

## Cluster expansion of the wave function. Potential energy curves of the ground and excited states of CO

O KITAO and H NAKATSUJI\*

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

**Abstract.** The SAC (symmetry-adapted cluster) and SAC-CI (SAC-configurational interactions) theories have been applied to the calculations of the potential curves of the ground and excited states of the CO molecule. The states studied are valence type  $X^1\Sigma^+$ ,  $(4)^1\Sigma^+$ ,  $A^1\Pi$ ,  $I^1\Sigma^-$ ,  $D^1\Delta$ ,  $a^3\Pi$ ,  $a^3\Sigma^+$ ,  $d^3\Delta$ , and  $e^3\Sigma^-$ , and of Rydberg type  $B^1\Sigma^+$ ,  $C^1\Sigma^+$ , and  $F^1\Sigma^+$ . For the description of the  $X^1\Sigma^+$  and  $(4)^1\Sigma^+$  states, we took advantage of the fact that the SAC and SAC-CI solutions satisfy orthogonality and Hamiltonian orthogonality to each other. Near the avoided crossing region of these states, however, the SAC theory fails because of the multi-reference nature of the correlation. Our theoretical potential curves of the ground and various excited states are very similar to the RKR (Rydberg-Klein-Rees) potential curves based on experimental data. The spectroscopic constants calculated also agree well with experimental values.

**Keywords.** Symmetry-adapted-cluster theory; symmetry-adapted-cluster-configurational-interaction theory; Rydberg and valence excited states; Thouless theorem; non-variational method; coupled-cluster-many-electron theory; quasi-degenerate correlation; Dunham theory; Rydberg and valence transitions.

### 1. Introduction

Adequate description of electron correlation is very important for the study of open-shells and excited states of molecules. This is especially so when we study potential energy curves of the ground and excited states. For this purpose several approaches have been developed, for example, MR (multi-reference)-CI (configuration interaction) (Beunker and Peyerimhoff 1983), MC-SCF (Das 1973; Grein and Banerjee 1975) and cluster expansion (Mukherjee *et al* 1975, 1977; Nakatsuji 1978, 1979; Nakatsuji and Hirao 1978; Paldus *et al* 1978; Mukherjee and Mukherjee 1979; Adnan *et al* 1980, 1982; Haque and Mukherjee 1984). In the cluster expansion approach, the multi-reference type theories are also being developed (Mukherjee *et al* 1975, 1977; Jeziorski and Monkhorst 1981; Nakatsuji 1985) in order to apply to quasi-degenerate states.

In this series of studies, we have developed and applied that SAC (symmetry-adapted-cluster) and SAC-CI theories (Nakatsuji 1978, 1979; Nakatsuji and Hirao 1978). The SAC theory is based on the cluster expansion of the wave function (Čížek 1960; Čížek and Paldus 1971; Bartlett 1981; Paldus 1983) and we usually apply it to the ground state of a molecule. The SAC-CI theory is the CI theory within the sub-space of the SAC wave function (Nakatsuji 1978, 1979; Nakatsuji and Hirao 1978). It has been effectively applied to various kinds of excited and ionized states. (see for example, Nakatsuji 1984, Nakatsuji *et al* 1985, and references therein). The success is basically due to the

---

Dedicated to Professor Sadhan Basu on the occasion of his 65th birth anniversary.

\* To whom correspondence should be addressed.

orthogonality and the Hamiltonian orthogonality between the SAC and SAC-CI wave functions. The linear response theory due to Mukherjee and co-workers (Mukherjee and Mukherjee 1979; Adnan *et al* 1980, 1982; Haque and Mukherjee 1984) seems to be related incidentally to the SAC-CI theory.

In this paper, we report a calculation of the potential curves of the ground and various excited states of the CO molecule. This molecule is interesting because of the following reasons. In figure 1, we explain intuitively the electronic structures of the two  ${}^1\Sigma^+$  states (ground  $X^1\Sigma^+$  and  $(4)^1\Sigma^+$  states) within the double excitations from the HF (Hartree-Fock) configuration. Near the equilibrium geometry, the HF configuration is a main configuration of the ground state  $X^1\Sigma^+$ . As the distance increases, the weight of the HF configuration decreases and finally becomes zero at the dissociation limit. There, the molecule dissociates into the  ${}^3P$  state of oxygen and the  ${}^3P$  state of carbon, i.e.,  $C({}^3P) + O({}^3P)$ . This state corresponds to a doubly excited configuration from the HF configuration. On the other hand, the  $(4)^1\Sigma^+$  state is an ordinary singly excited state

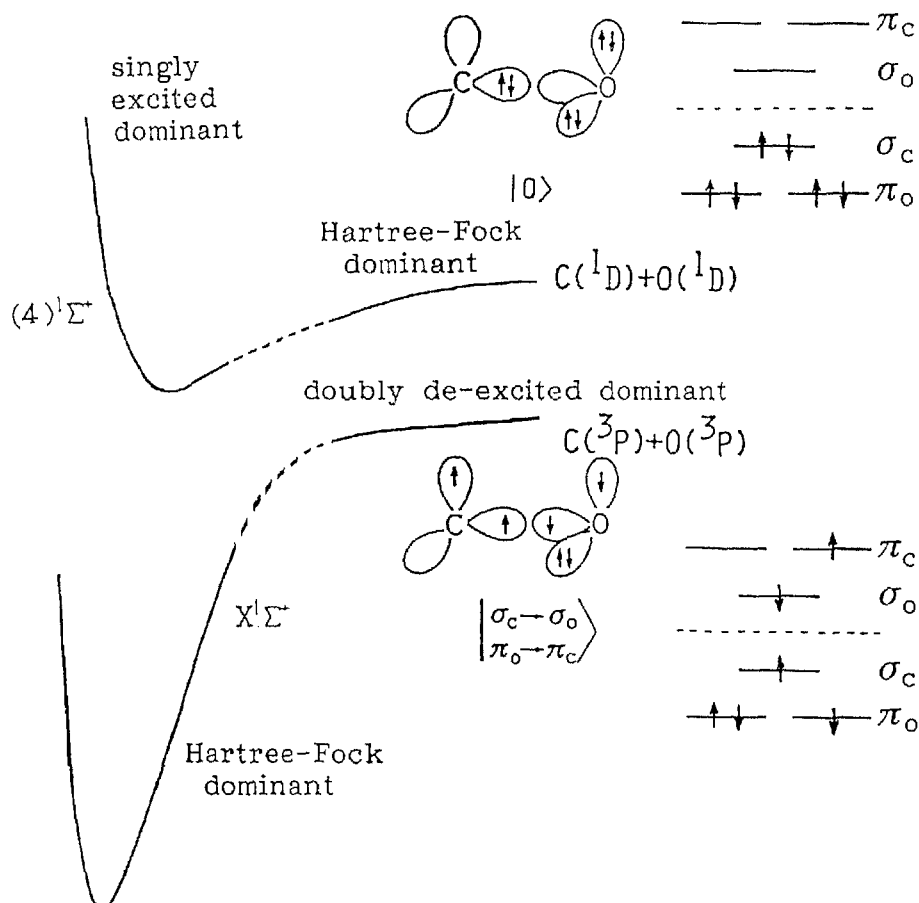


Figure 1. Nature of the potential curves of the two  ${}^1\Sigma^+$  states of the CO molecule.

near the equilibrium geometry. The main configuration of this state also changes substantially as the CO distance increases and finally the HF configuration becomes a main configuration near the dissociation limit. There the state is essentially  $C(^1D) + O(^1D)$ . Thus, the ground state and the  $(4)^1\Sigma^+$  state should suffer strong avoided crossing in the intermediate region. We study the potential curves of these states by the SAC and SAC-CI theories. We apply the SAC theory to the HF dominant state and calculate the other state by the SAC-CI theory. The basis of the study is the theoretical consistency of these two theories which we discuss in the next section. The other states of the CO molecule studied here, Rydberg excited states  $B^1\Sigma^+$ ,  $C^1\Sigma^+$ ,  $F^1\Sigma^+$ , and valence excited states  $A^1\Pi$ ,  $I^1\Sigma^-$ ,  $D^1\Delta$ ,  $a^3\Pi$ ,  $a'^3\Sigma^+$ ,  $d^3\Delta$ ,  $e^3\Sigma^-$  are essentially singly excited states near the equilibrium geometry. They are calculated by the SAC-CI theory.

The potential curves of the CO molecule have been studied by several authors. O'Neil and Schaefer (1970) reported extensive full-CI calculations within the valence MO's of the minimal STO basis. They explained rough natures of the various excited states, though the crudeness of the basis set may be serious in clarifying the actual system. Caughram *et al* (1973) applied the equations-of-motion method to several excited states of the CO molecule, with the aid of the experimental potential curves of the ground states. Cooper and Langhoff (1981) reported the MRSD-CI calculation for several states of the CO molecule, using extensive STO basis set. This calculation seems to be the most reliable one so far reported. We have calculated the potential curves of the lower four  $^1\Sigma^+$  states (Nakatsuji and Hada 1985), using minimal STO-3G basis, as the test calculation of the multi-reference version of the SAC (Nakatsuji 1985). The MR-SAC calculation reproduced well the full-CI potential curves of the ground and excited states.

## 2. SAC and SAC-CI theories

In this section, we briefly explain the SAC and SAC-CI theories. Major emphasis shall be laid on the non-variational formulation of the theoretical consistency of these two theories. The variational formulation was given before (Nakatsuji 1978, 1979). The SAC wave function for the singlet (ground) state is written as

$$\Psi_{\text{SAC}} = \exp \left[ \sum_I C_I S_I^\dagger \right] |0\rangle, \quad (1)$$

$$|0\rangle = \|\psi_{1\alpha}\psi_{1\beta} \cdots \psi_{i\alpha}\psi_{i\beta} \cdots \psi_{n\alpha}\psi_{n\beta}\|. \quad (2)$$

As a reference function  $|0\rangle$ , we usually adopt a restricted Hartree-Fock solution, but this is not essential because the SAC theory satisfies the Thouless theorem, i.e., the self-consistency (Thouless 1960). The operator  $S_I^\dagger$  is a symmetry-adapted excitation operator. A single excitation from occupied orbital  $i$  to virtual orbital  $a$  is given by

$$S_i^a = \frac{1}{\sqrt{2}} (a_{a\alpha}^\dagger a_{i\alpha} + a_{a\beta}^\dagger a_{i\beta}) \quad (3)$$

where  $a_{\alpha\alpha}^\dagger$  and  $a_{\alpha\alpha}$  mean the creation and annihilation operators for spin  $\alpha$ . The double and higher excitation operators can be written by the products of these excitation operators.

We use a non-variational method to determine the expansion coefficients  $C_I$  in (1). We require the Schrödinger equation  $(H-E)|\Psi_{\text{SAC}}\rangle = 0$  to be satisfied in the space of

the linked configurations and we get (Nakatsuji 1979)

$$\langle 0 | H - E | \Psi_{\text{SAC}} \rangle = 0 \quad (4)$$

$$\langle 0 | S_I (H - E) | \Psi_{\text{SAC}} \rangle = 0. \quad (5)$$

Because the Hamiltonian includes up to two body operators, the energy is calculated exactly from (4) as

$$E_{\text{SAC}} = E_0 + \sum_I C_I \langle 0 | HS_I^\dagger | 0 \rangle + \frac{1}{2} \sum_{IJ} C_I C_J \langle 0 | HS_I^\dagger S_J^\dagger | 0 \rangle. \quad (6)$$

For the excited states, we consider the SAC-CI expansion (Nakatsuji 1978, 1979). We define the configuration function as

$$\Phi_K = R_K^\dagger \Psi_{\text{SAC}} \quad (7)$$

and define the SAC-CI wave function by a linear combination of these configuration functions.

$$\Psi_{\text{SAC-CI}} = \sum_K d_K \Phi_K. \quad (8)$$

In (7) the operators  $\{R_K^\dagger\}$  consist of the identity operator  $I \equiv R_0^\dagger$  and the symmetry-adapted excitation operators. When we consider the excited states which belong to the same symmetry as the SAC solution, the operators  $\{R_K^\dagger\}$  are the same as the operators  $\{S_I^\dagger\}$  used in the SAC expansion. With an appropriate choice of the operators  $\{R_K^\dagger\}$ , we can deal with not only the excited states of different spin-space symmetry, but also ionized and electron attached states (Nakatsuji 1979; Nakatsuji and Hirao 1981). We use the non-variational method to determine the coefficients  $d_K$  in (8). Requiring the Schrödinger equation  $(H - E) | \Psi_{\text{SAC-CI}} \rangle = 0$  in the space of the linked configurations, we get (Nakatsuji 1979)

$$\langle 0 | H - E | \Psi_{\text{SAC-CI}} \rangle = 0 \quad (9)$$

$$\langle 0 | R_K (H - E) | \Psi_{\text{SAC-CI}} \rangle = 0. \quad (10)$$

We note that the SAC and SAC-CI wave functions  $\Psi_{\text{SAC}}$  and  $\Psi_{\text{SAC-CI}}$  satisfy the common set of equations, (4) and (5), and (9) and (10). Especially, when we consider the excited states belonging to the same symmetry as the ground state, the operators  $\{R_K^\dagger\}$  represent the same set of the operators as the operators  $\{S_I^\dagger\}$ . The solutions of the Schrödinger equation belonging to different eigenvalues are orthogonal and Hamiltonian orthogonal. The SAC-CI wave function defined by (8) can represent the SAC wave function as a special case ( $d_0 = 1$  and  $d_I = 0, I \geq 1$ ). Therefore, the SAC-CI solution belonging to different energy from the SAC solution should satisfy

$$\langle \Psi_{\text{SAC}} | \Psi_{\text{SAC-CI}} \rangle = 0 \quad (11)$$

$$\langle \Psi_{\text{SAC}} | H | \Psi_{\text{SAC-CI}} \rangle = 0 \quad (12)$$

within the space under consideration. Similarly, different SAC-CI solutions should satisfy

$$\langle \Psi_{\text{SAC-CI}}^a | \Psi_{\text{SAC-CI}}^b \rangle = 0, \quad (13)$$

$$\langle \Psi_{\text{SAC-CI}}^a | H | \Psi_{\text{SAC-CI}}^b \rangle = 0. \quad (14)$$

Equations (11)–(14) are the necessary conditions the exact state functions should satisfy

and therefore are important prerequisites for the theory dealing with the properties involving different states (e.g., transition energy, transition moment, etc.).

### 3. Computational details

The basis set used in the present calculations is the [4s2p] set of Huzinaga-Dunning (Dunning 1970; Dunning and Hay 1977) for the valence part. For the Rydberg part, diffuse *s* and *p* functions with exponents 0.023 (*s*), 0.021 (*p*) for carbon and 0.032 (*s*), 0.028 (*p*) for oxygen were placed at the nuclear position. The number of the basis set is 28. The HF MO's of the closed-shell system were used as reference MO's for all of the states calculated here. They were calculated by the HONDOG program (King *et al* 1979). The space of the active MO's consists of all the valence and Rydberg orbitals. The number of active MO's is 24.

We applied the SAC method to the HF dominant state and the SAC-CI method to generate the other states. In the short internuclear distance we calculated the ground state by the SAC method and the excited states by the SAC-CI method. At the long internuclear distance we calculated the HF dominant (4)<sup>1</sup>Σ<sup>+</sup> excited state by the SAC method. The ground state was calculated by the SAC-CI method as a de-excited state.

In the SAC calculations we considered single and double excitations as linked operators and only the products of double excitations (quadruple excitations) in the unlinked terms. We obtain from (5) (Nakatsuji 1979)

$$H_{I0} + \sum_J C_J (G_{IJ} - E_{\text{SAC}} T_{IJ}) = 0, \quad (15)$$

where

$$H_{I0} = \langle 0 | S_I H | 0 \rangle,$$

$$G_{IJ} - E_{\text{SAC}} T_{IJ} = \langle 0 | S_I (H - E_{\text{SAC}}) S_J^\dagger | 0 \rangle + \frac{1}{2} \sum_K C_K \langle 0 | S_I (H - E_{\text{SAC}}) S_K^\dagger S_J^\dagger | 0 \rangle.$$

Equations (6) and (15) were solved iteratively. For closed shells, the solution is equivalent to that of the CCMET (coupled-cluster many-electron theory) (Čížek 1960; Čížek and Paldus 1971). The SAC theory itself is equally applicable to open-shell systems (Nakatsuji 1978; Nakatsuji and Hirao 1978; Hirao and Nakatsuji 1981).

In the SAC-CI calculation, the wave function was truncated at the second order for the coefficients  $d_k$  and  $C_I$ .

$$\Psi_{\text{SAC-CI}} = \sum_K d_K \left[ R_K^\dagger + \sum_I C_I R_K^\dagger S_I^\dagger \right] | 0 \rangle \quad (16)$$

where  $C_I = n_{\text{SAC}} C_I$ . We include single and double excitations to  $R_K^\dagger$  and only double excitations to  $S_I^\dagger$ . The unlinked terms therefore consist of triple and quadruple excitations. Inserting (16) into (9) and (10), we obtain

$$\sum_L (H_{KL} - E_{\text{SAC-CI}} T_{KL}) d_L = 0, \quad (17)$$

where

$$H_{KL} - E_{\text{SAC-CI}} T_{KL} = \langle 0 | R_K (H - E_{\text{SAC-CI}}) R_L^\dagger | 0 \rangle$$

$$+ \sum_I C_I \langle 0 | R_K (H - E_{\text{SAC-CI}}) R_L^\dagger S_I^\dagger | 0 \rangle.$$

This equation constitutes an eigenvalue problem of a non-symmetric matrix (Hirao and Nakatsuji 1982).

In (16), we renormalized the coefficient  $C_I$  by the renormalization factor  $n_{\text{SAC}}$  of the SAC wave function. This factor was introduced from the following consideration. In the SAC-CI formalism, we calculate the wave functions using an approximate transferability of the electron correlation from the SAC wave function. The SAC wave function is intermediate normalized, taking the weight of the Hartree-Fock part to be unity. On the other hand, the SAC-CI wave function is normalized to unity. Therefore when the electron correlation becomes relatively large, it would be better to transfer the normalized quantity of the electron correlation of the SAC wave function in order to maintain a balance in the SAC-CI wave function. Note however that this modification is rather temporary because the single reference SAC theory itself will breakdown when  $n_{\text{SAC}}$  is considerably larger than unity (Nakatsuji 1985). Actually in the region of the avoided crossing between the  $X^1\Sigma^+$  and  $(4)^1\Sigma^+$  states, the SAC solution was unreliable, so that we could not obtain the SAC-CI solution either.

To diminish the size of calculations, we selected the linked operators in the way reported before (Nakatsuji 1983). In this calculation the thresholds  $\lambda_g$  and  $\lambda_e$  were  $1 \times 10^5$  and  $2 \times 10^{-5}$  au, respectively, for singlet states and  $\lambda_e$  for triplet states was  $5 \times 10^{-5}$  au. We included both single and double excitations as main reference configurations used in the selection procedure (Nakatsuji 1983). As the result the practical dimension to be solved is approximately 1600 at the most. As for the  $S_I^\dagger$  operators included in the unlinked terms, we adopted double excitations whose coefficients in the SD-CI are larger than  $5 \times 10^{-3}$  for SAC and  $1 \times 10^{-3}$  for SAC-CI. The  $R_K^\dagger$  operators in the unlinked terms of SAC-CI consists of single and double excitations whose coefficients in the SD-CI are larger than  $8 \times 10^{-2}$ .

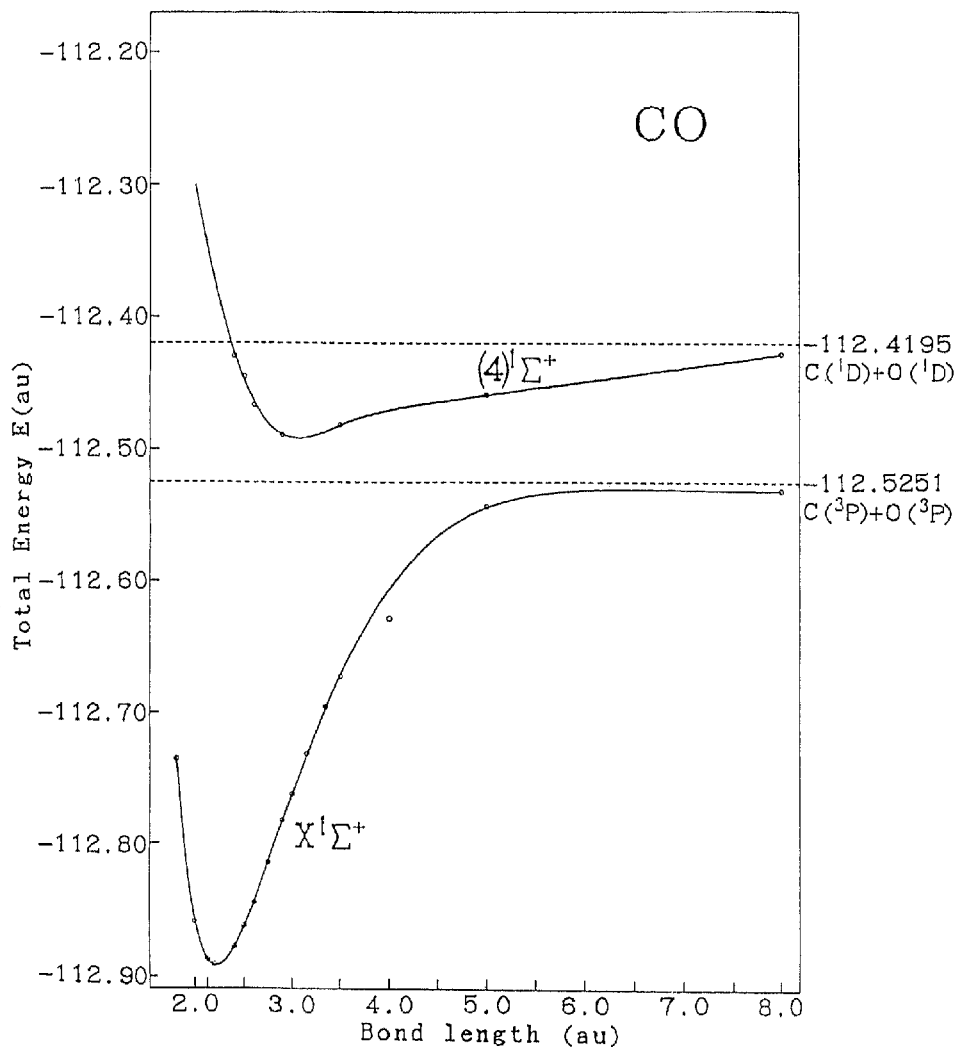
We note that in the present calculations, we include only single and double excitations as the *linked* operators of the SAC and SAC-CI methods. This space is not enough for the description of the  $^1\Sigma^+$  valence excited states. Within the present space, the  $(4)^1\Sigma^+$  state is the lowest valence excited state. However, due to the full-CI calculations based on the minimal basis sets (O'Neil and Schaefer 1970; Nakatsuji and Hada 1985), there are two other  $^1\Sigma^+$  states in the energy region studied here. Our lowest valence excited  $^1\Sigma^+$  state is close to the  $(4)^1\Sigma^+$  state studied by Cooper and Langhoff (1981). Hence, we denoted this state as  $(4)^1\Sigma^+$ .

#### 4. Potential curves of the CO molecule

The potential curves of the  $X^1\Sigma^+$  and  $(4)^1\Sigma^+$  states of the CO molecule calculated by the present method are shown in figure 2. For the  $X^1\Sigma^+$  state, the curve from 1.8 au to 3.5 au was calculated by the SAC method and the curve from 5.0 au to 8.0 au by the SAC-CI method. For the  $(4)^1\Sigma^+$  state, we used the SAC-CI method for the curve from 1.8 au to 3.5 au and the SAC method for the curve from 5.0 au to 8.0 au.

First we discuss the  $X^1\Sigma^+$  state. Since we did not use  $d$ -polarization functions, the calculated equilibrium bond length (1.17 Å) is little longer than the experimental data (1.13 Å). The experimental RKR (Rydberg-Klein-Rees) potential curves of the CO molecule (Krupenie 1966; Tilford and Simmons 1972) are shown in figure 4.

Near the avoided crossing region, our calculated result at 4.0 au shows a large deviation from the whole potential curve. One may think that the point at 5.0 au is not



**Figure 2.** Potential energy curves of the  $X^1\Sigma^+$  and  $(4)^1\Sigma^+$  states of the CO molecule calculated by the SAC and SAC-Cl methods.

adequate and the potential curve goes through the calculated point at 4.0 au. From the following two reasons we think that the potential curve drawn in figure 2 is better and the point calculated at 4.0 au is out of order.

First is the consideration on the breakdown of the single reference theory. In table 1, we collected the norm of the SAC-NV wave function. A remarkable feature is seen at 4.0 au in the problem. If the single-reference cluster expansion theory is appropriate, the norm of the wave function should not exceed unity by very much. However, at 4.0 au, the norm is much larger than those of any other calculated points. This indicates

**Table 1.** Norm of SAC-NV wave function of the HF dominant state of the CO molecule.

Bond length (au)	norm	Bond length (au)	norm
1.8	1.04	2.9	1.11
2.0	1.05	3.0	1.13
2.132	1.05	3.15	1.16
2.2	1.06	3.35	1.27
2.4	1.07	3.5	1.40
2.5	1.07	4.0	2.49 <sup>a</sup>
2.6	1.08	5.0	1.39
2.75	1.09	8.0	1.17

<sup>a</sup>This value indicates that the result at 4.0 au is unreliable (see text).

that the quasi-degenerate correlation which is not described by the single reference theory occurs in this region of the internuclear separation (Nakatsuji 1985).

The second reason is based on the spectroscopic constants calculated by the two different potential curves. We analyzed the potential curves by the Dunham theory (Dunham 1932). The results are compared in table 2 where the values given in the second row in parentheses were obtained from the curve going through the calculated point at 4.0 au. The vibrational anharmonicity  $\omega_e x_e$  reflects the shape of the potential curve very sensitively. The upper figure in table 2,  $\omega_e x_e = 15.7 \text{ cm}^{-1}$  almost reproduces the experimental value,  $13.3 \text{ cm}^{-1}$ . The same value from the curve going through the calculated point at 4.0 au is 5.48, which is only a half of the experimental value.

Next we discuss the  $(4)^1\Sigma^+$  state. Because an appropriate SAC solution was unavailable at 4.0 au, we could not calculate the SAC-CI solution at this point. The potential curve was extrapolated from the reliable curves in shorter and longer regions. The avoided crossing part is therefore unreliable. We assign this state to the valence  $\pi \rightarrow \pi^*$  excitation. No experimental data seems to have been given about this state; for example, see the RKR curves shown in figure 4. Cooper and Langhoff (1981) calculated this state by the MRSD-CI method, so that we compare our spectroscopic results with their results in table 2. The equilibrium bond length  $r_e$  is almost the same. Remarkable differences are seen in the term energy  $T_e$  and the vibrational anharmonicity  $\omega_e x_e$ . For the former, our result is lower than theirs by 0.6 eV, and for the latter our result is almost twice as large as theirs. This is probably due to the lack of the *linked* three and four excitation terms in the present calculation.

In figure 3, we draw all the potential curves calculated with the SAC and SAC-CI theory. In figure 4, the potential curves drawn by the RKR method based on the experimental data (Krupenie 1966; Tilford and Simmons 1972) are displayed. The arrow in the upper right corner shows the lower dissociation limit of figure 3. The agreement of the RKR curves and our calculated curves is very good. The theoretical and experimental spectroscopic constants are summarized in table 2. The agreement between theory and experiment is satisfactory.

At the upper left corner of figure 3, we see three typical Rydberg transitions,  $B^1\Sigma^+$ ,  $C^1\Sigma^+$ , and  $F^1\Sigma^+$ . The natures are predominantly  $n \rightarrow 3s$ ,  $n \rightarrow 3p_\sigma$  and  $n \rightarrow 3d_\sigma$ , respectively. The equilibrium internuclear distances of these states are slightly shorter



Table 2. Spectroscopic constants of the ground and the excited states of CO<sup>a</sup>.

State		$T_e$ (eV)	$r_e$ (Å)	$\omega_e$ (cm <sup>-1</sup> )	$\omega_e x_e$ (cm <sup>-1</sup> )	$B_e$ (cm <sup>-1</sup> )	$\alpha_e$ (cm <sup>-1</sup> )
$X^1\Sigma^+$	ground	Calc. <sup>c</sup>	0.0 <sup>b</sup>	1.17	2012	15.7	1.79
		Calc. <sup>d</sup>	(0.0)	(1.18)	(1896)	(5.48)	(1.77)
		Expt.	0.0 <sup>b</sup>	1.13	2170	13.3	1.93
$I^1\Sigma^-$	$\pi \rightarrow \pi^*$	Calc.	7.74	1.46	1025	14.5	1.15
		Expt.	8.07	1.40	1092	10.7	1.27
$D^1\Delta$	$\pi \rightarrow \pi^*$	Calc.	7.79	1.46	1041	13.5	1.15
		Expt.	8.17	1.40	1094	10.2	1.26
$A^1\Pi$	$n \rightarrow \pi^*$	Calc.	7.89	1.29	1390	19.1	1.47
		Expt.	8.07	1.24	1518	19.4	1.61
$(4)^1\Sigma^+$	$\pi \rightarrow \pi^*$	Calc.	10.89	1.62	795	14.5	0.93
		C-L <sup>e</sup>	11.49	1.52	974	7.3	—
$B^1\Sigma^+$	$n \rightarrow 3s$	Calc.	10.66	1.14	2070	11.9	1.89
		Expt.	10.78	1.12	2113	15.2	1.96
$C^1\Sigma^+$	$n \rightarrow 3p_\sigma$	Calc.	11.19	1.15	2252	16.4	1.86
		Expt.	11.40	1.12	2176	14.7	1.95
$F^1\Sigma^+$	$n \rightarrow 3d_\sigma$	Calc.	12.68	1.13	2059	15.3	1.91
		Expt.	(12.37)	(1.15)	(2034)	(198 <sup>f</sup> )	(1.86)
$a^3\Pi$	$n \rightarrow \pi^*$	Calc.	5.74	1.25	1728	16.9	1.58
		Expt.	6.05	1.21	1743	14.3	1.69
$d^3\Sigma^+$	$\pi \rightarrow \pi^*$	Calc.	6.40	1.42	1164	8.01	1.21
		Expt.	6.92	1.35	1229	10.5	1.35
$d^3\Delta$	$\pi \rightarrow \pi^*$	Calc.	7.18	1.44	1092	7.79	1.18
		Expt.	7.58	1.37	1172	10.6	1.31
$e^3\Sigma^-$	$\pi \rightarrow \pi^*$	Calc.	7.48	1.45	1089	8.81	1.17
		Expt.	7.96	1.38	1118	10.7	1.28

<sup>a</sup>Experimental values are taken from Huber and Herzberg (1979); <sup>b</sup>dissociation energy is 9.98 eV (calculation) and 11.226 eV (experiment, Krupenie 1966); <sup>c</sup>our final results (see text); <sup>d</sup>calculated values obtained if we assume that the potential curves goes through the calculated point at 4.0 au (see text); <sup>e</sup>theoretical result due to Cooper and Langhoff (1951); <sup>f</sup>this experimental data might be unreliable (see text).

than that of the ground state, and they have a sharp curvature. As seen from the spectroscopic constants shown in table 2, our potential curves reproduce well the experimental results. For the  $F^1\Sigma^+$  state, the experimental vibrational anharmonicity  $\omega_e x_e$  is extraordinarily large (Krupenie 1966), i.e., 198 cm<sup>-1</sup>. Our results indicate that this state has the potential curve very similar to the  $B^1\Sigma^+$  state, so that this value might be incorrect.

Around the middle left of figure 3, several  $\pi \rightarrow \pi^*$  valence transitions are seen. In this region, the states,  $^1\Delta$ ,  $^1\Sigma^-$ ,  $^3\Sigma^-$ ,  $^3\Delta$ ,  $^3\Sigma^+$  have the potential minima. These states have the curves of relatively shallow minima. The average internuclear distance of these states is longer than that of the ground state. The singlet pair  $D^1\Delta$ ,  $I^1\Sigma^-$  and the triplet pair  $d^3\Delta$ ,  $e^3\Sigma^-$  have similar spectroscopic constants but these two pairs cross around 4.0 au. At the shorter bond length region the singlet pair lies at higher energy level than the triplet pair, but is the reverse at the longer bond length region. This crossing is also seen in the experimental RKR curves.

The  $A^1\Pi$  and  $a^3\Pi$  states are from  $n \rightarrow \pi^*$  transition. The average internuclear distance is slightly longer than that of the ground state. We did not calculate the longer

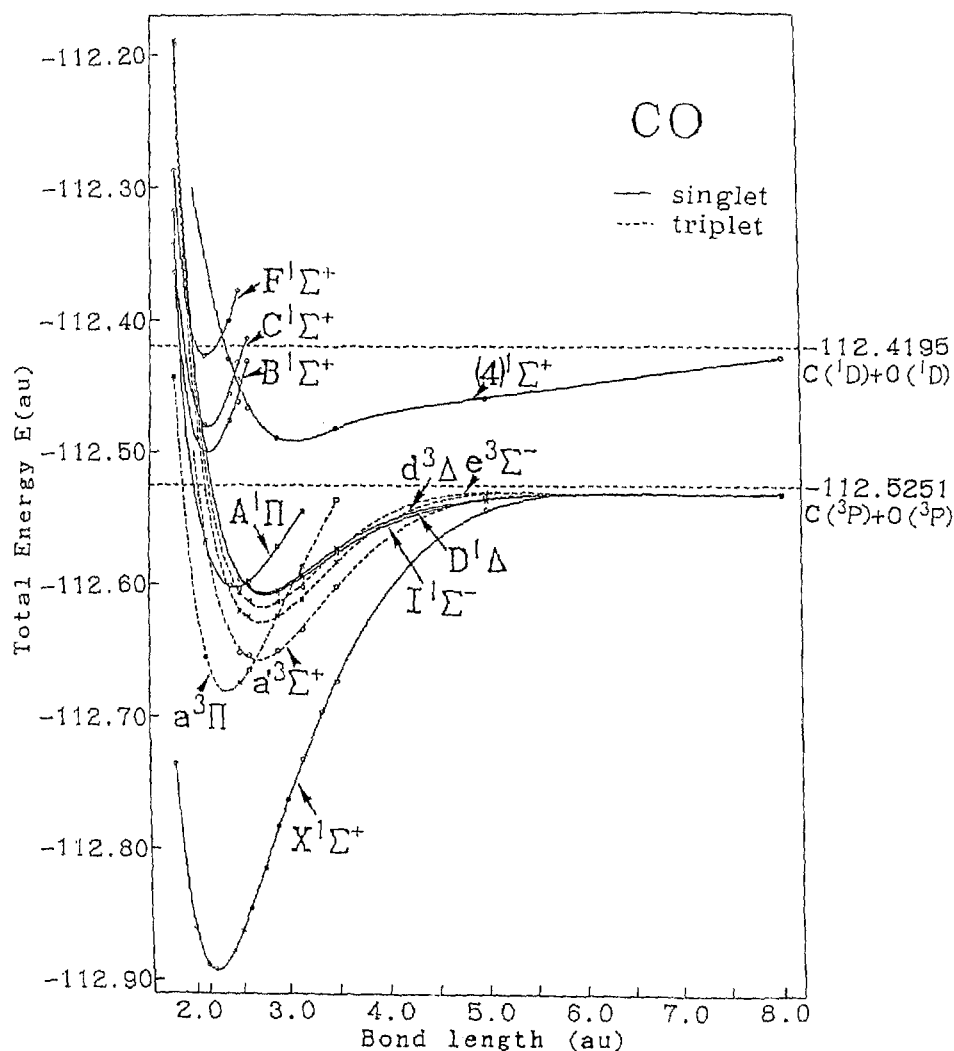


Figure 3. Potential energy curves of the CO molecule calculated by the SAC and SAC-CI methods.

internuclear region of these potential curves. The reason is as follows. In the present calculations we considered up to double excitations as *linked* operators. From the full- $\text{CI}$  study (Cooper and Langhoff 1981), in order to describe these states appropriately at longer internuclear distance it is necessary to include triple and higher excitations in the *linked* operators.

#### Acknowledgements

The authors thank Dr J Ushio for valuable discussions. The calculation was carried out with the HITAC M200H computer at the Institute for Molecular Science, and the FACOM

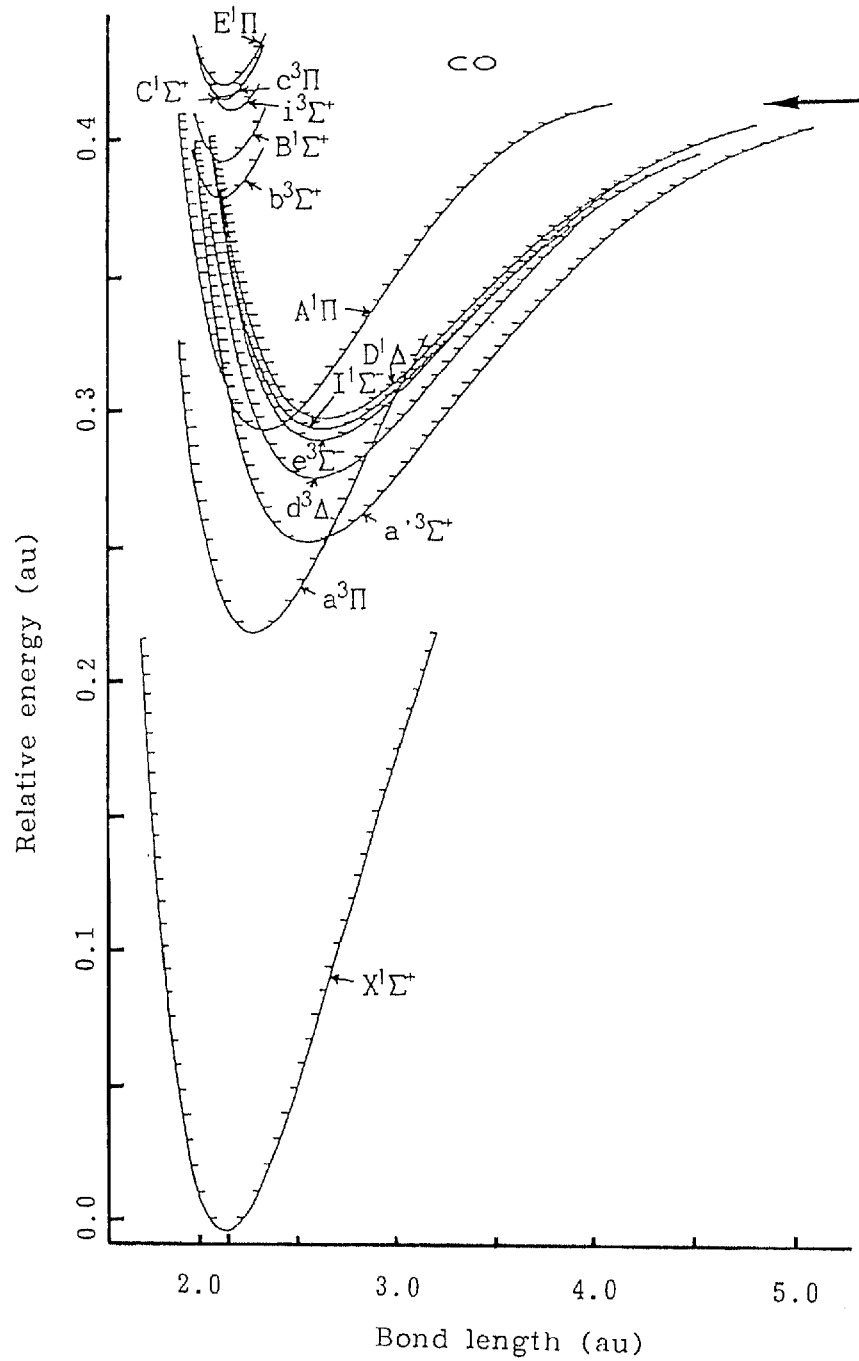


Figure 4. Experimental RKR curves of the CO molecule.

M380, M382, and VP100 computers at the Data Processing Center of Kyoto University. The authors thank these computer centers for the grants of computing time. Part of this study was supported by a Grant from the Japanese Ministry of Education, Science, and Culture.

## References

- Adnan S S Z, Bhattacharya S and Mukherjee D 1980 *Mol. Phys.* **39** 519  
 Adnan S S Z, Bhattacharya S and Mukherjee D 1982 *Chem. Phys.* **85** 204  
 Bartlett R J 1981 *Ann. Rev. Phys. Chem.* **32** 359  
 Buenker R J and Peyerimhoff S D 1983 in *New horizons of quantum chemistry* (ed.) by P O Löwdin and B Pullman (Dordrecht: Reidel) p. 183, and references cited therein  
 Čížek J 1960 *J. Chem. Phys.* **45** 225  
 Čížek J and Paldus J 1971 *Int. J. Quantum Chem.* **5** 359  
 Cooper D M and Langhoff S R 1981 *J. Chem. Phys.* **74** 1200  
 Coughran W, Rose J, Shibuya T and Mckoy V 1973 *J. Chem. Phys.* **58** 2699  
 Das G 1973 *J. Chem. Phys.* **58** 5104  
 Dunham J L 1932 *Phys. Rev.* **41** 713, 721  
 Dunning T H Jr 1970 *J. Chem. Phys.* **53** 2823  
 Dunning T H Jr and Hay J P 1977 in *Modern theoretical chemistry, Vol. 2, methods of electronic structure theory* (ed.) Schaefer H F III (New York: Plenum Press) p. 1  
 Grein G and Banerjee A 1975 *Int. J. Quantum Chem. Symp.* **9** 147  
 Haque M A and Mukherjee D 1984 *J. Chem. Phys.* **80** 5058  
 Hirao K and Nakatsuji H 1981 *Chem. Phys. Lett.* **79** 292  
 Hirao K and Nakatsuji H 1982 *J. Comput. Phys.* **45** 246  
 Huber K P and Herzberg G 1979 *Molecular spectra and molecular structure IV. Constants of diatomic molecules* (Princeton: D. Van Nostrand)  
 Jeziorski B and Monkhorst H J 1981 *Phys. Rev.* **A24** 1668  
 King H F, Dupuis M and Rys J 1979 Program Library HONDOG (No. 343) of the Computer Center of the Institute for Molecular Science  
 Krupenie P H 1966 *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. (US)* **5**  
 Mukherjee D, Moitra R K and Mukhopadhyay A 1975 *Mol. Phys.* **30** 1861  
 Mukherjee D, Moitra R K and Mukhopadhyay A 1977 *Mol. Phys.* **33** 955  
 Mukherjee D and Mukherjee P K 1979 *Chem. Phys.* **39** 325  
 Nakatsuji H 1978 *Chem. Phys. Lett.* **59** 362  
 Nakatsuji H 1979 *Chem. Phys. Lett.* **67** 329, 334  
 Nakatsuji H 1983 *Chem. Phys.* **75** 425  
 Nakatsuji H 1984 *J. Chem. Phys.* **80** 3703, and references therein  
 Nakatsuji H 1985 *J. Chem. Phys.* **83** 713  
 Nakatsuji H and Hada M 1985 in *Proceeding of the nobel laureate symposium on applied quantum chemistry (PAC' CHEM '84, Honolulu)* (ed.) Smith V H Jr. (Dordrecht: Reidel)  
 Nakatsuji H and Hirao K 1978 *J. Chem. Phys.* **68** 2053  
 Nakatsuji H and Hirao K 1981 *Int. J. Quantum Chem.* **21** 301  
 Nakatsuji H, Kitao O and Yonezawa T 1985 *J. Chem. Phys.* **83** 723  
 O'Neil S V and Schaefer H F III 1970 *J. Chem. Phys.* **53** 3994  
 Paldus J 1983 in *New horizons of quantum chemistry* (ed.) by P O Löwdin and B Pullman (Dordrecht: Reidel) p. 81  
 Paldus J, Čížek J, Saute M and Laforgue A 1978 *Phys. Rev.* **17** 805  
 Thouless D J 1960 *Nucl. Phys.* **21** 225  
 Tifford S G and Simmons J D 1972 *J. Phys. Chem. Ref. Data* **1** 147