	21 833

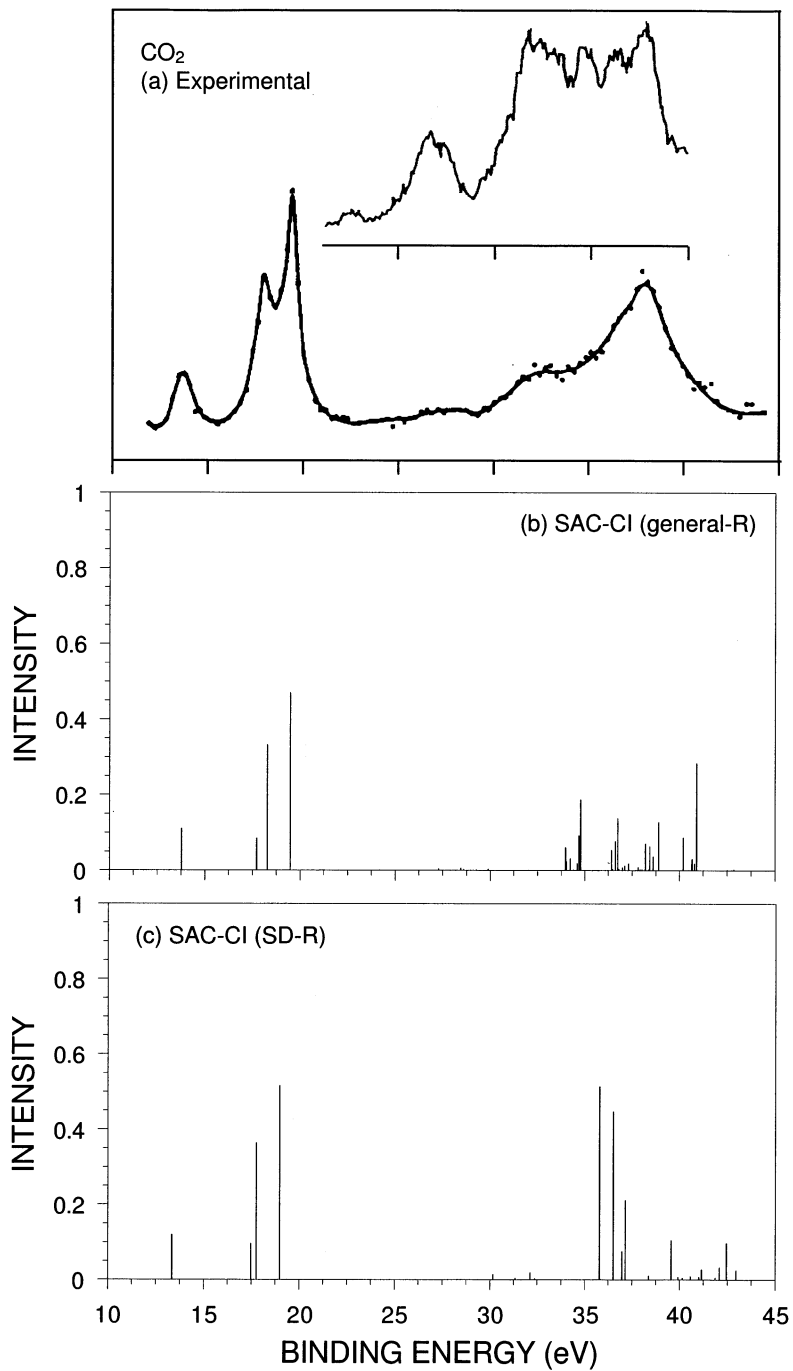


Fig. 1. (a) Experimental photoelectron spectrum [1,5] of CO<sub>2</sub> and the ionization spectra calculated by the (b) SAC-CI general-R and (c) SD-R methods.

The two peaks observed experimentally at 29.7 and 30.5 eV were assigned to the  ${}^2\Pi_g$  and  ${}^2\Pi_u$  states, respectively [5]. In this region, the SAC-CI general-*R* method calculates one  ${}^2\Pi_g$  state at 30.64 eV and two  ${}^2\Pi_u$  states at 32.02 and 33.09 eV. Some of the states have a three-electron-pro-

cess character. In the SAC-CI general-*R* calculation, the  ${}^2\Sigma_u^+$  states are also obtained in this energy region, although their monopole intensities are small.

In the inner-valence region of 30–45 eV, five [5] or seven [4] satellite peaks were observed. These

Table 2

Excitation level, ionization potential (in eV), and monopole intensity for the ionized states of CO<sub>2</sub> calculated by the SAC-CI general-*R* and SD-*R* methods

State	Experimental		SAC-CI general- <i>R</i>			SAC-CI SD- <i>R</i>	
	FKS <sup>a</sup>	RNMMR <sup>b</sup>	Excitation level	I.P.	Intensity	I.P.	Intensity
${}^2\Pi_g$	–	13.78	1	13.77	0.85	13.35	0.92
${}^2\Pi_u$	–	17.59	1	17.72	0.78	17.48	0.88
${}^2\Sigma_u^+$	–	18.08	1	18.28	0.83	17.77	0.91
${}^2\Sigma_g^+$	–	19.40	1	19.48	0.81	18.99	0.89
${}^2\Pi_u$	22.8	22.7	2	24.19	0.008	27.19	0.008
–	25.1	25.0	2	25.04	0.002	–	–
–	–	–	2	25.63	0.002	–	–
–	26.9	27.3	2	28.45	0.055	32.37	0.035
–	30.7	30.5	2	32.02	0.012	35.51	0.005
–	–	–	2+3	33.09	0.012	35.86	0.016
${}^2\Pi_g$	29.8	29.7	2	30.64	0.002	33.71	0.005
–	–	–	2+3	34.40	0.018	–	–
${}^2\Sigma_u^+$	–	–	2	29.26	0.003	32.13	0.025
–	32.2	31.9	2	29.89	0.005	35.79	0.659
–	33.4	33.7	2	33.98	0.079	36.97	0.097
–	–	–	2	34.23	0.041	38.38	0.014
–	–	–	2+3	34.61	0.024	39.92	0.009
–	35.0	34.9	2+3	34.70	0.119	40.57	0.012
–	35.5	–	2+3	36.62	0.100	41.15	0.036
–	–	–	2+3	36.75	0.178	41.87	0.008
–	–	–	2	37.32	0.023	42.10	0.043
–	–	–	2	37.82	0.011	–	–
–	–	–	2	38.61	0.047	–	–
–	–	–	2+3	40.20	0.112	–	–
–	–	–	2	40.63	0.023	–	–
–	–	–	2	40.67	0.040	–	–
–	–	–	2	40.79	0.023	–	–
${}^2\Sigma_g^+$	–	–	2	27.29	0.005	30.17	0.015
–	–	–	2	34.04	0.024	31.34	0.005
–	–	–	2	34.78	0.188	36.52	0.447
–	36.9	36.5	2	36.41	0.054	37.14	0.212
–	–	–	2+3	36.47	0.005	39.56	0.105
–	–	–	2	37.00	0.008	40.15	0.005
–	–	–	2	37.13	0.015	41.02	0.007
–	38.0	38.0	2+3	38.20	0.071	42.45	0.098
–	–	–	2	38.43	0.064	42.96	0.026
–	–	–	2+3	38.90	0.129	–	–
–	40.6	–	2+3	40.90	0.284	–	–

<sup>a</sup> [4]<sup>b</sup> [5]

peaks consist of the shake-up states whose intensities are due to the  $(2\sigma_u)^{-1}$  and  $(3\sigma_g)^{-1}$  single-hole states. In a previous SAC-CI study [7], many shake-up states originated from these states. Roy et al. [5] assigned the three lower peaks at 31.9, 33.7, and 34.9 eV to the  ${}^2\Sigma_u^+$  states and the two higher peaks at 36.5 and 38 eV to the  ${}^2\Sigma_g^+$  states using the photon energy-dependent behavior of the relative intensities. Freund et al. [4] observed the corresponding states and the two additional peaks at 35.5 and 40.6 eV. The SAC-CI general-*R* results show that there are many  ${}^2\Sigma_u^+$  and  ${}^2\Sigma_g^+$  shake-up states with considerable intensities in the energy region of 34–40 eV. Prominent  ${}^2\Sigma_u^+$  states are calculated at 33.98, 34.23, 34.70, 36.62, 36.75, and 40.20 eV, and  ${}^2\Sigma_g^+$  states with certain intensities are calculated at 34.78, 36.41, 38.20, 38.43, 38.90, and 40.90 eV. While these states are attributed to the peaks in the inner-valence region, a one-to-one assignment would appear to be meaningless. Some of shake-up states have the nature of three-electron processes and have considerable intensities around 40 eV. In Table 2, the excitation level '2 + 3' means that these states have more than 10% three-electron-process character. These shake-up states were also obtained by the CIPSI method [5], although the pattern of the calculated peaks was different from that presented here.

#### 4. Conclusion

The SAC-CI general-*R* and SD-*R* methods were applied to the ionization spectrum of CO<sub>2</sub>. The main peaks were well described by both the SAC-CI general-*R* and SD-*R* methods. However, there are remarkable differences between the results of the SAC-CI general-*R* and SD-*R* methods for the inner-valence region. The SAC-CI general-*R* method reproduces well the structures of the satellite peaks observed by PES, while the results of the SD-*R* method are inadequate for describing these peaks. With the SAC-CI general-*R* method, the IPs of the shake-up states are about 3 eV lower than those obtained by the SD-*R* method. The outer-valence satellite peaks were assigned to the  ${}^2\Pi_u$  and  ${}^2\Pi_g$  states and the inner-valence

satellite peaks were assigned to numerous  ${}^2\Sigma_u^+$  and  ${}^2\Sigma_g^+$  states. The present results support, in general, the assignments of Roy et al. [5], but the pattern of the calculated peaks is different, especially for the inner-valence shake-up states.

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