

Structures and Bonding Character of $\text{Ge}\cdots\text{CO}$ Weakly Bonding ComplexesYuxiang Bu^{*,†,‡} and Zhaohua Cao^{‡,§}

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The structural properties and the bonding character of the subcarbonyl Ge, GeCO, and $\text{Ge}(\text{CO})_2$ in their singlet and triplet states have been investigated using B3LYP, B3P86, B3PW91, and MP2 methods at 6-311+G* basis set level. Results indicate that GeCO species possesses a $^3\Sigma$ ground state with a singlet $^1\Sigma$ excited state above by 17 kcal/mol at CCSD(T)/6-311+G* level. The ground-state GeCO may be classified as carbene-like, and its $\text{CO}^{\delta-}$ moiety possesses CO^- character. Formation of GeCO causes the weakening of CO bonding; the produced Ge–C bond is weakly bonding consisting of a weak σ -bond and two weak π -bonds. The calculated dissociation energy is 16.8 kcal/mol at CCSD(T)/6-311+G* level. The corresponding potential well for the bending mode is shallow; therefore, GeCO molecule is easily bent. For $\text{Ge}(\text{CO})_2$, there exist two v-type structures for singlet state and one for triplet state; no linear ones are found for either state. The singlet state (1^1A_1) is more stable by 24.1 kcal/mol than the 2^1A_1 state and by 36.6 kcal/mol than the $^3\text{B}_1$ state at CCSD(T)/6-311+G* level; thus it may be considered as the ground state. The bond lengths in the 1^1A_1 ground state are very close to those in GeCO species, but the $\angle\text{GeCO}$ angle is bent by $\sim 10^\circ$ and the $\angle\text{CGeC}$ angle is only $\sim 76^\circ$. The Ge–C bond lengths in the 2^1A_1 state are longer by 0.03–0.07 Å than those of the 1^1A_1 state, and the $\angle\text{GeCO}$ and $\angle\text{CGeC}$ angles are 140 – 144° and 119 – 125° , being significantly different from those of the ground state. The corresponding triplet state has $\sim 50^\circ$ of $\angle\text{CGeC}$ angle and 162 – 166° of $\angle\text{GeCO}$ angle, but its Ge–C and C–O bonds are longer than those in the 1^1A_1 state by ~ 0.07 and 0.03 Å, respectively. These $\text{Ge}(\text{CO})_2$ species have essentially carbene-like character and should be referred to as bicarbonyl carbene-like. Comparison of the CO-dissociating energies between GeCO and $\text{Ge}(\text{CO})_2$ in their ground states indicates that the first-CO-dissociating energy of $\text{Ge}(\text{CO})_2$ is smaller by ~ 8.7 kcal/mol than that of GeCO; the averaged one over two COs is also smaller than that of GeCO. Detailed bonding analysis has implied that the possibility is small for the existence of the polycarbonyl Ge with more than two COs. This prediction may be also true for similar carbonyl complexes containing other nonmetal and nontransition metal atoms or clusters. Further study is very necessary.

1. Introduction

In view of the importance in industry and biological processes, many investigations have focused on the interaction of carbon suboxides with functional biological and material molecules. One of the species of interest is carbon monoxide, CO; it is a pervasive ligand and surface adsorbate. Due to its special coordination property, it is easily absorbed over isolated transition metal clusters, polynuclear transition metal complexes, and transition metal surfaces, perhaps changing the surface structural properties of material molecules. It also can be easily bounded to metalloporphyrins, heme proteins, and transition metal containing model compounds of biological interest, leading to a change of the biological functionality. On the other hand, a series of new progresses have also confirmed the absorption and coordination character to the nontransition metal and nonmetal clusters, compounds, and the polar molecules. Therefore, detailed investigations regarding the interaction between CO and various clusters and compounds are very

interesting for the approaches to the functionality and its control mechanism of the biological and material molecules.

A recent survey of the stretching frequencies of CO bounded to biological molecules has shown that there is an interesting change in the vibrational frequency for CO;¹ the affecting factors resulting in the frequency shift mainly involve the ring-ligand substituents,² CO ligand binding geometry and steric effects,^{3–5} redox potentials,⁶ CO binding affinities,⁷ and charge and polar interactions in the protein pocket.^{1,8,9} To interpret the dependence of the CO binding on these factors, many interesting models have been established. However, despite this, the interaction details and their nature are still unknown. Fortunately, many very important conclusions have been drawn for the interaction character between CO and many small transition metal clusters such as mono transition metal carbonyl complexes and bi transition metal carbonyl complexes, and much valuable information has also been provided for further approaches to the interaction between carbonyl and the active center of transition metal centered biological molecules. However, compared with the studies on transition metal carbonyl complexes, the studies on the interaction nature between CO and nontransition metals or nonmetals has appeared to be seriously absent. Obviously the continuously increased attention to these kinds of studies

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about the irregular bonding interaction have indicated that it is very important to explore these kinds of slight–weakly bound systems for the investigations of the interaction between CO and the nonmetal-centered active sites in biological and large molecules.

Due to the lack of bonding active d orbitals, when interacting with carbonyl complexes, the nonmetal and nontransition metal atoms cannot follow the bonding mechanism occurring in transition metal carbonyl complexes. Therefore, it may be predicted that the bonding interaction between CO and nontransition metals is significantly different from that between CO and transition metals. At least it is very difficult to form polycarbonyl complexes although CO is a very strong donor–acceptor ligand. This prediction has been confirmed by an early experiment. That early experimental report indicated that even if a strong-field ligand CO was used to interact with Si atom, only the single and double carbonyl Si complexes (SiCO and $\text{Si}(\text{CO})_2$) were experimentally found under the cryogenic condition.¹⁰ The corresponding electron spin resonance and optical spectra also confirmed the existence of these two species. Later, Stolvik also further determined experimentally the SiCO molecular geometry.¹¹ Although they claimed that SiCO and $\text{Si}(\text{CO})_2$ were linear molecules, they also implied the existence of the bent structures for SiCO with some uncertainty. However, their further semiempirical quantum chemistry CNDO calculations on SiCO molecule gave some information regarding the unstability of the nonlinear SiCO structure.¹⁰ A reasonable interpretation for this interference is that the molecular bending force constant is quite low and some constraints in the matrix sites induce bending. Similarly, the structure of $\text{Si}(\text{CO})_2$ species being a linear is also doubtful, because there was no certain experimental information to support this claim. Further, there also have not been any reports regarding the structures of Si carbonyl coordinations with more than two ligands before now.

Due to the importance of silicon and germanium elements in the fields of semiconductor and noncrystal materials, studies have still focused on structural properties of silicon-containing compounds. However, studies on germanium-containing compounds are relatively absent. Obviously, Ge is different not only from C and the other nonmetal elements but also from the transition metals in nature, although it has two kinds of d orbitals (fully occupied and fully empty d orbitals). Therefore, in forming polyligand complexes like transition metals, Ge does certainly exhibit some special bonding character.

The aim of this work is to give a detailed theoretical investigation on the geometric parameters, harmonic frequencies, dissociation energies, ionization potentials, and other relevant properties for GeCO and $\text{Ge}(\text{CO})_2$ species, the analogues of the carbonyl complexes of Si and the transition metals, and further to analyze the possibility of the existence for $\text{Ge}(\text{CO})_3$ or other polycarbonyl Ge complexes, using density functional theory methods and the wave function correlated ab initio method with a relatively large one-particle basis set.

2. Computational Details

The geometric optimizations on GeCO and $\text{Ge}(\text{CO})_2$ species at the singlet and triplet states have been performed using the density functional theory (DFT) and the second-order Moller–Plesset perturbation theory (MP2) at an extensive large 6-311+G* basis set level. The three density functionals methods used are B3LYP, B3P86, and B3PW91, as implemented in Gaussian 94.¹² These three models combine Becke three-parameter hybrid functional, which is a linear combination of Hartree–Fock exchange, Slater exchange, and B88 gradient-corrected ex-

change,¹³ with the correlation functionals of Lee et al.,^{14,15} Perdew (P86),^{16,17} and Perdew and Wang (PW91),¹⁸ respectively.

In recent years DFT has emerged as a reliable and computationally inexpensive method capable of successfully predicting the properties of difficult systems.^{19–24} It has been demonstrated that this method, especially on nonlocal functionals, can accurately predict the molecular properties of the systems that exhibit multireference character. It is desirable to employ it for the calculations on these weak interaction systems.

Therefore, the geometries are first optimized using DFT models described above. The harmonic vibrational frequencies are then obtained from analytic second derivative methods. Using the second-order Moller–Plesset perturbational theory, the geometries are reoptimized, and the harmonic vibrational frequencies are calculated via finite differences of analytic gradients. The corresponding energy quantities are also calculated using the third-order and fourth-order Moller–Plesset theories (MP3, MP4) with single, double, and quadruple substitutions and the coupled cluster singles and doubles including a perturbational estimate of the triples [CCSD(T)]. The calculations are performed with the Gaussian 94 program package, and all electrons are included in the electron correlation correction of the relevant energy quantities.

The calculations are mainly limited to the singlet and the triplet states of these two species for the bonding and charge distribution analysis and determinations of the ground states. The dissociation energies (D_e) and the ionization potentials (IP) are then obtained by comparing the energy differences between the ground states and the corresponding dissociated species ($\text{Ge} + \text{CO}$) for GeCO and ($\text{Ge} + 2\text{CO}$ or $\text{GeCO} + \text{CO}$) for $\text{Ge}(\text{CO})_2$, and those between the ground states and the corresponding monovalent cations GeCO^+ and $\text{Ge}(\text{CO})_2^+$.

In addition to the numerical error occurring in Hartree–Fock calculations, the accuracy of DFT calculations also depends on the number of points used in the numerical integration, therefore finer grids have been employed. In all DFT calculations performed here, the numerical integration of the functionals are carried out using a Gaussian 94 default grid consisting of 75 radial shells and 302 angular points per shell, resulting in about 7000 points per atom.

3. Results and Discussion

Tables 1 and 2 give the geometric parameters and harmonic frequencies obtained using three DFT (B3LYP, B3P86, and B3PW91) methods and the second-order Moller–Plesset perturbational theory (MP2) with a relatively large basis set (6-311+G*) for GeCO and $\text{Ge}(\text{CO})_2$ at their singlet and triplet states. The corresponding spin-density distributions, charge populations, and zero-point vibrational energies for all the stable species are collected in Table 3. Tables 4 and 5 list the calculated total energies (E_T) and the dissociation energies (D_e) for GeCO and $\text{Ge}(\text{CO})_2$ in their ground states and the corresponding state–state energy separations (ΔE) relative to the ground states, respectively. To test the bonding situation of these species, the ionization potentials (IP) are also determined by comparing the energy difference between the ground-state species and their corresponding monovalent cations; the results are also given in Tables 4 and 5. In the following subsections, discussions will be made according to the structural classification.

3.1. GeCO Species. The geometric optimizations have indicated that there are two conformers for GeCO species in the singlet ($^1\Sigma$) and triplet ($^3\Sigma$) states; the triplet state is more stable than the singlet state and thus may be assigned to the

TABLE 1: Optimized Geometric Parameters (Å, deg) and Harmonic Vibrational Frequencies (cm⁻¹) at Four Theoretical Levels with a 6-311+G* Basis Set for GeCO Species at Two States and Those for Free State CO and CO⁻ Molecules

state	method	$r_{\text{Ge-C}}$	$r_{\text{C-O}}$	$\angle\text{GeCO}$	ω_1	ω_2	ω_3	ω_4
GeCO (³ Σ)	B3LYP	1.9401	1.1549	180.0	286.2	286.4	399.0	1967.0
	B3P86	1.9230	1.1532	180.0	292.5	292.6	421.8	1995.1
	B3PW91	1.9274	1.1537	180.0	292.9	293.0	417.2	1991.4
	MP2	1.9503	1.1557	180.0	289.0	289.0	400.1	2009.8
	expt							
GeCO (¹ Σ)	B3LYP	1.9421	1.1581		238.5	334.0	409.0	1964.7
	B3P86	1.9233	1.1570		238.1	341.0	432.4	1987.9
	B3PW91	1.9270	1.1576		238.9	340.5	429.1	1984.0
	MP2	1.9194	1.1712		223.2	319.2	462.9	1906.6
	expt							
CO (¹ Σ)	B3LYP		1.1277					2212.8
	B3P86		1.1268					2225.9
	B3PW91		1.1273					2222.9
	MP2		1.1393					2129.3
	expt		1.1283					2144.0
CO (² Π)	B3LYP		1.1889					1649.6
	B3P86		1.1870					1671.4
	B3PW91		1.1853					1667.6
	MP2		1.1815					1796.7
	expt							

TABLE 2: Optimized Geometric Parameters (Å, deg) and Harmonic Vibrational Frequencies (cm⁻¹) at Four Theoretical Levels with a 6-311+G* Basis Set for Ge(CO)₂ Species at Two States

	Ge(CO) ₂ (1 ¹ A ₁) (v-type)				Ge(CO) ₂ (³ B ₁) (v-type)				Ge(CO) ₂ (2 ¹ A ₁) (v-type)			
	B3LYP	B3P86	B3PW91	MP2	B3LYP	B3P86	B3PW91	MP2	B3LYP	B3P86	B3PW91	MP2
$r_{\text{Ge-C}}$	1.9535	1.9296	1.9331	1.9276	2.0259	2.0041	2.0077	2.0185	2.0221	1.9622	1.9677	1.9401
$r_{\text{C-O}}$	1.1479	1.1473	1.1478	1.1603	1.1781	1.1795	1.1799	1.1782	1.1504	1.1498	1.1505	1.1665
$\angle\text{GeCO}$	170.25	170.83	170.84	171.20	163.60	166.81	162.79	161.95	140.80	144.30	144.35	144.07
$\angle\text{CGeC}$	77.84	76.31	76.46	75.46	51.26	49.71	49.75	49.99	125.28	118.84	118.69	118.93
ω_1 (A ₁)	87.80	86.63	86.58	77.96	137.26	182.88	181.97	163.22	37.09	67.58	67.83	
ω_2 (B ₁)	310.41	322.22	32.05	310.99	259.14	266.17	265.64	271.26	211.92	236.99	273.68	
ω_3 (B ₂)	311.82	326.89	325.45	325.95	279.76	295.37	294.63	306.42	215.59	303.78	302.50	
ω_4 (A ₁)	382.21	403.55	401.93	397.81	311.60	312.74	511.00	325.78	282.77	268.99	266.05	
ω_5 (A ₂)	390.37	411.93	408.33	424.64	359.96	407.11	402.99	413.05	339.86	392.62	391.06	
ω_6 (B ₂)	408.66	438.18	435.38	464.99	459.52	500.60	498.70	500.69	362.63	430.01	424.34	
ω_7 (A ₁)	522.70	536.80	534.98	524.84	520.35	544.59	542.25	621.44	455.08	473.19	471.82	
ω_8 (B ₂)	1999.84	2022.11	2019.27	1937.22	1824.21	1826.79	1823.10	1995.87	1959.36	1980.57	1976.33	
ω_9 (A ₁)	2072.15	2090.49	2087.33	1995.04	1832.26	1831.54	1829.27	2152.35	2016.73	2043.22	2038.70	

TABLE 3: Calculated Spin-Density Distribution (ρ), Charge Population (Q) and Zero-Point Vibrational Energies (ZPVE, kcal/mol) for GeCO and Ge(CO)₂ Species at DFT/6-311+G* and MP2(full)/6-311+G* Levels

state	method	Q_{Ge}	Q_{C}	Q_{O}	ρ_{Ge}	ρ_{C}	ρ_{O}	ZPVE
GeCO (¹ Σ)	B3LYP	0.227	-0.139	-0.088				4.2122
	B3P86	0.203	-0.127	-0.076				4.2878
	B3PW91	0.200	-0.119	-0.080				4.2781
	MP2(full)	0.217	-0.025	-0.192				4.1629
	expt							
GeCO (³ Σ)	B3LYP	0.198	-0.111	-0.087	1.397	0.342	0.261	4.2010
	B3P86	0.174	-0.100	-0.074	1.398	0.333	0.269	4.2914
	B3PW91	0.167	-0.088	-0.079	1.406	0.327	0.266	4.2809
	MP2(full)	0.123	0.047	-0.170	1.579	0.103	0.318	4.2713
	expt							
Ge(CO) ₂ (1 ¹ A ₁) (v-type)	B3LYP	0.255	-0.019	-0.109				9.2722
	B3P86	0.221	-0.008	-0.103				9.4907
	B3PW91	0.216	0.002	-0.110				9.4642
	MP2(full)	0.229	0.104	-0.218				9.2342
	expt							
Ge(CO) ₂ (2 ¹ A ₁) (v-type)	B3LYP	0.274	-0.115	-0.021				8.4074
	B3P86	0.230	-0.111	-0.004				8.8295
	B3PW91	0.240	-0.114	-0.006				8.8590
	MP2(full)	0.167	-0.002	-0.082				
	expt							
Ge(CO) ₂ (³ B ₁) (v-type)	B3LYP	0.407	-0.014	-0.190	0.854	0.228	0.345	8.5546
	B3P86	0.375	-0.003	-0.184	0.837	0.208	0.373	8.8173
	B3PW91	0.369	0.004	-0.189	0.844	0.205	0.373	8.7912
	MP2(full)	0.399	0.074	-0.274	0.984	0.035	0.473	9.6497
	expt							

ground state. However, both two states are structurally linear and also similar.

In detail, the results in Table 4 indicate that the singlet state (¹Σ) is significantly higher than the triplet ground state (³Σ); the calculated state-state adiabatic energy separations between these two states are within 17–20 kcal/mol at several different

theoretical levels. Three DFT methods (B3LYP, B3P86, and B3PW91) give good agreement results (17.6–20.1 kcal/mol) with a small deviation of ca. 2.5 kcal/mol. The results at three MP levels (MP2, MP3, and MP4) also agree well with each other. They are very close to the CCSD value and are slightly greater than the CCSD(T) value (17 kcal/mol). This good

TABLE 4: Calculated Total Energies (E_T , au), Dissociation Energies (D_e , kcal/mol), and Vertical Ionization Potentials (IP_v , kcal/mol) of GeCO in the Ground State and the Corresponding State–State Energy Separations (ΔE , kcal/mol) Relative to the Ground State at 6-311+G* Basis Set Level

	E_T ($^3\Sigma$)	ΔE ($^1\Sigma$)	D_e ($^3\Sigma$)	IP_v ($^3\Sigma$)	IP_a ($^3\Sigma$)
B3LYP	−2190.322 944 8	17.66	27.88	192.95	187.08
B3P86	−2191.284 141 3	19.74	32.57	208.29	202.75
B3PW91	−2190.242 914 3	20.18	30.50	195.52	189.87
PMP2	−2188.863 115 3	20.06	19.86	183.36	177.14
PMP3	−2188.808 035 2	19.93	15.74		176.55
MP4 _{SDQ}	−2188.851 171 3	18.37	14.41		175.05
CCSD	−2188.837 211 9	18.83	14.08		174.83
CCSD(T)	−2188.862 938 4	17.04	16.81		176.22

TABLE 5: Calculated Total Energies (E_T , au), Dissociation Energies (D_e , kcal/mol) and Vertical Ionization Potentials (IP_v , in kcal/mol) of Ge(CO)₂ in the Ground State and the Corresponding State–State Energy Separations (ΔE , kcal/mol) Relative to the Ground State at 6-311+G* Basis Set Level^a

	E_T (1^1A_1)	ΔE (3B_1)	ΔE (2^1A_1)	$D_{e,1}$ (1^1A_1)	$D_{e,T}$ (1^1A_1)	IP_v (1^1A_1)
B3LYP	−2303.693 470 8	31.71	24.41	13.45	41.33	185.29
B3P86	−2304.897 224 2	29.34	20.56	17.50	50.07	200.40
B3PW91	−2303.563 957 2	29.07	20.32	15.36	45.86	187.09
PMP2	−2301.998 839 3	37.46	21.74	12.94	32.80	176.89
PMP3	−2301.924 821 6	33.10	23.64	8.29	24.03	
MP4 _{SDQ}	−2301.981 037 6	37.36	21.99	7.20	21.61	
CCSD	−2301.961 388 4	34.87	22.51	5.46	19.54	
CCSD(T)	−2302.010 279 2	36.58	24.12	8.10	24.91	

^a $D_{e,1}$ denotes the first CO dissociation energy, while $D_{e,T}$ denotes total CO dissociation energy.

agreement, together with that found for the other special systems,^{19–24} has indicated that the state–state energy separation falling within 17–20 kcal/mol is reliable.

Although the singlet state is higher than the triplet state, they are structurally similar. For the ground state ($^3\Sigma$), the optimized Ge–C bond length is within 1.9230–1.9401 Å at DFT theoretical levels; the largest deviation is ~0.013 Å. They are slightly smaller by 0.010–0.025 Å than the MP2 value (1.9503 Å). The optimized C–O bond length is within 1.1532–1.1557 Å with only a largest deviation of 0.0025 Å. This best agreement among the bond length results, together with the recent investigations about other weakly bound species, has implied that three DFT and MP2 methods are applicable here. For the singlet state ($^1\Sigma$), a similar tendency has also been observed. The optimized Si–C bond length is 1.9194–1.9421 Å, and the C–O bond length falls within 1.1570–1.1712 Å at four different theoretical methods. The calculated largest deviations are only 0.022 and 0.014 Å, respectively. The C–O bond in the singlet state is slightly longer than that of the triplet state by a very small amount. These C–O bond lengths in both states are longer by ca. 0.03 Å than those (1.1268–1.1393 Å) of the free state CO ($^1\Sigma$) at four theoretical levels. However, they are slightly shorter by ~0.03 Å than those of the CO[−] free state ($^2\Pi$). This phenomenon has indicated that the combination of Ge with CO ($^1\Sigma$) weakens the C–O bonding strength and causes the CO^{δ−} moiety in GeCO to possess CO[−] anion character. From the optimized Ge–C bond length, it also may be known that the Ge–C bonds in GeCO ($^3\Sigma$, $^1\Sigma$) species are slightly shorter than the common Ge–C singlet bond. This observation has implied that from the viewpoint of the bond length the Ge–C bond of the linear GeCO species in every state may be considered as a weak doublet bond composed of perhaps a σ bonding and a weak π bonding or weak σ and π bonding. This prediction may be confirmed by the following vibrational frequency analysis and the charge-transfer case.

For the ground-state GeCO ($^3\Sigma$), there are two degenerate bending vibrational modes (ω_1 and ω_2 in Table 1) and two stretching–compression modes (ω_3 and ω_4 in Table 1). The bending modes are referred to the distortions of the linear

molecule into a bent one by two end atoms (Ge and O) departing from the molecular axis according to two directions vertical to the molecular axis. No Renner–Teller effect exists for this state. The calculated bending vibrational frequencies are in the range from 286 to 292 cm^{−1} at the four theoretical levels. These small bending vibrational frequencies imply that the potential energy surface for the distortion to the bent molecule is flat. No experimental values have been reported for the vibrations of this molecule. However, an early experimental report on SiCO species had implied this low-bending vibrational mode.¹⁰ Actually, GeCO molecule with a small departure from linearity is slightly unstable with respect to the linear conformation. However, the energy derivative at the linear equilibrium configuration is very small; viz., the corresponding potential well is shallow. This is to say that the bending force constant is quite low and some constraints in the matrix sites may induce bending. This easy bending tendency may be also attributed to the fact that there are two weak π -bonding interactions between Ge and the CO moiety. Certainly, two weak π -bonds are degenerate for the $^3\Sigma$ ground state, while those for the $^1\Sigma$ state are not, causing the vibrational coupling to produce two nondegenerate bending vibrational modes (265 and 377 cm^{−1}). In other words, this singlet state is subject to the Renner–Teller effect. The following bonding analysis will give a detailed interpretation for this phenomenon.

The modes (ω_3 and ω_4) are actually referred to the Ge–C and C–O stretching–compression vibrations. Four theoretical methods estimate the harmonic frequencies to be within 399–421 and 1967–2010 cm^{−1} for the ground state ($^3\Sigma$) and within 409–469 and 1906–1987 cm^{−1} for the singlet state ($^1\Sigma$). Very good agreement can be observed for every vibrational mode of every species. No experimental spectroscopy data have been reported for GeCO species for its any states. Only the C–O mode of ground-state SiCO has been experimentally observed to be 1899.3 cm^{−1}.¹⁰ Although the calculated values are 573–587 cm^{−1} for the Si–C vibration, the corresponding IR intensity is very small and tends to zero. Thus it can be concluded that no signal can be experimentally observed for this mode. However, the absolute change in the C–O vibrational mode is

significant after CO is combined with Ge atom. The frequency red shift is 230–265 cm^{-1} at DFT/6-311+G* level and 120 cm^{-1} at MP2(full)/6-311+G* level. The considerable decrease in the C–O mode frequency implies weakening of the C–O bonding, and magnitude of the weakening is greater than that in the transition metal MCO systems. The difference between GeCO and transition metal MCO mainly originates from the electronic configuration difference between Ge and the transition metal atoms. The Ge–CO vibrational frequency reflects the binding strength of Ge with CO species, and is within 399–421 cm^{-1} . From this, it seems to imply that the Si–C bonding in GeCO species in the ground state is weak. Similar analysis may be true for the singlet state ($^1\Sigma$) of GeCO species; the Ge–CO vibrational red shifts are 220–267 cm^{-1} .

The dissociation energy is also an important quantity to measure Ge–CO bonding interaction. No experimental estimate of the dissociation energy has been reported for the linear ground-state GeCO species. The theoretically calculated dissociation energies of the GeCO in the ground state ($^3\Sigma$) using several different methods with 6-311+G* basis set are given in Table 4. No zero-point-energy and counterpoise corrections have been made for these D_e values. The corrections may slightly reduce the D_e values, but they do not significantly change the relative regularity. Thus the following discussions are based on uncorrected D_e values. The results obtained from three DFT methods are within 27.9–32.6 kcal/mol. They are considerably greater by 12–13 kcal/mol than the values obtained by the correlated wave function methods. The high-level CCSD(T) value is 16.8 kcal/mol, while the fourth-order MP4(SDQ) and CCSD methods without the contribution of the triple excitation underestimate the dissociation energy by 2.4–2.8 kcal/mol. Fortunately, the third-order MP3 gives a result very close to the CCSD(T) one. Together with the previous investigations, it can be predicted that three DFT methods slightly overestimate the ground-state dissociation energy, and the dissociation energy of GeCO ($^3\Sigma$) species of at least 17 kcal/mol is reliable. These D_e values have implied that the Ge–CO bonding should not be considered as a very weak interaction, but it also should not be considered as a chemical bond of interest. It is weaker than common chemical bonding but stronger than the intermolecular weak interaction. This prediction is basically in agreement with the analysis mentioned above.

Table 4 also lists the vertical ionization potential (IP_v) for GeCO in the ground state ($^3\Sigma$) calculated at several different levels of theory. Comparison among them indicates that three DFT methods yield an IP_v value greater by 13–28 kcal/mol than those using the MPn ($n = 2, 3, 4$) and CC methods. The B3P86 value is greater by 13–15 kcal/mol than the B3LYP and B3PW91 results. This deviation is only 7.8% of the total averaged IP_v ; thus it can be said that three DFT methods agree well in yielding IP_v . In addition, the best agreement is among several correlated wave function methods (MPn, $n = 2, 3, 4$, and CC): the largest deviation is only 3.3 kcal/mol. Therefore, it can be concluded that the values of 170–190 kcal/mol should be reliable for the ground-state GeCO species. These large IP_v values indicate that the frontier orbital energy level is very low, and the electrons occupying them are very stable, not being easily removed. These IP_v values are greater by only ~6 kcal/mol than the Ge atomic IP (181.92, 196.10, 183.95, and 174.37 kcal/mol at three DFT and CCSD(T,full) levels). This indicates that Ge moiety in GeCO ($^3\Sigma$) still possesses Ge atomic character to a large extent. The small increase amount for IP may be attributed to charge transfer from Ge to CO which increases

the attractive force of Ge core to the outer-shell electrons and makes ionization of the electrons around the Ge core difficult. In addition, this small increase may be also interpreted as the contribution from the ionization potential of CO moiety.

All these observations depend on special bonding character. The valence electronic configurations for the triplet ground state ($^3\Sigma$) and the singlet excited state ($^1\Sigma$) are, respectively

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

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

Of interest is that there are a couple of degenerate π orbitals in the frontier orbital zone. The main difference between the two electronic states is referred to the different occupations of these two degenerate π orbitals. If two electrons fill two π orbitals with the same spin directions, $^3\Sigma$ state may be yielded, while if two electrons occupy only one π orbital with opposite spin directions, $^1\Sigma$ state is produced. Obviously, this singlet state ($^1\Sigma$) should be energetically higher than the triplet state ($^3\Sigma$). Inspection of the orbital components reveals that these two π orbitals actually describe the interaction between Ge p orbitals and the antibonding π^* orbitals of CO, viz., the bonding interaction in the Ge–C bonding zone and the antibonding interaction in the C–O bonding zone.

Thus it can be predicted that, in the formation process, Ge uses the empty p orbital to accept the coordination lone-pair electrons of the donor CO, yielding the high-energy-level backbone σ -type bonding ($4\sigma^2$). In addition to this bonding, the Si π -type p orbitals interact with the π^* antibonding orbitals to form three-center conjugated π bonds. This conjugated π coupling further strengthens the Si–C bond, but it reduces the C–O bond. This bonding interaction mechanism is basically similar to those occurring in the transition metal carbonyl complexes but with a major difference in the components. That is, for GeCO species Ge uses its p-type orbitals to form the feedback π bond instead of the d-type orbitals. Since 4p orbitals are energetically higher than 3d orbitals for the third-row elements, electron transfer from Ge 4p to CO π^* orbitals is easier than that from 3d to CO π^* orbitals as occurred in the transition metal MCO. Thus the weakening of C–O bonding in GeCO species is greater than that in the transition metal carbonyl complexes, MCO. This prediction may be confirmed by Mulliken population analysis. The net charge transfers from Ge to CO are 0.12–0.20 e at the MP2(full) level for GeCO ($^3\Sigma$) species; the transferred charges mainly distribute over the O center and should involve some amount of CO π -electron component.

However, comparison of the spin density reflects that GeCO ($^3\Sigma$) should also exhibit carbene-like character and may be named as carbonyl germene (viz., H_2Ge), an analogue of carbene H_2C : and silene H_2Si :). Of two spin-single electrons 1.4–1.6 e (70–80%) distribute over the Ge center, while the remaining is equivalently over the C (~0.33 e, ~17%) and O (~0.27 e, ~14%) centers. This indicates that two degenerate HOMOs with two spin-unpaired electrons mainly describe the Ge π -type orbital character. This prediction agrees well with the analysis about vertical ionization potentials. As mentioned above, the IP_v of GeCO ($^3\Sigma$) is close to the first IP of Ge atom. Calculations on the ionized GeCO^+ species indicates that, when an electron is removed, the $\text{GeCO } ^3\Sigma$ state becomes the $\text{GeCO}^+ ^2\Pi$ state. In the latter, the positive charge is mainly over the Ge center with +0.79 to +0.83. The spin density distribution also reflects that the spin-unpaired electron is over the Ge center with an

amount of ~ 0.86 . From this it can be distinctly seen that the ionized electron is certainly the HOMO π electron with a significant Ge p_{π} -type orbital character. Comparison of HOMO coefficients also supports this analysis.

A similar analysis is also true for the GeCO ($^1\Sigma$) state, although its electronic configuration is different from that of the $^3\Sigma$ state. In addition, it should be noted that although in the bond length aspect $\text{CO}^{\delta-}$ moiety in GeCO exhibits CO^- character, the spin density is considerably different from that of the CO^- species ($\text{C} \sim 1.0$ and $\text{O} \sim 0.0$) and there is also a large charge distribution difference between them. Thus from this point it cannot be classified as a CO^- anion compound.

3.2. $\text{Ge}(\text{CO})_2$ Species. The above analysis regarding GeCO species indicates that the Ge–CO bond is weak relative to the usual chemical bonds; the corresponding bonding energy is ~ 16 kcal/mol. This bonding energy value for Ge–CO species implies that Ge is seemingly capable of combining two carbonyls to form $\text{Ge}(\text{CO})_2$ compound. In an early experiment Weltner demonstrated the existence of the bicarbonyl Si, $\text{Si}(\text{CO})_2$ and found a slight weak band at 1928 cm^{-1} which was attributed to the formation of OCSiCO , and this molecule was assigned to be linear. However, no detailed IR vibrational analysis has been given. Our recent primary investigations on $\text{Si}(\text{CO})_2$ have indicated that $\text{Si}(\text{CO})_2$ molecule is not linear, whether in the triplet state or in the singlet state. Not only C–Si–C is not linear, but also Si–C–O is not linear. As mentioned above, GeCO possesses carbene-like property and a very flat bending potential well; thus it is a problem worthy of consideration whether $\text{Ge}(\text{CO})_2$ is linear or not. To explore the structure and bonding at four theoretical levels mentioned above, the molecular geometries have also been optimized for $\text{Ge}(\text{CO})_2$ species in its singlet and triplet states, respectively. Results have indicated that whether in the singlet or triplet state $\text{Ge}(\text{CO})_2$ species possess v-type structures and both molecular fragment units (C–Ge–C and Ge–C–O) are bent. The linear structure search told us that there exists only a second-order saddle point. All attempts to find other stable isomers for $\text{Ge}(\text{CO})_2$ species have been unsuccessful. In optimizations, three stable structures have been found which are referred to two $^1\text{A}_1$ states and one $^3\text{B}_1$ state. The corresponding optimized geometric parameters and vibrational frequencies are given in Table 2, the charge population and the spin density distribution are listed in Table 3, and some relevant energy quantities are collected in Table 5.

For the singlet state, there are two $^1\text{A}_1$ states, both of which are of v-type structure, while for the triplet state there is only one state. Opposite to the GeCO species, both singlet states are more stable than the triplet state by 29–31 and 7–9 kcal/mol, respectively. Between these two $^1\text{A}_1$ states, the energy difference is 20–24 kcal/mol. Thus to distinguish these two states, 1^1A_1 is used to denote the ground state, while 2^1A_1 denotes the first singlet excited state (see Figure 1). According to the analysis about the applicability of three DFT methods (B3LYP, B3P86, and B3PW91) and Moller–Plesset perturbation theory and a good agreement among the state–state energy separations, it can be concluded that the state–state energy separations for $\text{Ge}(\text{CO})_2$ species of 30–36 kcal/mol for $^3\text{B}_1$ – 1^1A_1 state and 20–24 kcal/mol for 2^1A_1 – 1^1A_1 state are reliable. For the linear states, whether the $^1\Sigma_g$ or the $^3\Pi_u$ state, no stable minimum exists on the global potential energy surface. In addition, the optimized geometries by the linear constraint have very great energy separations relative to the ground state (1^1A_1).

For the ground state (1^1A_1), the data in Table 2 have shown that the key angle $\angle\text{CGeC}$ reflecting the molecular nonlinear

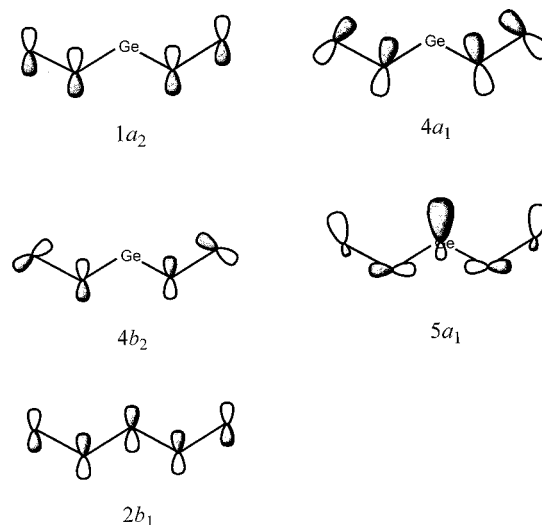


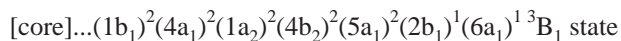
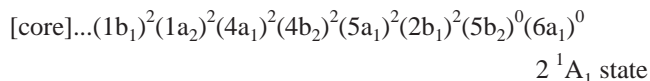
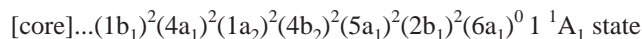
Figure 1. Orbital interaction diagram for the 2^1A_1 state ($1a_2$ and $2b_1$ are p-type orbitals and the others are s-type orbitals).

character is only 75 – 78° at three DFT and MP2 levels with 6-311+G* basis set. Another very interesting bond angle is $\angle\text{GeCO}$, whose value is ca. 171° . This molecule belongs to C_{2v} symmetry, two GeCO moieties are symmetrically laid in two sides of C_2 axis, and every O atom departs from its Ge–C axis by 9 – 10° outside. The optimized Ge–C bond lengths fall within 1.9276 – 1.9535 \AA and are very close to those in GeCO ($^3\Sigma$) and GeCO ($^1\Sigma$) species, while the C–O bond lengths are within 1.1473 – 1.1603 \AA and are also very close to those in monocarbonyl Ge species. This observation indicates that there is bonding character in the bicarbonyl Ge systems similar to that in the monocarbonyl Ge system. The very small deviation in Ge–C and C–O bonds between GeCO and $\text{Ge}(\text{CO})_2$ species may be attributed to the breaking of a weak π bonding (there are two weak π bonds for GeCO but there is only one for $\text{Ge}(\text{CO})_2$). Optimization searches have also found another $^1\text{A}_1$ state, viz., the 2^1A_1 state in this work. The corresponding state–state energy separation relative to the ground state (1^1A_1 state) is about 20–24 kcal/mol at four theoretical levels. Another apparent difference of 2^1A_1 state from the 1^1A_1 state is embodied in the molecular geometries. The optimized $\angle\text{CGeC}$ angle is 119 – 125° , and is significantly greater than that ($\sim 77^\circ$) of the ground state (1^1A_1). The angle $\angle\text{GeCO}$ ($\sim 144^\circ$) in the 2^1A_1 state is also significantly smaller than that ($\sim 170^\circ$) in the 1^1A_1 state. Although the C–O bond length is very close to that of the ground state, the Ge–C bond length is slightly longer by $\sim 0.033\text{ \AA}$ than that of the ground state.

However, for the triplet state ($^3\text{B}_1$), there are also obvious changes compared with the ground state and GeCO species, and also there is a significant difference from the 2^1A_1 state. First, the bond angle $\angle\text{CGeC}$ is reduced by ca. 27° ; the $\angle\text{GeCO}$ bond angle is also reduced by 4 – 10° . In particular, the Ge–C bond length is significantly longer by $\sim 0.07\text{ \AA}$ than that in the 1^1A_1 ground state and GeCO ($^3\Sigma$, $^1\Sigma$) states, and also longer by 0.04 – 0.06 \AA than that in the 2^1A_1 state, while the C–O bond becomes longer by about 0.03 \AA . It should be noted that all attempts to find other low-lying triplet excited states have been unsuccessful.

Obviously all these considerable structural difference among the three electronic states should be attributed to the bonding differences among them. At the MP2(full)/6-311+G* level, the

determined frontier orbital valence electronic configurations for the three states are



It is easily understood that the excitation of an electron from $2b_1$ to $6a_1$ orbitals of $1^1 A_1$ state may directly yield the $3B_1$ excited state. Inspection of the high-energy-level bonding orbitals reveals that the HOMO ($2b_1$) denotes the interaction of Ge π -type p orbital with the antibonding π^* orbital of CO and mainly reflects the π -bonding interaction between Ge and C centers and the π^* -antibonding interaction between C and O centers, while the lowest unoccupied molecular orbital (LUMO), $6a_1$ orbital, describes the σ^* -type antibonding interaction between the s orbital of Ge and the σ^* -type orbital of CO species. In addition, several other interacting bonds in interest are $4a_1$, $1a_2$, $4b_2$, and $5a_1$ orbitals. The $4a_1$ and $1a_2$ orbitals depict the σ -bonding and π -bonding interactions 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 Ge—C σ -bonding orbital.

Obviously, the key molecular orbitals describing the bonding interaction between Ge and CO moieties are $5a_1$ and $2b_1$ for the ground state and $5a_1$, $2b_1$, and $6a_1$ for the excited state ($3B_1$). The excitation of an electron from $2b_1$ to $6a_1$ orbital significantly weakens the Ge—C π -bonding interaction and increases the Ge—C σ^* -antibonding interaction. The net effect by $2b_1 \rightarrow 6a_1$ excitation on the Ge—C bond is the weakening of Ge—C bond, and it causes the Ge—C bond to become long. The calculated considerable bond length increase in the $3B_1$ state compared with the $1^1 A_1$ ground state has provided powerful evidence for the analysis mentioned above. At the same time, although transferring a $2b_1$ orbital electron to $6a_1$ orbital also reduces the π^* -antibonding interaction between C and O centers; this transfer greatly increases the σ^* -antibonding interaction between them. Thus, the overall effect of this transfer on the C—O bond is the weakening of the C—O bond. This prediction has also fully been proven by the optimized geometric parameters given in Table 2 (the C—O bond in $\text{Ge}(\text{CO})_2$ ($3B_1$) is longer than that in $\text{Ge}(\text{CO})_2$ ($1^1 A_1$) by ~ 0.03 Å).

However, for the $2^1 A_1$ state, although the electronic configuration is the same as that of the $1^1 A_1$ state, the bonding situation is different for each. As discussed for the $1^1 A_1$ state, the key molecular orbitals describing the bonding interaction of Ge—CO are also $5a_1$ and $2b_1$. The $2b_1$ is same as those in the $1^1 A_1$ and $3B_1$ states and describes the π -type interaction between Ge p orbital and π^* of CO moieties, but $5a_1$ is a bent σ -type bonding orbital. The other bonding orbitals ($1b_1$, $1a_2$, $4a_1$, and $4b_2$ orbitals) also have some significant differences from those of the ground state ($1^1 A_1$) in orbital components. This point may be proven by the following bonding analysis.

Another interesting characteristic for these bicarbonyl Ge compounds is that there are different $\angle \text{CGeC}$ and $\angle \text{GeCO}$ bond angles for three different states. As exhibited in Table 2, they are to some extent similar to those of H_2Ge , an analogue of carbene, but are different from those of GeCO species and some transition metal carbonyl compounds. For H_2Ge species, the singlet state ($1^1 A_1$) is also more stable than the triplet state ($3B_1$), but its $\angle \text{HGeH}$ bond angle ($1^1 A_1$, $\sim 91.5^\circ$) is smaller than that

for the triplet state ($3B_1$, $\sim 120.0^\circ$). Obviously $\text{Ge}(\text{CO})_2$ may be classified as an analogue of carbene, but its bonding is different from the carbene-like species. The difference between them is certainly attributed to the participation of CO as ligand. Inspection of the natural bond orbital (NBO) reveals that for the ground-state species Ge utilizes two hybrid orbitals ($\text{sp}^{8.25\text{d}^{0.1}}$) to interact with two C ($\text{sp}^{0.54}$) hybrid orbitals to form two Ge—C bonds. In addition, conjugated π bonding is also formed to strengthen the Ge—C interaction. Obviously if Ge uses its pure p orbitals to form Ge—C bonds, the $\angle \text{CGeC}$ angle should be 90° . Due to the participation of Ge s orbital, and under the consideration of the increase of Ge p_z orbital component along with the molecular axis, the $\angle \text{CGeC}$ bond angle becomes smaller than 90° . Another dominant factor to cause the small $\angle \text{CGeC}$ is the repulsion interaction from the lone-pair electrons of Ge. In addition, the change of the hybrid index of C center also plays an arbitrary role in forming a small $\angle \text{CGeC}$ angle. For the triplet state, from analysis mentioned above, it can be easily understood that there is a $\angle \text{CGeC}$ angle much smaller than that for the singlet ground state. The electron exchange between $2b_1$ and $6a_1$ orbitals increases the s-orbital component of the hybrid orbital used to form Ge—C bonds. Combining the antibonding character of Ge—C in $6a_1$ orbital, a small $\angle \text{CGeC}$ angle is completely reasonable. At the same time, the decrease of $\angle \text{CGeC}$ angle also results in the further bending of $\angle \text{GeCO}$ angle to a larger extent. However, for the $2^1 A_1$ state, the hybrid orbital for Ge used to form Ge—C σ bonding is sp^2 , while the hybrid orbital of C used to form this bond is also basically sp^2 . The orbital index of the hybrid orbital occupied by the lone-pair electrons (~ 1.75 e) is $\text{sp}^{0.14}$. Thus, the $\angle \text{CGeC}$ angle tending to 120° is reasonable. Analysis of the natural bond orbital character has also revealed that for all these states ($1^1 A_1$, $2^1 A_1$, and $3B_1$) the σ -type hybrid orbital of every C is $\text{sp}^{\sim 1.8}$ in the C—O bond, while that of every O is sp. Namely, the effective bonding orbital of C center obviously deviates from the associating C—O axis by $\sim 13^\circ$, therefore resulting in the C—O bond apart from the Ge—C axis by $\sim 13^\circ$. Of course, outside deviation may be due to the repulsion interaction between two —C=O moieties.

Table 2 also lists nine vibrational mode frequencies obtained using four theoretical methods for every species. Obviously, ω_8 (B_2) and ω_9 (A_1) may be undoubtedly assigned to two C=O character absorption peaks with asymmetric and symmetric stretching vibrations, while ω_6 (B_2) and ω_7 (A_1) correspond to the Ge—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 ω_1 (A_1) mode. The remaining modes are the $\angle \text{GeCO}$ angle 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). As noted in the analysis concerning geometric parameters, very good agreement among the data obtained using four theoretical methods can also be observed. Further, a very interesting observation is the changes of the vibrational frequencies for C—O stretching mode. For the $1^1 A_1$ ground state, although the C—O bond length change is close to that of GeCO species, the stretching frequencies are greater by 40 – 120 cm^{-1} than those of GeCO , and are close to those of the free state CO ($1^1 \Sigma$) molecule. They are significantly larger by 200 – 240 cm^{-1} than those of CO^- ($2^1 \Pi$) in its free state. This indicates that the weakening of the C=O moiety in the $\text{Ge}(\text{CO})_2$ ground state is smaller than that in the monocarbonyl Ge, and the CO of $\text{Ge}(\text{CO})_2$ possesses the free-state CO molecular character. From this it can be predicted that the CO moieties in polycarbonyl

Ge such as $\text{Ge}(\text{CO})_3$ or $\text{Ge}(\text{CO})_4$, etc. are essentially close to the free-state CO ($^1\Sigma$). However, these kinds of polycarbonyl Ge compounds exist with very weak molecular interaction, so they may be unstable as complexes. Perhaps this is why there are no experimental reports regarding the existence of tricarbonyl Ge or other polycarbonyl Ge complexes. In addition, there is no apparent frequency change for the Ge–C vibrations in $\text{Ge}(\text{CO})_2$ (1^1A_1) compared with that in GeCO ($^3\Sigma$), but a very low vibrational frequency corresponding to $\angle\text{CGeC}$ angle scissor-cutting mode has implied the weak bonding interaction between Ge and two COs, indicating that the potential energy surface is flat with respect to the bending of the $\angle\text{CGeC}$ angle, and these polycarbonyl molecules are facile.

Similarly for the excited state ($^3\text{B}_1$), also no apparent change for Ge–C vibration can be observed, but the C–O vibrational frequency is obviously smaller than that in $\text{Ge}(\text{CO})_2$ ground state (1^1A_1) by 175–200 cm^{-1} at DFT/6-311+G* levels, and it is also smaller than that of GeCO species (by 140–170 cm^{-1}). According to the discussion mentioned above regarding the geometric parameters, it can be believed that this observation is reasonable.

To further determine the bonding strength of this bicarbonyl Ge complex and to predict the stability of the polycarbonyl Ge complexes, the monocarbonyl dissociation energies, the bicarbonyl dissociation energies, and the corresponding vertical ionization potentials of the ground-state $\text{Ge}(\text{CO})_2$ species are also calculated by using four theoretical methods with 6-311+G* basis set, and are also calibrated by the higher-level electron correlation methods such as MP3, MP4_{SDQ}, and CCSD and including triple excitations (see Table 5).

For the first CO dissociation energy, $D_{\text{e},1}$, three DFT methods give $D_{\text{e},1}$ values within 13.5–17.5 kcal/mol, which are slightly greater than that for the MP2(full) result (12.9 kcal/mol). The further electronic correlation calculations at MP3, MP4_{SDQ}, CCSD, and CCSD(T) levels give results significantly smaller than the DFT and MP2 ones. The highest level CCSD(T) method used here produces a $D_{\text{e},1}$ of 8.1 kcal/mol. Due to the limitation of these DFT methods and the intramolecular weak interaction character, it can be predicted that results falling within 7–12 kcal/mol are reliable. Comparison of these values with those of GeCO ($^3\Sigma$) indicates that the first CO adiabatic dissociation energy (8–13 kcal/mol) is significantly smaller than the second CO adiabatic dissociation energy (14–16 kcal/mol), viz., the CO adiabatic dissociation energy of GeCO ($^3\Sigma$). In other words, the dissociation of $\text{Ge}(\text{CO})_2$ into GeCO ($^3\Sigma$) and CO ($^1\Sigma$) is easier than that of GeCO into Ge (^3P) and CO ($^1\Sigma$). That is, the first CO binding energy of Ge atom is greater than the second CO one. It may be predicted that the third CO binding energy of Ge will be smaller than the second CO one, and so is true for the fourth or fifth CO binding energies. From the viewpoint of averaged single CO binding energy, the averaged value (12.5 kcal/mol at CCSD(T)/6-311+G* level) for $\text{Ge}(\text{CO})_2$ species is also smaller than that (16.8 kcal/mol at the same level) for GeCO species; therefore, for the tricarbonyl Ge the averaged binding energy should be smaller than that of $\text{Ge}(\text{CO})_2$. This tendency has implied that polycarbonyl Ge complexes with more than two COs should be unstable, and are very easily dissociated to subcarbonyl Ge complexes. This further confirms fact that up to now there have not been reports regarding $\text{Ge}(\text{CO})_3$, $\text{Ge}(\text{CO})_4$, etc. even at very low temperatures.

Another important energy quantity is IP_v . The IP_v of $\text{Ge}(\text{CO})_2$ is slightly smaller than that of GeCO by ~ 2 kcal/

mol. The ionized electron mainly comes from the Ge center, having indicated the carbene-like character of $\text{Ge}(\text{CO})_2$ species.

4. Conclusion

The structural properties and the bonding character for subcarbonyl Ge, GeCO and $\text{Ge}(\text{CO})_2$, in their singlet and triplet states have been investigated in detail using three DFT and MP2 methods with a 6-311+G* basis set. Results indicate that GeCO species has a stable triplet ground state and the corresponding singlet state is higher than the ground state by 17.1 kcal/mol at CCSD(T)/6-311+G* level. Combination of Ge with CO yields a weak Ge–CO bond and simultaneously reduces the C–O bond. The formed GeCO ($^3\Sigma$) has carbene-like character, and especially its $\text{CO}^\delta-$ moiety possesses CO^- property. The main interaction between Ge and CO is a weak σ bond and two weak π bonds. Although the Ge–C bond length is similar to the single bond, the bond strength is weaker than the common Ge–C bonds. The calculated dissociation energy is 16.8 kcal/mol at CCSD(T)/6-311+G* level. The corresponding potential well for the bending mode is shallow; therefore this GeCO molecule is facile.

For the bicarbonyl Ge systems, $\text{Ge}(\text{CO})_2$, two v-type structures are found for singlet state and only one for the triplet state. These configurations are significantly different from the linear one. The singlet state (1^1A_1) is more stable by ~ 24.1 kcal/mol than the 2^1A_1 state and by 36.6 kcal/mol than the triplet state ($^3\text{B}_1$) at CCSD(T)/6-311+G* level, being the ground state. The bond length in the ground state is very close to that in GeCO species, but every GeCO moiety is bent by $\sim 10^\circ$, and the $\angle\text{CGeC}$ angle is significantly smaller than 180° and is only $\sim 76^\circ$. The 2^1A_1 state has a bond length slightly longer by 0.03 Å, a $\angle\text{CGeC}$ angle significantly larger by $\sim 42^\circ$, and a $\angle\text{GeCO}$ angle smaller by 26° , compared with the 1^1A_1 ground state. The corresponding triplet state has a $\angle\text{CGeC}$ angle of $\sim 49^\circ$ and a $\angle\text{GeCO}$ angle of $\sim 166^\circ$. However, its Ge–C and C–O bonds are longer than those in ground state by ~ 0.07 and 0.03 Å, respectively. The linear constraint singlet ($^1\Sigma_\text{g}$) and triplet ($^3\Pi_\text{u}$) states are also considerably higher than the ground state (1^1A_1) and also than the v-type triplet state ($^3\text{B}_1$). These $\text{Ge}(\text{CO})_2$ species have essentially carbene-like character and should be referred to the analogue of carbene. Comparison of the CO dissociation energies between GeCO and $\text{Ge}(\text{CO})_2$ in the ground states indicates that the first CO dissociation energy of $\text{Ge}(\text{CO})_2$ is smaller by ~ 8.7 kcal/mol than that of GeCO ; the averaged one over two COs is also smaller than that of GeCO . Detailed bonding analysis has implied that the possibility of the existence of polycarbonyl Ge with more than three COs is small. Perhaps this is why no experimental observations have been reported up to now for polycarbonyl Ge complexes. These nonmetal and nontransition metal atoms or clusters are very different from the transition metals: they cannot form polycarbonyl complexes and detailed interaction character is also still unclear. Thus further studies are very necessary.

In addition, it should be noted that due to the importance of investigations regarding the weak interaction in biological and materials fields, detailed studies of 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 and Notes

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