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Theoretical study of the structural character of weakly bonding silicon carbonyl complexes

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Abstract. The structures, properties and the bonding character for sub-carbonyl Si, SiCO and Si(CO)₂, in singlet and triplet states have been investigated using complete-active-space self-consistent field (CASSCF), density functional theory and second-order Møller–Plesset methods with a 6-311+G* basis set. The results indicate that the SiCO species possesses a $^3\Sigma^-$ ground state, and the singlet $^1\Delta$ excited state is higher in energy than the $^3\Sigma^-$ state by 17.3 kcalmol⁻¹ at the CASSCF–MP2/6-311+G* level and by 16.4 kcalmol⁻¹ at the CCSD(T)/6-311+G* level. The SiCO ground state may be classified as silene (carbonylsilene), and its CO^{δ-} moiety possesses CO⁻ property. The formation of SiCO causes the weakening of CO bonds. The Si–C bond consists of a weak σ bond and two weak π bonds. Although the Si–C bond length is similar to that of typical Si–C bonds, the bond strength is weaker than the Si–C bonds in Si-containing alkanes; the calculated dissociation energy is 26.2 kcalmol⁻¹ at the CCSD(T)/6-311+G* level. The corresponding bending potential-energy surface is flat; therefore, the SiCO molecule is facile. For the bicarbonyl Si systems, Si(CO)₂, there exist two V-type structures for both states. The stablest state is the singlet state (1A_1), and may be referred to the ground state. The triplet state (3B_1) is energetically higher in energy than the 1A_1 state by about 40 kcalmol⁻¹ at the CCSD(T)/6-311+G* level. The bond lengths in the 1A_1 state are very close to those of the SiCO species, but the SiCO moieties are bent by about 10°, and the CSiC angles are only about 78°. The corresponding 3B_1 state has a CSiC angle of about 54° and a SiCO angle of about 165°, but its Si–C and C–O bonds are longer than those in the 1A_1 state by about 0.07 and 0.03 Å, respectively. This Si(CO)₂ (1A_1) has essentially silene character and should be referred to as a bicarbonyl silene. Comparison of the CO dissociation energies of SiCO and Si(CO)₂ in their ground states indicates that the first CO dissociation energy of Si(CO)₂ is smaller by about 7 kcalmol⁻¹ than that of SiCO; the average one over both CO groups is also smaller than that of SiCO. A detailed

bonding analysis shows that the possibility is small for the existence of polycarbonyl Si with more than three CO. This prediction may also be true for similar carbonyl complexes containing other nonmetal and non-transition-metal atoms or clusters.

Key words: Silicon carbonyl complexes – Weakly bonding interaction – Density functional calculations – Ab initio calculations

1 Introduction

Over recent years, there has been considerable interest concerning the binding of carbon monoxide (CO) to functional biological and material molecules. CO is a pervasive ligand and surface adsorbate. Not only it is easily absorbed over isolated transition-metal clusters, polynuclear transition-metal complexes, and transition-metal surfaces, leading to changes of the surface structural properties of these kinds of clusters and transition-metal-containing large molecules, but it can also be bound to metalloporphyrins, heme proteins, and transition-metal-containing model compounds of biological interest, leading to changes in their biological functionality. CO may also be significantly bonded to non-transition-metal and nonmetal clusters, compounds, and molecules containing nucleophilic and electrophilic centers, because of its strong ability of donating and accepting electrons. Therefore, detailed investigations regarding the interaction between CO and various clusters and compounds are very interesting for approaches to the functionality and its control mechanism of biological and material molecules. On the other hand, the binding of CO to the donor and acceptor active sites changes not only the structural properties of the donor and acceptor, but also the electronic configurations and the spectroscopic character and other properties. A recent survey of CO stretching frequencies for heme proteins and model compounds has shown an

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interesting change in the CO vibrational frequency [1]. Many factors commonly held to affect these frequencies are fully recognized as ring-ligand substituents [2], CO ligand binding geometry and steric effects [3, 4, 5], redox potentials [6], CO binding affinities [7], and the charge and polar interactions in the protein pocket [1, 8, 9]. Although some interesting interpretations have been given for the dependence of the CO binding on these factors, the interaction details and nature among them are still unknown. Fortunately, great progress has been made in investigations of the interaction between CO and many small transition-metal clusters, many important conclusions have been made and have also provided much valuable information for further approaches to the interaction between carbonyl and the active centers of the transition-metal-centered biological molecules. However studies on the interaction between CO and non-transition metals or nonmetals appear to be absent. To our knowledge, only a few theoretical and experimental studies on such kinds of systems have been reported. These works have mainly focused on the alkali carbonyls, $[M^+(\text{CO})_n, M(\text{CO})_n, n = 1, 2, 3$ and $M = \text{H, Li, Na, K}$] [10, 11, 12, 13, 14]. The emphasis has been on the bond dissociation energies of $X^+ - \text{CO}$ ($X = \text{H, Li, Na}$ and K) [11], the lithium and sodium cation affinities of CO [12], and the sequential bond energies of $M^+(\text{CO})_n$ ($n = 1, 2, 3; M = \text{Li, Na, K}$) [13]. Especially in recent years, increasing attention has also been paid to the interactions of CO with alkali metals and nontransition metals [14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29]. The electronic structures and relevant properties have been investigated in detail using different theoretical methods for Li carbonyls $\{\text{Li}_2 - \text{CO}$ [14], LiC_2O_2 [15], $\text{Li}(\text{CO})_n$ ($n = 1, 2, 3$) [16]), Na and K carbonyls, Al carbonyls $[\text{AlCO}, \text{Al}(\text{CO})_2]$ [17, 18, 19, 20] and its isocarbonyl (AlOC) and the AlCO cyclic structures [18, 20], etc. However, relatively little work has been done on the non-metal carbonyls. Subcarbonyl complexes that have been detected experimentally include AsCO^- , AsCO [21], SiCO^- , GeCO^- [22], BCO , $(\text{BCO})_2$, $\text{B}(\text{CO})_2$ [23], SCO [24, 25], CCO [26, 27] and $\text{Si}(\text{CO})_n$ ($n = 1, 2$) [28, 29], but no detailed theoretical reports have been given on their properties. Obviously such studies are important for the investigation of the interactions between CO and the non-metal-centered active sites in large biological and material molecules.

Compared with transition-metal atoms and compounds, non-transition-metal atoms obviously lack active bonding d orbitals. They cannot use their empty d orbitals to accept the σ -coordination lone-pair electrons coming from CO and at the same time use their occupied d orbitals to interact with empty π^* antibonding molecular orbitals and to feed back the electron to CO owing to the large energy level difference between π^* and the fully empty or fully occupied d orbitals of the nontransition metals and nonmetals. Therefore, it may be expected that the bonding interaction between CO and nontransition metals is significantly different from that between CO and transition metals.

Owing to the importance of Si in semiconductor and noncrystalline materials, many works have focused on Si-containing hydrocarbon-like compounds, and great

progress has been made. Investigations indicate that Si behaves very differently from carbon in forming chemical bonds. The single, double and triple bonds of Si-Si or Si-C are obviously weaker than those of the corresponding C-C bond. In addition to the difference from C and the other non-metal elements, Si is also obviously different from transition metals in nature, although it has slightly higher level d orbitals. In the aspect of forming polyligand coordinations like transition metals, it can be predicted that Si does not form polyligand complexes, owing to the weak binding interaction between Si and ligands. An early experimental report indicated that even if a strong-field ligand CO is used to coordinate the Si atom, only the single and double ligand Si-carbonyl coordinations, SiCO and $\text{Si}(\text{CO})_2$, are found experimentally under cryogenic condition [28]. In that experiment, SiCO and $\text{Si}(\text{CO})_2$ were prepared by using high-temperature vaporized Si atoms to react with CO in $(\text{Ar}/\text{CO}) = 100\text{--}200$ or pure CO matrices and trapping them in solid argon at 4 K. The corresponding electron spin resonance and optical spectra were also measured, and were further used to confirm the existence of these two species. Later, Stolvik [29] also further determined experimentally the SiCO molecular geometry. Although it was claimed that SiCO and $\text{Si}(\text{CO})_2$ were linear molecules, the existence of bent structures for SiCO was also implied with some uncertainty. Semiempirical quantum chemistry complete neglect of differential overlap calculations on the SiCO molecule confirmed that structures with small departures from linearity can be expected to be unstable with respect to the linear conformation [28]. One interpretation for this interference is that the molecular bending force constant is quite small and some constraints in the matrix sites induce bending. Similar to SiCO , the linear structure for $\text{Si}(\text{CO})_2$ is also doubtful. To explain the relevant phenomena, Schaefer's group has made interesting progress in studies regarding these Si carbonyls [30, 31, 32, 33]. Using coupled-cluster with single and double excitations (CCSD), configuration interaction with single and double excitations and triple-zeta (CISD/TZ) basis sets, they investigated systematically the electronic structural characterization of silaketenylidene SiCO (carbonylsilene) [33] and 2-silaketenylidene CSiO [30] for their $^3\Sigma^-$ and $^3\Pi$ states, and indicated that there is obviously a Renner - Teller effect only for the linear $^3\Pi$ state. They also reassigned the structure of dicarbonyl Si, $\text{Si}(\text{CO})_2$, on the basis of theoretically predicted IR spectra [32]. These studies have provided much valuable information for further investigation regarding the nonmetal carbonyls. However, these recent works have focused on only two low-lying triplet states ($^3\Sigma^-$, $^3\Pi$) for monocarbonyl Si and the low-lying singlet states ($^1\Sigma_g^+$, 1A_1) for dicarbonyl Si, but no studies have been reported for the singlet state of SiCO and the triplet state of $\text{Si}(\text{CO})_2$. In addition, no evidence regarding the existence of Si polycarbonyls has appeared.

The aim of this work is to give a detailed theoretical investigation on the geometrical parameters, the harmonic frequencies, the dissociation energies, the ionization potentials, and other relevant properties for SiCO and $\text{Si}(\text{CO})_2$ species in their different states, and to

analyze the probability of the existence of $\text{Si}(\text{CO})_3$, using density functional theory (DFT) methods and wavefunction-correlated ab initio methods with a relatively large one-particle basis set. Fortunately, in recent years DFT has emerged to be a reliable and computationally inexpensive method capable of successfully predicting the properties for many systems [34–39], especially, the methods using nonlocal functionals can accurately predict the molecular properties of the systems that exhibit multireference character. The main objective is to accurately predict the geometries and the relevant quantities, and to compare the calculated frequencies with the experimental findings and to give some reliable estimates of those fundamentals which are either masked or too weak to observe in the matrix experiments.

2 Computational details

Before the calculational methods are introduced, a preliminary analysis about electronic configurations is necessary. For SiCO in the triplet state and $\text{Si}(\text{CO})_2$ in both the singlet and the triplet states, the single determinant wavefunction can work well in describing the electronic states, but for the linear singlet state there are some limitations in the calculations. For the singlet state of SiCO , the highest-occupied molecular orbitals are the degenerate π orbitals with two electrons. This π^2 configuration may generate two states: $^1\Delta$ and $^1\Sigma^+$. The proper description of these two states requires at least two Slater determinants. In the multireference space, the first root corresponds to the $^1\Delta$ state and the second corresponds to the $^1\Sigma^+$ state. This implies that all methods which are based on the single determinant wavefunction are not suitable to treat the singlet state of SiCO species. Therefore, in our calculations, the DFT and the second-order Møller–Plesset perturbation theory (MP2) methods with the 6-311 + G* basis set were used for the optimizations on SiCO in the triplet state and $\text{Si}(\text{CO})_2$ in the singlet and triplet states. For the singlet state SiCO species, at the 6-311 + G* basis set level, the complete-active-space self-consistent-field (CASSCF) method was used. For the sake of comparison, SiCO in the triplet state was also optimized at the CASSCF/6-311 + G* level. However, a special case should be noted for the SiCO linear singlet state. When SiCO is bending, one component of the $^1\Delta$ state will be reduced to a $^1A'$ state and another component will be reduced to $^1A''$ state, while the $^1\Sigma^+$ will be reduced to a $2^1A'$ state. This implies that the geometry and energy of the $^1\Delta$ state may be estimated from the $^1A'$ state of its quasi-linear molecule. Thus, the $^1\Delta$ state was also optimized at the DFT and MP2 level with the same basis set by using its quasi-linear geometry with the $^1A'$ symmetry constraint. The three density functionals used were B3LYP, B3P86, and B3PW91, as implemented in Gaussian 94 [40]. These three models combine Becke's three-parameter hybrid functional, which is a linear combination of Hartree–Fock exchange, Slater exchange, and B88 gradient-corrected exchange [41] with the correlation functionals of Lee, Yang and Parr [42, 43], Perdew (P86) [44, 45], and Perdew and Wang (PW91) [46], respectively.

The geometries were first optimized using the DFT and MP2 models described previously. The harmonic vibrational frequencies were then obtained from analytic second derivative methods and finite differences of analytic gradients, respectively. In particular, for the SiCO system in the singlet and triplet states, the CASSCF(4,6) method was also used for the reoptimizations. In the CASSCF method, the active space consists of four electrons and six orbitals, which are 4σ , $2\pi^+$, $2\pi^-$, 5σ , $3\pi^+$, and $3\pi^-$. The corresponding energy quantities were also calculated using the third-order and the fourth-order Møller–Plesset theories (MP3, MP4) with all substitutions, the CCSD including a perturbational estimate of the triples [CCSD(T)] for all species, and the CASSCF-MP2 method for SiCO species. The calculations were performed with the Gaussian 94 program package, and all electrons were

included in the electron correlation corrections of the relevant energy quantities.

The calculations were mainly limited to singlet and the triplet states of these two species for the bonding and charge distribution analysis and the determinations of the ground states. The dissociation energies, D_e , and the ionization potentials (IP) were obtained by calculating the energy differences between the ground states and the corresponding dissociated species for SiCO ($\text{Si} + \text{CO}$) and for $\text{Si}(\text{CO})_2$ ($\text{Si} + 2\text{CO}$ or $\text{SiCO} + \text{CO}$), and those between the ground states and the corresponding monovalent cations SiCO^+ and $\text{Si}(\text{CO})_2^+$. On the basis of studies on SiCO and $\text{Si}(\text{CO})_2$, some properties of the $\text{Si}(\text{CO})_3$ species are predicted using the same theoretical methods, although no experimental data have been reported so far.

In addition, for the numerical integration grid in the DFT calculations, the Gaussian default grid was used, which consists of 75 radial shells and 302 angular points per shell, resulting in about 7,000 points per atom.

3 Results and discussions

The geometry optimizations and harmonic frequency analysis were first performed for SiCO and $\text{Si}(\text{CO})_2$ in their singlet and triplet states using B3LYP, B3P86, B3PW91, and MP2 methods with the 6-311 + G* basis set, and then at the CASSCF/6-311 + G* level, the linear SiCO species were reoptimized. To detect the possibility of the existence of the linear bicarbonyl Si complexes, the linear OCSiCO conformers in the singlet and triplet states were also optimized and the geometries were then proved by the harmonic vibrational frequency analysis to be stable minima on the global potential-energy surfaces or not. All these geometrical parameters and the harmonic frequencies are given in Tables 1 and 2. The corresponding spin-density distributions, charge populations, and the zero-point vibrational energies for all the stable species are collected in Table 3. The calculated total energies, E_T , and the dissociation energies (for SiCO and $\text{Si}(\text{CO})_2$ in their ground states and the corresponding state–state energy separations, ΔE , relative to the ground states are listed in Tables 4 and 5 as well as the vertical IPs.

In addition, the geometrical optimization and the vibrational analysis were also made for tricarbonyl Si, $\text{Si}(\text{CO})_3$.

3.1 SiCO species

3.1.1 The relative stability

The detailed geometrical optimizations yielded stable singlet ($^1\Delta$) and triplet ($^3\Sigma^-$) states for the SiCO species. The $^3\Sigma^-$ state is significantly stabler than the $^1\Delta$ state; their adiabatic energy separation is within 16–21 kcalmol $^{-1}$ at several different theoretical levels. Thus, the $^3\Sigma^-$ state may be assigned to the ground state. Both these states are linear and are structurally similar.

In detail, at the 6-311 + G* level, the results calculated (18.2–20.8 kcalmol $^{-1}$) with three DFT methods (B3LYP, B3P86, and B3PW91) are in good agreement with each other. They are also very close to the MP2 and MP3 values (about 19.6 kcalmol $^{-1}$). They are slightly higher than the MP4 value with singles, doubles and quadruples substitutions, and are also slightly higher than the CCSD and

Table 1. The optimized geometrical parameters (angstrom, degree) and the harmonic frequencies (cm^{-1}) at four theoretical levels with a 6-311+G* basis set for the linear SiCO species at two states and those for CO and CO⁻ molecules in their free states

States	Methods	$r_{\text{Si-C}}$	$r_{\text{C-O}}$	ω_1	ω_2	ω_3
SiCO ($^3\Sigma^-$)	CASSCF	1.835	1.152	2,178.1	360.2	548.7
	B3LYP	1.8169	1.1598	1,955.2	321.6	573.7
	B3P86	1.8104	1.1574	1,985.9	326.3	588.0
	B3PW91	1.8135	1.1576	1,984.2	326.3	584.4
	MP2	1.8253	1.1611	1,996.6	337.9	573.4
	Expt. [28]			1,899.3		
SiCO ($^1\Delta$)	CASSCF	1.829	1.132	2,155.8	338.7	578.2
	B3LYP ^a	1.8235	1.1622	1,958.5	265.5	576.4
	B3P86 ^a	1.8154	1.1606	1,983.6	264.7	591.9
	B3PW91 ^a	1.8179	1.1611	1,980.9	265.0	589.7
	MP2 ^a	1.8143	1.1756	1,907.0	266.1	610.5
SiCO ($^3\Pi$)	B3LYP	1.6955	1.1734	1,942.3	459.0	775.5
	B3P86	1.6914	1.1707	1,977.7	463.9	785.7
	B3PW91	1.6944	1.1711	1,975.1	463.3	781.3
	MP2	1.7037	1.1614	1,936.5	455.2	762.4
	CCSD(T) ^b	1.7061	1.1758	1,908	428	758
	Expt. [28]			1,857		750
CO ($^1\Sigma$)	B3LYP		1.1277	2,212.8		
	B3P86		1.1268	2,225.9		
	B3PW91		1.1273	2,222.9		
	MP2		1.1393	2,129.3		
	Expt. [26]		1.1283	2,144.0		
CO ⁻ ($^2\Pi$)	B3LYP		1.1889	1,649.6		
	B3P86		1.1870	1,671.4		
	B3PW91		1.1853	1,667.6		
	MP2		1.1815	1,796.7		

^aEstimated from quasi-linear molecule by reducing $^1\Delta$ symmetry to $^1A'$ symmetry of the bent species

^bThe CCSD(T)/TZ3P(2f) results from Ref. [33]

Table 2. The optimized geometrical parameters (angstrom, degree) and the harmonic vibrational frequencies (cm^{-1}) at four theoretical levels with a 6-311+G* basis set for the Si(CO)₂ species at two states

	Si(CO) ₂ (1A_1) (V-type)				Si(CO) ₂ (3B_1) (V-type)			
	B3LYP	B3P86	B3PW91	MP2	B3LYP	B3P86	B3PW91	MP2
$R_{\text{Si-C}}$	1.8262	1.8133	1.8160	1.8149	1.8919	1.8819	1.8852	1.9007
$R_{\text{C-O}}$	1.1507	1.1500	1.1504	1.1638	1.1795	1.1810	1.1812	1.1781
$\angle\text{SiCO}$	170.68	171.44	171.48	171.83	165.00	164.03	164.03	163.36
$\angle\text{CSiC}$	79.43	77.47	77.67	75.39	56.00	53.71	53.77	54.18
ω_1 (A_1)	102.7	100.2	100.3	94.3	130.3	181.6	180.4	160.5
ω_2 (B_1)	359.6	368.9	368.1	352.6	291.7	294.7	293.8	299.4
ω_3 (B_2)	386.6	397.7	396.4	400.8	372.2	388.6	387.6	386.3
ω_4 (A_2)	440.4	448.3	446.9	436.0	359.4	358.9	356.9	362.1
ω_5 (A_1)	509.7	526.8	524.4	515.6	381.7	450.0	446.6	457.9
ω_6 (B_2)	571.8	591.2	589.2	609.7	573.8	596.6	593.6	631.4
ω_7 (A_1)	641.9	659.1	656.3	664.7	559.5	586.0	582.6	581.2
ω_8 (B_2)	2,005.5	2,027.8	2,025.6	1,962.2	1,835.2	1,834.5	1,831.8	2,032.3
ω_9 (A_1)	2,073.6	2,090.8	2,088.2	1,992.3	1,837.3	1,835.5	1,834.1	2,161.3

CCSD(T) results. The CASSCF–MP2 method yields results in good agreement with those from the MP4 and CCSD(T) methods. This relative regularity for the results at these DFT and CCSD(T) levels is very similar to that found for other systems [34–39]. Thus, it can be concluded that the state–state energy separation falls within 17–20 kcalmol⁻¹.

3.1.2 Geometrical parameters

Although these two states have a large energy difference, they possess similar structures. For the ground state

($^3\Sigma^-$), the optimized Si–C bond length falls within 1.810–1.825 Å at five theoretical levels, the largest deviation is about 0.025 Å, while the optimized C–O bond length is within 1.157–1.161 Å with a largest deviation of about 0.009 Å. This good agreement among the bond length results suggests the appropriateness of the theoretical methods used here. Since the experimental detection of linear SiCO ($^3\Sigma^-$) by Weltner and coworkers, there have been several theoretical investigations which focus on its structural properties [31, 47]. Using a double-zeta plus polarization (DZP) basis set, Cai et al. [47] optimized the Si–C bond length of SiCO

Table 3. The calculated spin-density distribution (ρ), the charge population (Q) and the zero-point vibrational energies (ZPVE, kcalmol⁻¹) for SiCO and Si(CO)₂ species at DFT/6-311+G* and MP2(full)/6-311+G* levels

States	Methods	Q_{Si}	Q_{C}	Q_{O}	ρ_{Si}	ρ_{C}	ρ_{O}	ZPVE
SiCO (³ Σ ⁻)	B3LYP	0.180	-0.069	-0.111	1.311	0.361	0.329	4.53
	B3P86	0.144	-0.044	-0.100	1.319	0.352	0.329	4.61
	B3PW91	0.117	-0.014	-0.103	1.329	0.344	0.327	4.62
	MP2(full)	0.158	0.019	-0.177	1.496	0.103	0.402	4.64
SiCO (¹ Δ)	B3LYP	0.194	-0.084	-0.110				4.54
	B3P86	0.155	-0.054	-0.101				4.60
	B3PW91	0.134	-0.031	-0.103				4.59
	MP2(full)	0.216	-0.012	-0.205				4.49
SiCO (³ Π)	B3LYP	0.175	-0.035	-0.139	1.859	0.012	0.128	5.19
	B3P86	0.154	-0.021	-0.133	1.937	-0.048	0.112	5.27
	B3PW91	0.138	-0.001	-0.138	1.973	-0.078	0.105	5.26
	MP2(full)	0.194	0.045	-0.239	2.098	-0.105	0.007	5.27
Si(CO) ₂ (¹ A ₁) (V-type)	B3LYP	0.300	-0.029	-0.122				10.14
	B3P86	0.252	-0.007	-0.189				10.31
	B3PW91	0.227	-0.011	-0.124				10.29
	MP2(full)	0.252	0.093	-0.219				10.07
Si(CO) ₂ (³ B ₁) (V-type)	B3LYP	0.399	-0.014	-0.186	0.774	0.242	0.371	9.06
	B3P86	0.348	0.008	-0.183	0.763	0.222	0.396	9.33
	B3PW91	0.323	0.024	-0.186	0.773	0.218	0.396	9.30
	MP2(full)	0.434	0.039	-0.255	0.855	0.059	0.513	10.11
Si(CO) ₂ (¹ Σ _g) (linear)	B3LYP	0.667	-0.234	-0.099				10.07
	B3P86	0.653	-0.234	-0.092				10.18
	B3PW91	0.649	-0.228	-0.097				10.32
	MP2(full)	0.658	-0.131	-0.198				9.71

Table 4. The calculated total energies (E_{T} , au), the dissociation energies (D_{e} , kcalmol⁻¹), and the vertical ionization potentials (IP_{v} , kcalmol⁻¹) of SiCO in the ground state and the corresponding state-state energy separations (ΔE , kcalmol⁻¹) relative to the ground states at the 6-311+G* basis set level

	E_{T} (³ Σ ⁻)	ΔE (¹ Δ)	ΔE (³ Π)	D_{e} (³ Σ ⁻)	IP_{v} (³ Σ ⁻)
B3LYP	-402.8014836	18.21	71.90	36.50	202.12
B3P86	-403.2931744	20.23	69.65	41.50	217.32
B3PW91	-402.6998963	20.80	69.09	39.56	205.05
MP2	-402.1787529	19.84	71.85	28.89	190.01
MP3	-402.1804922	19.52	72.40	26.11	192.02
MP4 _{SDQ}	-402.1926862	17.26	76.42	23.71	189.73
CCSD	-402.1903524	17.90	70.81	23.57	189.68
CCSD(T)	-402.2104139	16.36	70.01	26.17	189.83
CASSCF	-402.1799287	17.26		42.52	188.78
CCSD(T) ^a			68.5		

^aThe CCSD(T)/cc-PVQZ value from Ref. [33]

(³Σ⁻) to 1.835 Å and the C–O bond to 1.167 Å at the multireference single and double excitation CI level, while Dekoek et al. [31] obtained bond lengths of 1.886 Å and 1.145 Å at the CASSCF level. At the CISD/TZ + double polarization (2P) level, the later group obtained these two bond lengths as 1.839 and 1.139 Å [31]. In recent detailed studies on this species, Schaefer and coworkers also used a higher-level [CCSD(T)] method and a larger basis set [TZ + 3P(2f)] and obtained Si–C and C–O bond lengths of 1.8249 and 1.1589 Å, respectively. No experimental values for these two bonds in the linear SiCO (³Σ⁻) molecule have been reported so far. Therefore, the highest-level theoretical

Table 5. E_{T} (au), D_{e} (kcalmol⁻¹) and IP_{v} (kcalmol⁻¹) of Si(CO)₂ in the ground state and the corresponding ΔE (kcalmol⁻¹) relative to the ground states at the 6-311+G* basis set level. $D_{\text{e},1}$ denotes the first CO dissociation energy, while $D_{\text{e},\text{T}}$ denotes total CO dissociation energy

	E_{T} (¹ A ₁)	ΔE (³ B ₁)	ΔE (¹ Σ _g)	$D_{\text{e},1}$ (¹ A ₁)	$D_{\text{e},\text{T}}$ (¹ A ₁)	IP_{v} (¹ A ₁)
B3LYP	-516.1882462	36.17	61.09	23.62	60.12	195.55
B3P86	-516.9234370	34.34	60.38	28.26	69.76	210.31
B3PW91	-516.0381580	34.14	60.16	26.15	65.71	197.29
PMP2	-515.3334127	42.14	58.14	24.80	53.68	186.76
PMP3	-515.3150556	35.89	76.79	15.10	41.21	187.02
MP4 _{SDQ}	-515.3401226	40.13	72.83	15.21	38.91	186.05
CCSD	-515.3316740	37.44	73.87	13.20	36.77	185.10
CCSD(T)	-515.3758652	40.21	65.21	19.45	45.62	187.53

value may be taken as the reference standard. Obviously, comparison indicates that the DZ basis set overestimated the bond length of Si–C by 0.01–0.06 Å and slightly underestimated the C–O bond length. At the TZ level, the electronic correlation effect significantly shortens the Si–C bond by 0.02–0.04 Å, and elongates the C–O bond. Our DFT and MP2 results at 6-311+G* basis set level are in good agreement with Schaefer's CCSD(T)/TZ + 3P(2f) values. This phenomenon has implied that the theoretical methods used in this work are reliable, and can give results very close to those from the highest-level correlation correction method.

For the singlet state (¹Δ), a similar tendency has also been observed. The estimated Si–C bond length from the

quasi-linear geometry is 1.814–1.824 Å, and the C–O bond length falls within 1.161–1.176 Å for four different theoretical methods. The calculated largest deviations are only 0.01 and 0.015 Å, respectively. The C–O bond in the ${}^1\Delta$ state is slightly longer than that of the ${}^3\Sigma^-$ state. No experimental and theoretical values have been reported so far. From the analysis of the ${}^3\Sigma^-$ state geometries, we can affirm the accuracy of our DFT and MP2 results of Si–C and C–O bond lengths. Compared with the calculated C–O bond length values (1.1268–1.1393 Å) of the free state CO (${}^1\Sigma$), the C–O bond becomes longer by about 0.036 Å after combining with an Si atom, and the values are very close to the C–O bond lengths (1.1815–1.1889 Å) of the free state CO[−] (${}^2\Pi$) anion. This phenomenon indicates that the combination of Si with CO (${}^1\Sigma$) via a singlet-state mechanism has weakened the C–O bonding strength and causes the CO[−] moiety in SiCO to possess CO[−] anionic character. The Si–C bonds in SiCO (${}^3\Sigma^-$, ${}^1\Delta$) species are slightly shorter than the common Si–C single bond by about 0.05 Å compared to 1.865 Å reported in Ref. [29], and are significantly longer than the common triple bond (1.588 Å [48]) by about 0.23 Å. This observation implies that the Si–C bond of the linear SiCO species in both states may be considered as a weak double bond composed of perhaps a σ bond and a weak π bond or weak σ and π bonds. The following vibrational frequency analysis and the charge transfer case can further substantiate this prediction.

3.1.3 Harmonic vibrational frequencies

For the ${}^3\Sigma^-$ ground state of SiCO, there are degenerate bending vibrational modes (ω_2 in Table 1) and two stretching–compression modes (ω_1 and ω_3 in Table 1). The bending modes distort the linear molecule into a bent one by departing from the molecular axis of two terminal atoms (Si and O) according to two directions vertical to the molecular axis. The calculated bending vibrational frequencies are in the range from 322 to 360 cm^{−1} at the five theoretical levels. The three DFT methods give very similar results (322–326 cm^{−1}) to each other. They are slightly smaller than the value (338 cm^{−1}) at the MP2 level, and those (336–350 cm^{−1}) calculated by Petraco et al. [33] at the CCSD(T) level with different basis sets [TZ2P–TZ3P(2f)]. This good agreement also reflects that DFT/6-311+G* methods are reliable in predicting the structural properties. Actually, these bending vibrational frequencies are relatively small; they imply that the potential-energy surface for bending is relatively flat. No experimental values have been reported [28] for these vibrational modes, but an early experimental report implied this low-bending vibrational mode. From the electron spin resonance data [28], it appears that the SiCO molecule may also be bent in some sites in some matrices, and SiCO in argon is a case where almost all the molecules appeared to be nonlinear. However, our all calculations on SiCO species have confirmed that a small departure from linearity can be expected to be slightly unstable with respect to the linear conformation, but the energy increase is very small when the SiCO bond angle changes

from 180° to 170° or smaller. The calculated relaxed potential energy surface with respect to the SiCO bond angle indicates that when the SiCO bond angle decreases by 10° from 180°, the total energy of the SiCO species increases only about 0.6 kcalmol^{−1} at the B3LYP/6-311+G* level, while when it decreases by 30° the systemic energy increase is less than 6 kcalmol^{−1}. This is to say that the bending force constant is quite small and some constraints in matrix sites may induce bending. This easy bending tendency may also be attributed to the fact that there are two weak π -bonding interactions between Si and CO moieties.

A similar analysis holds for the ${}^1\Delta$ state. At the CASSCF/6-311+G* level, our calculated ω_2 is 338.7 cm^{−1}. Considering the fact that ${}^1\Delta$ is reduced to ${}^1A'$ when SiCO is bent, the frequencies of the ${}^1\Delta$ state are also estimated from the quasi-linear molecule ${}^1A'$ state. At the DFT and MP2 levels, ω_2 is predicted to be about 265 cm^{−1}. It is smaller than that in the ${}^3\Sigma^-$ state by about 60 cm^{−1}. It may be predicted that the potential-energy surface in the ${}^1\Delta$ state is also flat, and the bonding between Si and CO moieties is also weak like that in the ${}^3\Sigma^-$ state.

The other two vibrational modes are the Si–C (ω_3) and C–O (ω_1) stretching vibrations; the CASSCF calculated frequency values are 548.7 and 2,178.1 cm^{−1} for the ${}^3\Sigma^-$ state and 578.2 and 2,155.8 cm^{−1} for the ${}^1\Delta$ state, respectively. At the DFT and MP2 levels, the harmonic frequencies are predicted to be 573–584 and 1,955–1,996 cm^{−1} for the ${}^3\Sigma^-$ state and 577–610 and 1,906–1,984 for the ${}^1\Delta$ state, respectively. Only the C–O mode of SiCO in the ${}^3\Sigma^-$ state was experimentally observed to be 1,899.3 cm^{−1}; no report on the Si–C vibrational mode has been given [28]. The experimental estimate for the later is about 800 cm^{−1}. Our calculated value is 573–587 cm^{−1}, but the corresponding IR intensity is very small. Perhaps this is why no experimental signal has been observed [28]. For the C–O stretching vibration in the ${}^3\Sigma^-$ state, the calculated results fall within 1,955–1,996 cm^{−1}; they are slightly greater than the experimental value (1,899.3 cm^{−1}) by 56–96 cm^{−1}. Obviously this deviation between the theoretical and the experimental values for the C–O mode of SiCO (${}^3\Sigma^-$) is almost equivalent to that (within 80 cm^{−1}) occurring in the free-state CO (${}^1\Sigma$). For the ${}^3\Sigma^-$ state, there are several investigations regarding the structures and frequencies at various wavefunction-correlated levels [31, 33, 47]. Among these studies, the highest level is the CCSD(T) method with a TZ plus triple polarization [TZ + 3P(2f)] function basis set. This method yields stretching frequencies of 564 cm^{−1} for Si–C stretching and 1,927 cm^{−1} for C–O. Obviously our calculated values are very close to those obtained by Schaefer and coworkers with a high-level method and a large basis set: however, the absolute change in the C–O vibrational mode is significant after CO is combined with an Si atom. The frequency redshift is 238–258 cm^{−1} at the DFT/6-311+G* level and 133 cm^{−1} at the MP2/6-311+G* level. These values, especially the DFT results, are very close to the experimental redshift value (245 cm^{−1}). The considerable decrease in the C–O mode frequency implies a weakening of the C–O bond, and this

weakening is greater than that in the transition-metal *MCO* systems. The Si–CO vibrational frequency reflects the binding strength of Si with the CO species. From the value of this frequency, we conclude that the Si–C bonding in the SiCO species in the $^3\Sigma^-$ state is weak. A similar situation is true for the $^1\Delta$ state.

3.1.4 Dissociation energies

No experimental estimates of the dissociation energy have been reported for the linear ground-state SiCO species. Although the structure and vibrational frequencies have been theoretically predicted by Dekook et al. [31] and Petraco et al. [33] at CC and CI levels with different basis sets for the $^3\Sigma^-$ state of SiCO, D_e and IP values have not been theoretically determined. D_e values of SiCO in the $^3\Sigma^-$ state using several different methods with the 6-311+G* basis set are listed in Table 4. No zero-point-energy and counterpoise corrections were made for the D_e values in Table 4. The corrections may slightly reduce the values, but they do not significantly change the relative regularity. Thus, the discussions will emphasize the qualitative results. The three DFT methods yield D_e values within 36.5–41.5 kcalmol $^{-1}$, and close to the CASSCF–MP2 value (42.5 kcalmol $^{-1}$). The high-level method CCSD(T) yields D_e to be 26.1 kcalmol $^{-1}$, while MP4(SDQ) underestimates D_e by 2.5 kcalmol $^{-1}$. Fortunately, MP3 gives a very close result to the CCSD(T) one; the MP2 result is also in good agreement with the CCSD(T) result, with a deviation of 2.7 kcalmol $^{-1}$. Together with the previously calculated results, it can be concluded that the three DFT methods slightly overestimate D_e of the $^3\Sigma^-$ state. Although there is a significant difference between the DFT values and those from the correlated-wavefunction methods, we can confidently conclude that D_e of the SiCO ($^3\Sigma^-$) species is at least 26 kcalmol $^{-1}$. These D_e results of SiCO ($^3\Sigma^-$) indicate that the Si–CO bonding should not be considered as a very weak interaction. It is weaker than the common chemical bonding, but much stronger than the intermolecular van der Waals interactions.

3.1.5 Ionization potential

Another important quantity is the IP. The vertical IP for SiCO in the $^3\Sigma^-$ state calculated at several different levels of theory is listed in Table 4. As in the analysis regarding D_e of the $^3\Sigma^-$ state, the three DFT methods yield an IP_v value slightly greater than those using the MP n ($n = 2,3,4$) and CC methods. The largest deviation from each other for the three DFT methods is 15 kcalmol $^{-1}$, only 7.1% of the total IP_v , and it can be recognized that the agreement among the three DFT results is good. There is also good agreement among several correlated-wavefunction methods (MP n , $n = 2,3,4$, and CC). They yield IP_v values of 189–192 kcalmol $^{-1}$. The results from the correlated-wavefunction methods are slightly smaller than the DFT values by 10–18 kcalmol $^{-1}$. These deviations are only 5–9% of IP_v . Therefore it can be concluded that the value of 190–210 kcalmol $^{-1}$ is reliable for the $^3\Sigma^-$ SiCO species. IP_v denotes the energy required for removing an electron from the frontier orbital under the Franck–

Condon condition. These large IP_v values indicate that the frontier orbital energy level is very low. These IP_v values are by about 16 kcalmol $^{-1}$ greater than the Si atomic IP results [186.74, 201.24, 190.45, and 179.19 kcalmol $^{-1}$ for the three DFT and CCSD(T,full) methods], indicating that the Si moiety in SiCO ($^3\Sigma^-$) still retains atomic character. The ionized electron mainly comes from the Si center.

3.1.6 Bonding analysis

The valence electronic configurations for the triplet ground state ($^3\Sigma^-$) and the singlet excited state ($^1\Delta$) are, respectively

$$^3\Sigma^- : (1\sigma^2)(2\sigma^2)(3\sigma^2)(1\pi^4)(4\sigma^2)(2\pi_+^1)(2\pi_-^1)(5\sigma^0)$$

and

$$^1\Delta : (1\sigma^2)(2\sigma^2)(3\sigma^2)(1\pi^4)(4\sigma^2)(2\pi_+^2)(2\pi_-^0)(5\sigma^0).$$

The major difference between the two electronic states lies in the different occupation of the highest occupied molecular orbital (HOMO), a pair of degenerate π orbitals. The π^2 configuration generates three electronic states: $^3\Sigma^-$, $^1\Delta$ and $^1\Sigma^+$. Obviously, the $^1\Delta$ state is energetically higher than the $^3\Sigma^-$ state, but lower than the $^1\Sigma^+$ state. Inspection of the frontier orbitals reveals that these two degenerate π orbitals (HOMO) are essentially Si p orbitals combined with the antibonding π^* orbitals. These orbitals describe the bonding interaction between Si and C centers and the antibonding interaction between C and O centers. Thus, it can be predicted that in the formation process, Si is an acceptor using its empty p orbital to accept the coordination lone-pair electrons of the donor CO, yielding the high-energy-level backbone σ -type bonding ($4\sigma^2$); at the same time, the formation of the π bonds further strengthens the Si–C bonding interaction and weakens the C–O interaction owing to the feedback of Si π -type electrons to the π^* orbitals of CO. This bonding mechanism is similar to that in transition-metal carbonyl complexes, but a major difference of SiCO from *MCO* is that Si uses its p -type orbitals to form the feedback π bond instead of the d -type orbitals. Owing to the electronic structural difference between Si and transition-metal atoms, the weakening of the C–O bond in the SiCO species is greater than that in the transition-metal carbonyls. The analysis of the charge population also reveals that the net charge transfer from Si to CO is 0.12–0.18e for SiCO ($^3\Sigma^-$), and the transferred charge is mainly distributed over the O center. However inspection of the spin density reflects that SiCO ($^3\Sigma^-$) also exhibits the character of silene (carbene-like) and may be named carbonylsilene. There are two unpaired electrons for the SiCO $^3\Sigma^-$ state, 1.3–1.5e (65–75%) of them distribute over the Si center, while the remainder are spread over the C (about 0.35e, about 17%) and O (about 0.33e, about 16%) centers. This distribution implies that two degenerate HOMOs with two spin unpaired electrons mainly describe the Si π -type orbital character. This prediction has been confirmed by IP_v . Calculations on the ionized SiCO $^+$ species indicate that when an electron is removed, the SiCO ($^3\Sigma^-$) state becomes the SiCO $^+$ ($^2\Pi$)

state. In the later, the positive charge is mainly on the Si center with 0.7–0.8e, and the one spin unpaired electron is also distributed over the Si center with an amount of about 0.79e. Compared with the distribution of SiCO ($^3\Sigma^-$), it can be distinctly seen that the ionized electron is certainly the HOMO π electron with a significant Si p_π -type orbital character.

Similar analysis holds for the SiCO $^1\Delta$ state, although with the exception of its different electronic configuration. In addition, it should be noted that although with respect to the bond length the CO $^{\delta-}$ moiety of SiCO exhibits CO $^-$ character, the spin density is considerably different from the CO $^-$ species (C about 1.0 and O about 0.0), and there is also a large charge distribution difference between them. Thus, from this point it cannot be classified as the CO $^-$ anion species.

3.1.7 $^3\Pi$ state

At different wavefunction-correlated levels, the first triplet excited state ($^3\Pi$) has been characterized. Obviously, this state originates from an electron excitation from 4σ to 2π , and the corresponding valence electronic configuration is

$$[\text{core}](1\sigma^2)(2\sigma^2)(3\sigma^2)(1\pi^4)(4\sigma^1)(2\pi_+^2)(2\pi_-^1)(5\sigma^0).$$

The structural and vibrational frequencies for this state have been predicted by different groups [33, 47] using wavefunction-correlated levels with different DZ and TZ basis sets plus polarizations. The state–state excitation energy ($X^3\Sigma^- \rightarrow A^3\Pi$) was also estimated. Thus this is not main state considered in this paper. However, no discussion was made in those studies about the differences between the $^3\Pi$ state and the $^1\Delta$ state. On the other hand, although there is a structural property analysis on this $^3\Pi$ state at wavefunction-correlated levels, such as CCSD(T) [33] and MRSDCI [47] methods, etc., no similar studies at DFT levels are given. Therefore, it is important to introduce this $A^3\Pi$ state here to make a detailed comparison with the $^1\Delta$ state. The relevant parameters calculated at the three DFT and MP2 levels with the 6-311 + G* basis set are given in Tables 1 and 3. The state–state energy separation of this state relative to the ground state is listed in Table 4. As already noted, since this $^3\Pi$ state may be considered as one produced from the $^3\Sigma^-$ state by exciting a 4σ electron to the 2π orbital and the $^1\Delta$ state as one produced by forcing two 2π electrons to occupy the same spatial orbital, the comparison should be made with the $^1\Delta$ state, taking the $^3\Sigma^-$ state as the reference state. As mentioned in the discussion of the $^3\Sigma^-$ state, 4σ is a bonding orbital principally describing the weak bonding interaction between Si and C centers and that between C and O centers, while 2π denotes the bonding interaction between Si and C centers and the antibonding interaction between C and O centers. Obviously, the excitation $4\sigma \rightarrow 2\pi$ strengthens the Si–C bond and weakens the C–O bond. Consequently the Si–C bond becomes short and the C–O bond becomes long compared with those in the $^3\Sigma^-$ state. The effect of this excitation on the geometrical parameters is considerably different from that from the excitation $2\pi_+^1 2\pi_-^1 \rightarrow 2\pi_+^2 2\pi_-^0$ which almost does

not affect the geometrical parameters. Although the excitation $4\sigma \rightarrow 2\pi$ significantly shortens the Si–C bond, the 2π orbital is energetically higher than the 4σ orbital; consequently, the $^3\Pi$ state should be significantly higher in energy than the $^3\Sigma^-$ state. However, the excitation $2\pi_+^1 2\pi_-^1 \rightarrow 2\pi_+^2 2\pi_-^0$ involves only the electron transition between the orbitals with same energy levels instead of the transition between the orbitals with different energy levels; therefore, this excitation does not cause a large energy change in the system and only increases the electronic repulsive energy. From these two different excitations, it can be concluded that the excitation from the $^3\Sigma^-$ ($4\sigma^2 2\pi_+^1 2\pi_-^1$) to the $^1\Delta$ ($4\sigma^2 2\pi_+^2 2\pi_-^0$) state needs a smaller excitation energy than that from the $^3\Sigma^-$ ($4\sigma^2 2\pi_+^1 2\pi_-^1$) to the $^3\Pi$ ($4\sigma^1 2\pi_+^2 2\pi_-^0$) state, viz., the $^1\Delta$ state should be energetically lower than the $^3\Pi$ state. Our calculated results given in Tables 1, 3, and 4 confirm this analysis. The calculated state–state energy separation ($^3\Pi$ – $^3\Sigma^-$) is about 70 kcalmol $^{-1}$ at several theoretical levels without zero-point-energy correction. No matter whether the zero-point-energy correction is taken into account or not, these results are only slightly greater, by 0.5–4.0 kcalmol $^{-1}$, than the value (68.5–69.0 kcalmol $^{-1}$) calculated by Schaefer's group using the highest level of theory with the largest basis set [CCSD(T)/cc-pVQZ]. In particular, the B3P86 and B3PW91 methods give an energy separation close to Schaefer's result. This observation demonstrates the applicability of DFT methods in studying these molecules.

As already mentioned, the excitation from the ground state may elongate the C–O bond and significantly shorten the Si–C bond. Our calculated Si–C bond length in the $^3\Pi$ state falls within 1.691–1.704 Å at four levels of theory; it is very close to the Schaefer CCSD(T)/TZ3P(2f) result (1.706 Å). This Si–C bond is significantly shorter than that of the $^3\Sigma^-$ state. The calculated C–O bond length falls within 1.161–1.173 Å, which is also very close to the CCSD(T)/TZ3P(2f) result (1.176 Å). It is slightly longer by about 0.01 Å than that in the $^3\Sigma^-$ state. The same variations may be seen by comparing the $^3\Pi$ state with the $^1\Delta$ state. From the frequency aspect, compared with the $^3\Sigma^-$ and $^1\Delta$ states, no apparent changes in the C–O stretching mode (ω_1) can be found for the $^3\Pi$ state, but the Si–C stretching mode is obviously blueshifted. The blueshift magnitude is about 200 cm $^{-1}$. This change implies that the Si–C bond in the $^3\Pi$ state is stronger than those in both the $^1\Delta$ and $^3\Sigma^-$ states, while the C–O bond is almost equivalent for the three states. Another important observation concerns the bending vibrational mode (ω_2). As noted by Schaefer and coworkers this $^3\Pi$ state displays two different real vibrational frequencies along the bending coordinate, viz., this state is subject to the Renner–Teller effect. Our calculated Renner parameter, ϵ , is about –0.135. The average bending vibrational frequency is within 455.2–463.9 cm $^{-1}$ and is slightly greater by 27–35 cm $^{-1}$ than the CCSD(T)/TZ3P(2f) value (428 cm $^{-1}$) [33]. The frequencies are considerably greater by about 137 cm $^{-1}$ than those of the ground state and by about 199 cm $^{-1}$ than those of the singlet state ($^1\Delta$), respectively. This indicates that the bending potential-energy surface in the $^3\Pi$ state is less flat than those in the $^3\Sigma^-$ and $^1\Delta$ states.

3.2 Si(CO)₂ species

The previous analysis indicates that the Si–CO bonding energy is about 26 kcalmol⁻¹. This observation implies that in view of the bonding character in the SiCO species it may be possible to form polycarbonyl Si compounds. In an early experiment Lembke et al. [28] also demonstrated the existence of bicarbonyl Si, Si(CO)₂, and found a slightly weak band at 1,928 cm⁻¹, which was attributed to the formation of OCSiCO, the counterpart of carbon suboxide, and this molecule was assigned to be linear; however, no detailed IR vibrational analysis was given. Obviously this linear assignment for the molecular geometry of Si(CO)₂ lacks sufficient evidence. According to the discussion, SiCO possesses silene property and a very low bending isomerization barrier; thus, it is a problem worthy of consideration if Si(CO)₂ possesses a linear structure. In view of these observations and considerations, in 1989, Grev and Schaefer [32] made a reassignment for the structure of Si(CO)₂ on the basis of theoretically predicted IR spectra. At the CISD/DZP level, they optimized three assumed structures for the Si(CO)₂ species, and indicated that the linear OCSiCO structure did not correspond to the minimum on the potential-energy surface, and the ground state corresponded to a V-type structure. It should be noted that their searches were limited to only the singlet state; the triplet state was not considered. The calculated geometrical parameters are 1.871 Å (Si–C), 1.126 Å (C–O), 80.0° (∠C–Si–C), and 172.7° (∠Si–C–O) at the SCF/DZP level, and 1.842 Å (Si–C), 1.147 Å (C–O), 78.4° (∠C–Si–C), and 172.3° (∠Si–C–O) at the CISD/DZP level, respectively [32]. This V-type structure was verified by comparing the calculated frequencies with the experimental findings of Lembke et al. [28]. The predicted linear OCSiCO structure is significantly higher by 80.5 kcalmol⁻¹ than the V-type structure at the CISD/DZP level. In view of some differences in geometrical parameters and the lack of information regarding the triplet state and of the detailed bonding analysis, in this section, the results of the investigation of the Si(CO)₂ species at the DFT level with the 6-311 + G* basis set are reported.

At the four theoretical levels, the molecular geometries were first optimized for the Si(CO)₂ species in its singlet and triplet states, respectively. It can certainly be claimed that whether in the singlet state or in triplet state the Si(CO)₂ species possesses a bent structure (symmetric V-type structure with C_{2v} symmetry). Not only is the C–Si–C unit of Si(CO)₂ not linear, but also the two Si–C–O units are not linear. The linear structure was found to be a second-order saddle point with degenerate imaginary frequencies. All attempts to find other stable isomers for the Si(CO)₂ species were unsuccessful. For the singlet state Si(CO)₂ (¹A₁) and triplet state Si(CO)₂ (³B₁), the optimized geometric parameters and the vibrational frequencies are given in Table 2, the charge population and the spin density distribution are listed in Table 3, while relevant energy quantities are collected in Table 5.

Optimizations indicate that there are two stable isomers for Si(CO)₂, with one being the V-type singlet state (¹A₁) and the other is the V-type triplet state (³B₁). In

contrast to the SiCO species, the singlet state is stabler by 34–42 kcalmol⁻¹ than the triplet state, and thus may be assigned to the ground state. According to the analysis about applicability of the three DFT and the MP2 methods, it can be concluded that the state–state energy separation for the Si(CO)₂ species of about 40 kcalmol⁻¹ is reliable. For the linear configurations (¹Σ_g⁺ and ³Π_u), even if there are no imaginary frequencies, the significantly large state–state energy separations (¹Σ_g⁺ to ¹A₁ being 60.1–61.1 kcalmol⁻¹ and ³Π_u to ¹A₁ being 75.8–76.9 kcalmol⁻¹ at DFT levels) clearly show that the linear configurations are very unstable.

For the ground state (¹A₁), from the data in Table 2, it can be seen that the key angle ∠CSiC reflecting the molecular nonlinear character is only 75–79° at three DFT and MP2 levels with the 6-311 + G* basis set. Another interesting bond angle is ∠SiCO. At four theoretical levels, its optimized value is about 170°. The molecule possesses C_{2v} symmetry, with the two SiCO moieties symmetrically on the two sides of the C₂ axis, and both O atoms depart from the Si–C axis by 9–10° on the outside. These DFT results for the angles are in good agreement with those calculated by Grev and Schaefer using the CISD/DZP method. The optimized C–O bond lengths are within 1.1500–1.1638 Å and are also very close to the CISD/DZP result (1.147 Å) [32]. However, there is a large deviation between our DFT calculated values and the CISD/DZP value of Grev and Schaefer for the Si–C bond length. The optimized Si–C bond lengths fall within 1.8133–1.8262 Å at three DFT/6-311 + G* and MP2/6-311 + G* levels, being significantly shorter by 0.016–0.030 Å than the CISD/DZP value (1.842 Å) [32]. On the basis of the previous discussions regarding the Si–C bond of SiCO (³Σ⁻), it can be concluded that a Si–C bond length falling within 1.813–1.826 Å is reliable, and that the CISD/DZP method overestimates it. These Si–C and C–O bond lengths are very close to the those in the SiCO (³Σ⁻) and SiCO (¹Δ) species. This observation indicates that there is similar bonding character in the bicarbonyl Si systems as in the monocarbonyl Si systems. The very small deviations in Si–C and C–O bonds between SiCO and Si(CO)₂ species may be attributed to the breaking of a weak π bond ([here are two weak π bonds for SiCO and there is only one for Si(CO)₂]). However, for the ³B₁ state, there are obvious changes relative to the ¹A₁ state and SiCO species. No investigations have been reported up to now. Our calculations have indicated the following several changes. First the CSiC bond angle is reduced by about 24°, and the SiCO bond angles are also reduced by 5–8°. In particular, the Si–C bond lengths are significantly longer by 0.065–0.085 Å than those in the ¹A₁ state and SiCO (³Σ⁻, ¹Δ) states, while the C–O bonds become longer by about 0.03 Å.

Obviously these considerable changes should be attributed to differences in the bonding character. According to the frontier orbital valence electronic configuration of the ground state: [core].....(1b₁)²(4a₁)²(1a₂)²(4b₂)²(5a₁)²(2b₁)²(6a₁)⁰, the corresponding one of the ³B₁ state should be [core].....(1b₁)²(4a₁)²(1a₂)²(4b₂)²(5a₁)²(2b₁)¹(6a₁)¹. Namely, an electron is excited from 2b₁ to 6a₁, yielding the ³B₁ state. Inspection of the

high-energy-level bonding orbitals reveals that as in the SiCO species, the HOMO ($2b_1$) denotes the interaction of Si π -type p orbitals with the antibonding π^* orbital of CO and mainly reflects the π -bonding interaction between Si and C centers and the π^* -antibonding interaction between C and O centers, while the lowest unoccupied molecular orbital, $6a_1$ orbital, describes the σ^* -type antibonding interaction between an s orbital of Si and the σ^* -type orbital of the CO species. In addition, several other bonding orbitals are $4a_1$, $1a_2$, $4b_2$, and $5a_1$ orbitals. $4a_1$ and $1a_2$ depict the σ -bonding and π -bonding interaction localizing at the CO moiety, respectively, while $4b_2$ corresponds to the σ^* -antibonding interaction between C and O centers, and $5a_1$ is the Si–C σ -bonding orbital. Obviously, the key molecular orbitals describing the bonding interaction between Si and CO moieties are $5a_1$ and $2b_1$ for the 1A_1 state, while those for the 3B_1 state are $5a_1$, $2b_1$, and $6a_1$. The excitation of an electron from $2b_1$ to $6a_1$ yields the 3B_1 state. This electron transition significantly weakens the Si–C π -bonding interaction and increases the Si–C σ^* -antibonding interaction; the net effect of $2b_1 \rightarrow 6a_1$ excitation on the Si–C bond is the weakening of the Si–C bond. Thus, this excitation must cause the elongation of the Si–C bond. The calculated bond length increase in the 3B_1 state compared with the 1A_1 state provides evidence for the previous analysis. At the same time, although excitation of a $2b_1$ electron to $6a_1$ orbital also reduces the π^* -antibonding interaction between C and O centers, this excitation greatly increases the σ^* -antibonding interaction between them. Thus, the overall effect from this transfer on the C–O bond is the weakening of the C–O bond. This prediction has also been proved by the optimized geometrical parameters given in Table 2 [the C–O bonds in Si(CO)₂ (3B_1) are longer than those in the Si(CO)₂ 1A_1 state by about 0.03 Å].

Another interesting characteristic of these bicarbonyl Si compounds is that they have very small CSiC bond angles and a slightly bent SiCO angle. This is to some extent similar to silene such as H₂Si, etc., but is different from the SiCO species and some transition-metal carbonyl compounds. For the H₂Si species, the singlet state (1A_1) is also stabler than the triplet state (3B_1), but the HSiH bond angle in the triplet state (3B_1 , 118°) is greater than that in the singlet state (1A_1 , 91.4°). Obviously Si(CO)₂ may be classified as a silene, but it has bonding differences from H₂Si. This difference is attributed to the participation of CO as a ligand. Inspection of the natural bonding orbitals (NBO) reveals that for 1A_1 state species, Si utilizes two hybrid orbitals ($sp^{7.53}d^{0.13}$) to interact with two C ($sp^{0.53}$) hybrid orbitals to form two Si–C bonds. Obviously if Si uses its pure p orbitals to form Si–C bonds, the CSiC angle should be 90°. Owing to the participation of the Si s orbital, and under the consideration of the increase of the Si p_z orbital along the molecular axis, the CSiC bond angle becomes smaller than 90°. Of course, the repulsion interaction from a pair of lone electrons of Si is also a dominant factor. In addition, the change of the hybrid index of the C center also plays an arbitrary role in forming the small CSiC angle. For the 3B_1 state, from the previous analysis mentioned, it can be easily understood that its CSiC

angle is smaller than that in the singlet state. The electron exchange between the $2b_1$ and $6a_1$ orbitals increases the s -orbital component of the hybrid orbital used to form Si–C bonds. Combining the antibonding character of Si–C in the $6a_1$ orbital, it is reasonable that the CSiC angle becomes small. At the same time, the decrease of the CSiC angle also results in further bending of the SiCO angle. Analysis of the NBO character also reveals that in these states (1A_1 and 3B_1) every C σ -type hybrid orbital is $sp^{1.77}$, while every O is sp . Namely the effective bonding orbital of the C center obviously deviates from the associated C–O axis by about 15°, therefore resulting in the C–O bond deviating from the Si–C axis by about 15°. Of course, outside departure may be due to the repulsion interaction between the two –C=O moieties.

The vibrational frequencies obtained using the four theoretical methods are also listed in Table 2. ω_8 (B_2) and ω_9 (A_1) may be assigned to two C=O characteristic absorption peaks with asymmetric and symmetric stretching vibrations, while ω_6 (B_2) and ω_7 (A_1) correspond to the Si–CO asymmetric and symmetric stretching vibrations. These two groups of vibrational modes reflect the strength of the corresponding bonds, respectively. Another vibrational mode of interest is the ω_1 (A_1) mode. The remaining modes are the in-plane bending vibrational modes (ω_3 , B_2 and ω_5 , A_1) and the out-of-plane waggle modes (ω_2 , B_1 and ω_4 , A_2) for the SiCO angle. As noted in the analysis concerning the geometrical parameters, very good agreement among the data obtained using the four theoretical methods can also be observed. Further, an interesting observation is the changes of the vibrational frequencies for the C–O stretching mode. For the 1A_1 ground state, although the C–O bond-length change relative to that in the SiCO species is negligible, the stretching frequencies become larger by 40–120 cm⁻¹, and are close to that of the free state CO ($^1\Sigma$) molecule. This indicates that the weakening of the C=O moiety in the Si(CO)₂ ground state is smaller than that in the monocarbonyl Si, and the CO of Si(CO)₂ possesses free CO molecular character. From this it can be predicted that the CO moieties in polycarbonyl Si such as Si(CO)₃ or Si(CO)₄, etc. are essentially closer to the free state CO ($^1\Sigma$), if such complexes exist; however, these kinds of polycarbonyl Si compounds appear to be unstable as complexes. Perhaps this is why there are no experimental reports regarding the existence of the tricarbonyl Si or other polycarbonyl Si complexes. In addition, although no apparent frequency change has been observed for the Si–C vibrations in Si(CO)₂ (1A_1) compared with that in SiCO ($^3\Sigma^-$), a very low vibrational frequency corresponding to the CSiC angle scissor-cutting mode implies the weak bonding interaction between Si and two CO. This indicates that the potential-energy surface is flat with respect to the bending of the CSiC angle, and that these polycarbonyl molecules are facile.

Similarly for the excited state (3B_1), no apparent change for Si–C vibrations is observed, but the C–O vibrational frequencies are obviously smaller than those in the Si(CO)₂ ground state (1A_1) by 200–250 cm⁻¹ at DFT/6-311 + G* levels, and also are smaller than those of SiCO species (by 120–150 cm⁻¹). According to the

previous discussions regarding the geometrical parameters, it is believed that this observation is reasonable.

To further determine the bonding strength of this bicarbonyl Si complex and to examine the stability of the polycarbonyl Si complexes, the monocarbonyl dissociation energies and the bicarbonyl dissociation energies and the corresponding IP_v of the ground-state $Si(CO)_2$ species were also calculated by using the four theoretical methods with the 6-311 + G* basis set, and were also calibrated by the higher-level electron correlation methods such as MP3, MP4_{SDQ}, CCSD, and that including triple excitations (see Table 5). No investigations have been reported for these energy quantities; the following discussions focus on the theoretical analysis and the intrinsic relationship between the bonding and relevant energy parameters.

For the first CO dissociation energy, $D_{e,1}$, the three DFT methods give $D_{e,1}$ within 23.6–28.3 kcalmol⁻¹, which is very close to the MP2 result (24.8 kcalmol⁻¹). The MP3, MP4_{SDQ}, and CCSD values are significantly smaller than the DFT ones; only the CCSD(T) result (19.5 kcalmol⁻¹) is close to the DFT and MP2 values. According to the performance of the various methods, the results falling within 19–24 kcalmol⁻¹ are reliable. Comparison of these values with those of SiCO ($^3\Sigma^-$) indicates that the first CO adiabatic dissociation energy is smaller than the second CO adiabatic dissociation energy by about 13 kcalmol⁻¹ at the DFT levels and by about 7 kcalmol⁻¹ at the CCSD(T) level. Namely, dissociation of $Si(CO)_2$ into SiCO ($^3\Sigma^-$) and CO ($^1\Sigma$) is easier than that of SiCO into Si (3P) and CO ($^1\Sigma$). In other words, the first CO binding energy of an Si atom is greater than the second CO one. It may be predicted that the third CO binding energy of Si will be smaller than the second CO one, and the same regularity is true for the fourth or fifth CO binding energies. From the viewpoint of the average single CO binding energy, the average value [22.8 kcalmol⁻¹ at the CCSD(T)/6-311 + G* level] for the $Si(CO)_2$ species is also smaller than that (26.2 kcalmol⁻¹ at the same level) for the SiCO species; therefore, for the tricarbonyl Si the average binding energy should be smaller than that of $Si(CO)_2$. This tendency implies that polycarbonyl Si complexes with more than two CO ligands should be unstable, and are very easily dissociated to subcarbonyl Si complexes. This further confirms the fact that up to now there have been no reports about $Si(CO)_3$ or $Si(CO)_4$, etc., even at very low temperature.

Another important energy quantity is IP_v . The IP_v of $Si(CO)_2$ is slightly smaller than that of SiCO by 2–7 kcalmol⁻¹. The ionized electron mainly comes from the Si center, indicating the silene character of the $Si(CO)_2$ species.

4 Conclusion

The detailed structural properties and the bonding character for subcarbonyl Si, SiCO and $Si(CO)_2$, in their singlet and triplet states have been investigated using three DFT, MP2 and CASSCF methods with a

6-311+G* basis set. The results indicate that for the SiCO species the triplet state is stabler than the singlet state; the corresponding state-state energy separation is 16.4 kcalmol⁻¹ at CCSD(T)/6-311+G* level. The combination of Si with CO yields a weak Si–CO bond and simultaneously weakens the C–O bond. The resulting SiCO ($^3\Sigma^-$) may be classified as silene (carbonylsilene), and its $CO^{\delta-}$ moiety possesses CO^- property. The main interaction between Si and CO moieties is a weak σ bond and two weak π bonds. Although the Si–C bond length is similar to the single bond, the bond strength is weaker than the common Si–C bonds in Si-containing alkanes. The calculated dissociation energy is 26.2 kcalmol⁻¹ at the CCSD(T)/6-311+G* level. The corresponding bending potential-energy surfaces are flat; therefore, these SiCO molecules are facile. For the bicarbonyl Si systems, $Si(CO)_2$, two V-type structures are found for singlet and triplet states which are significantly different from the linear configuration. The singlet state (1A_1) is stabler by about 40 kcalmol⁻¹ than the triplet state (3B_1) at the CCSD(T)/6-311+G* level and may be assigned to the ground state. The bond length in the ground state (1A_1) is very close to that in the SiCO species, but its SiCO moieties are bent by about 10°, and the CSiC angle is only about 78°. The 3B_1 state has about 54° of the CSiC angle and about 165° of the SiCO angle; however, its Si–C and C–O bonds are longer than those in the 1A_1 ground state by about 0.07 and 0.03 Å, respectively. The linear constrained singlet ($^1\Sigma_g$) and triplet ($^3\Pi_u$) states are also considerably higher than the ground state (1A_1) and also than the V-type triplet state (3B_1). This $Si(CO)_2$ (1A_1) species has essentially silene character and should be referred to as a bicarbonyl silene. Comparison of the CO dissociation energies between SiCO and $Si(CO)_2$ in the ground states indicates that the first CO dissociation energy of $Si(CO)_2$ is smaller by about 7 kcalmol⁻¹ than that of SiCO; that averaged over two CO is also smaller than that of SiCO. The detailed bonding analysis implies that the possibility of the existence of the polycarbonyl Si with more than three CO is small. Perhaps this is why no experimental observations have been reported up to now for polycarbonyl Si complexes. These nonmetal and non-transition-metal atoms or clusters are very different from the transition metals, they cannot form the polycarbonyl complexes, and the detailed interaction character is also still unclear. Thus further studies are very necessary.

It should also be noted that owing to the importance of investigations regarding the weak interaction in biological and materials fields, detailed studies on not only the interaction among large molecules but also that between large and small molecules need further attention. Perhaps investigations on the interaction and bonding among such small molecules may provide some valuable information.

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References

1. Ray GB, Li X-Y, Ibers JA, Sessler JL, Spiro TG (1994) *J Am Chem Soc* 116: 162
2. Alben JO, Caughey WS (1968) *Biochemistry* 7: 175
3. Collman JP, Brauman JI, Halbert TR, Suslick KS (1976) *Proc Natl Acad Sci USA* 73: 3333
4. Li X-Y, Spiro TG (1988) *J Am Chem Soc* 110: 6024
5. Ramsden J, Spiro TG (1989) *Biochemistry* 28: 3125
6. Barlow CH, Ohlsson P-I, Paul K-G (1976) *Biochemistry* 15: 2225
7. Yoshikawa S, Choc MG, O'Toole MC, Caughey WS (1977) *J Biol Chem* 252: 5498
8. Jewsbury P, Kitagawa T (1994) *Biophys J* 67: 2236
9. Springer BS, Sligar SG, Olson JS, Phillips GN Jr (1994) *Chem Rev* 94: 699
10. Staemmler V (1975) *Chem Phys* 7: 17
11. Ikuta S (1984) *Chem Phys Lett* 109: 550
12. Del Bene JE (1986) *J Comput Chem* 7: 259
13. Walter D, Sievers MR, Armentrout PB (1998) *Int J Mass Spectrom Ion Processes* 175: 93
14. Alikani ME, Bouteiller Y (1997) *J Mol Struct (THEOCHEM)* 436: 481
15. Alikani ME (1998) *J Mol Struct (THEOCHEM)* 432: 263
16. Pullumbi P, Bouteiller Y, Perchard JP (1995) *J Chem Phys* 102: 5719
17. Pullumbi P, Bouteiller Y (1995) *Chem Phys Lett* 234: 107
18. Wesolowski SS, Galbraith JM, Schaefer HF III (1998) *J Chem Phys* 108: 9398
19. Balaji V, Sunil KK, Jordan KD (1987) *Chem Phys Lett* 136: 309
20. Wesolowski SS, Crawford TD, Ferman JT, Schaefer HF III (1996) *J Chem Phys* 104: 3672
21. Zhang L, Dong J, Zhou M (2001) *Chem Phys Lett* 335: 334
22. Zhang L, Dong J, Zhou M (2000) *J Chem Phys* 113: 8700
23. Burkholder TR, Andrews L (1992) *J Phys Chem* 96: 10195
24. Riemer WH, Zika RG (1998) *Marine Chem* 62: 89
25. Goldman A, Coffey MT, Stephen TM, Rinsland CP, Mankin WG, Hannigan JW (2000) *J Quant Spectrosc Radiat Transfer* 67: 447
26. Jacox ME, Milligan DE, Moll NG, Thompson WE (1965) *J Chem Phys* 43: 3734
27. Devillers MC (1966) *C R Acad Sci* 262c: 1485
28. Lembke RR, Ferrante RF, Weltner W Jr (1977) *J Am Chem Soc* 99: 416
29. Stolvik R (1985) *J Mol Struct* 124: 133
30. Petraco NDK, Brown ST, Yamaguchi Y, Schaefer III HF (2000) *J Phys Chem A* 104: 10165
31. Dekook RL, Grev RS, Schaefer III HF (1988) *J Chem Phys* 89: 3016
32. Grev RS, Schaefer III HF (1989) *J Am Chem Soc* 111: 5687
33. Petraco NDK, Brown ST, Yamaguchi Y, Schaefer HF III (2000) *J Chem Phys* 112: 3201
34. Archibong EF, St-Amant A (1998) *Chem Phys Lett* 284: 331
35. Bu Y, Song X (2000) *J Chem Phys* 113: 4216
36. Bu Y (2000) *Chem Phys Lett* 322: 503
37. Bu Y, Song X, Liu C (2000) *Chem Phys Lett* 319: 725
38. Bu Y (2001) *Chem Phys* 273: 103
39. Bu Y (2001) *Chem Phys Lett* 338: 142
40. Frisch MJ, Trucks GW, Schlegel HB, Gill PMW, Johnson BG, Robb MA, Cheeseman JR, Keith T, Petersson GA, Montgomery JA, Raghavachari K, Al-Laham MA, Zakrzewski VG, Ortiz JV, Foresman JB, Peng CY, Ayala PY, Chen W, Wong MW, Andres JL, Replogle ES, Gomperts R, Martin RL, Fox DJ, Binkley JS, Defrees DJ, Baker J, Stewart JP, Head-Gordon M, Gonzalez C, Pople JA (1995) *Gaussian 94*, revision B.2. Gaussian, Pittsburgh, Pa
41. Becke AD (1993) *J Chem Phys* 98: 5648
42. Lee C, Yang W, Parr RG (1988) *Phys Rev B* 37: 785
43. Stephens PJ, Devlin FJ, Ashvar CS, Chabalowki CF, Frish MJ (1994) *Faraday Discuss* 99: 103
44. Perdew JP (1986) *Phys Rev B* 33: 8822
45. Perdew JP (1986) *Phys Rev B* 34: 7406
46. Perdew JP, Wang Y (1992) *Phys Rev B* 45: 13244
47. Cai ZL, Wang YF, Xiao HM (1992) *Chem Phys Lett* 191: 533
48. Hoffmann R (1983) *J Am Chem Soc* 105: 1084
49. Huber KB, Herzberg G (1979) *Constants of diatomic molecules*. Van Nostrand, New York