

## Ab Initio Study on the Structure and Energetics of (CO)<sub>2</sub>

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The stationary point structures and relative energies between them as well as binding energies of (CO)<sub>2</sub> have been investigated at the CCSD(T) level using the correlation-consistent basis sets aug-cc-pVXZ (X=T, Q, 5). It is found that while the equilibrium structure corresponds to the C-bonded T-shaped configuration with intermolecular distance of 4.4 Å, there exists another minimum, slightly higher in energy (~10 cm<sup>-1</sup>) than the global minimum, corresponding to the O-bonded T-shaped configuration with the intermolecular distance of 3.9 Å. The CCSD(T) basis set limit binding energy of (CO)<sub>2</sub> is estimated to be 132 cm<sup>-1</sup>.

**Key Words :** (CO)<sub>2</sub>, Equilibrium structure, CCSD(T) CBS limit binding energy

### Introduction

Carbon monoxide has an interesting property. Despite its nonnegligible dipole moment (~0.1D), the bulk carbon monoxide has an unusually low boiling point (-193 °C), which is much lower than near-isoelectronic NO and even lower than O<sub>2</sub> (-183 °C). This feature appears to be related to the strong triple bond within the CO monomer which localizes the most electrons along the C-O bond, thereby leaving little electrons outside the bond to participate in the intermolecular interaction through van der Waals forces. Therefore, one would expect a very weak intermolecular interaction between the two CO molecules.

Experimentally, since the first detection of the microwave lines of CO dimer by means of molecular beam electron resonance spectroscopy by Van den Bout *et al.*<sup>1</sup> there has been an important progress recently concerning the equilibrium structure of (CO)<sub>2</sub>. From the analysis of vibrational-rotational transition lines of (CO)<sub>2</sub> infrared spectrum in the region of CO stretching vibration using a pulsed supersonic jet and a tunable diode laser probe, Brookes and McKellar<sup>2</sup> concluded that (CO)<sub>2</sub> must have two almost isoenergetic isomers with intermolecular separations of 4.4 Å and 4.0 Å, with the 4.4 Å isomer slightly lower in energy than the 4.0 Å isomer by less than 1 cm<sup>-1</sup>. On the basis of previous calculations on this dimer, they also suggested that both of these isomers may be roughly T-shaped, with the 4.4 Å isomer being a C-bonded configuration and the 4.0 Å isomer being an O-bonded configuration. Further study of (CO)<sub>2</sub> spectrum in the millimeter wave region by Roth *et al.*<sup>3</sup> revealed that there appear to be two other isomer states with intermolecular separations of 4.17 and 4.26 Å which are slightly higher in energy (~5 cm<sup>-1</sup>) than the aforementioned isomers with intermolecular separations of 4.4 and 4.0 Å.

Theoretically, due to the unusual floppiness and existence of many shallow wells in the potential energy surface (PES) of (CO)<sub>2</sub>, the progress toward understanding the equilibrium structure (along with other isomeric structures) and concurrent dynamics has been very slow and there also have been some controversies about the equilibrium and saddle

point structures of (CO)<sub>2</sub> over the past decade. Van der Pol *et al.*<sup>4</sup> constructed the potential energy surfaces of (CO)<sub>2</sub> using the *ab initio* values for the electrostatic and first-order exchange interactions as well as dispersion coefficients. The potential predicted the T-shaped global minimum structure with O-bonded configuration and several local minima differing slightly in energy and separated by small barriers. Later, Meredith and Stone<sup>5</sup> extended the potential of Van der Pol *et al.*<sup>4</sup> by adding more dispersion coefficients in the multipole expansion of the dispersion energy. This potential showed the two symmetry-equivalent T-shaped (C-bonded) global minimum structures and a local minimum of slipped anti-parallel structure. However, both potentials were found to have a deficiency in explaining the known experimental spectroscopic data of (CO)<sub>2</sub>.

More recently, Rode *et al.*<sup>6</sup> examined the equilibrium and saddle points structures of this dimer at the MP4 (Moller-Plesset Perturbation Theory at the fourth order<sup>7,8</sup>) level using the [6s4p3d1f] basis optimized for the monomer property and found the two minima corresponding to two anti-parallel structures of CO monomers for the planar dimer. The saddle point connecting the minima was found to have a similar structure as the minima structures except that the dipole moments of the monomers have the same sign (parallel-shaped) in case of the saddle point. Noting the relatively large difference between the MP4 and CCSD(T) (single and double excitation coupled cluster method with perturbative triples corrections<sup>9</sup>) results, the previous authors also suggested that even the CCSD(T) method would not provide the sufficiently accurate results for the CO-CO interaction potential due to the lack of important fifth order correlation contribution. However, Pedersen *et al.*<sup>10</sup> suggested that the residual correlation effect beyond CCSD(T) level appears to be small compared to the perturbative triples excitation contributions by the CCSD(T) method beyond the CCSD (single and double excitation coupled cluster method<sup>11-14</sup>) level. They emphasized the importance of using the basis set of sufficient quality in studying the CO-CO interaction and concluded that CCSD(T) method would yield sufficiently accurate interaction energies for this system as long as the

basis set convergence problem in the computed results is properly handled. Therefore, in view of the recent development in the experimental and theoretical findings concerning  $(\text{CO})_2$ , it is in order to examine the PES and binding energetics of  $(\text{CO})_2$  using the proper theoretical model which includes the important electron correlation and basis set effects necessary for describing the weak interaction in the  $(\text{CO})_2$ , although that appears to be a formidable task at the present time, considering the weak and complex nature of the PES of  $(\text{CO})_2$ .

In this article we explore the PES of  $(\text{CO})_2$  using the CCSD(T) method with correlation-consistent aug-cc-pVTZ basis set<sup>15</sup> which includes the multiple diffuse functions up to f type. Although it might be argued that the theoretical level employed here is not sufficiently high enough to elucidate the fine details of the PES of  $(\text{CO})_2$ , it will nevertheless be shown that using this method one can locate the equilibrium and other lower energy stationary structures relevant to the previous experimental finding of this dimer.<sup>2</sup> After characterizing the various stationary structures of this dimer at the CCSD(T)/aug-cc-pVTZ level, we determine the energy differences between the various structures and binding energy at the equilibrium with high accuracy using the large correlation-consistent basis sets and well-established extrapolation technique exploiting the basis set convergence property of correlation consistent basis sets. In the next section we explain how the stationary structures of  $(\text{CO})_2$  were obtained in this study.

### Characterization of the Stationary Structures

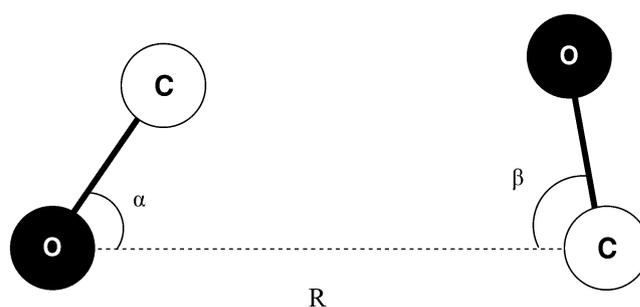
Since the PES of  $(\text{CO})_2$  has been known to be very floppy, we adopted both the optimization algorithm<sup>16</sup> and extensive scanning of PES to locate the equilibrium and saddle point structures of this dimer using the CCSD(T) method with aug-cc-pVTZ basis set which contains [5s4p3d2f].

Although this basis set may not be sufficiently large enough to locate all the stationary structures of  $(\text{CO})_2$ , it includes diffuse functions of each angular type which could be critical, in combination with CCSD(T) method, in locating the global minimum structure and computing the reliable binding energy of this dimer. This is generally supported by the results for the dipole moment and polarizability of CO monomer using the same theoretical method as dimer, which exhibit a very good agreement with

**Table 1.** Dipole moment ( $\mu$ ) and dipole polarizabilities ( $\bar{\alpha}$ ,  $\Delta\alpha$ ) of  $\text{CO}^a$

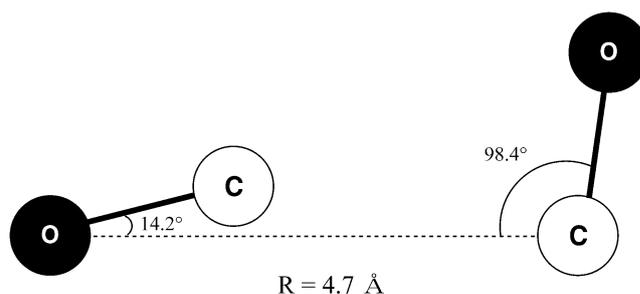
	This work <sup>b</sup>	Experiment
$\mu$	0.0497	0.0480 <sup>e</sup>
$\bar{\alpha}^c$	13.0894	13.0891 <sup>f</sup>
$\Delta\alpha^d$	3.6605	3.59 ± 0.07 <sup>g</sup>

<sup>a</sup>All values in Atomic Units. <sup>b</sup>CCSD(T)/aug-cc-pVTZ results at  $r_{\text{CO}} = 1.1282 \text{ \AA}$ . <sup>c</sup>Mean dipole polarizability ( $\bar{\alpha} = [\alpha_{zz} + 2\alpha_{xx}]/3$ ). <sup>d</sup>Anisotropy of dipole polarizabilities ( $\Delta\alpha = \alpha_{zz} - \alpha_{xx}$ ). <sup>e</sup>From ref. 17. <sup>f</sup>Dipole oscillator strength value in ref. 18. <sup>g</sup>From ref. 19.

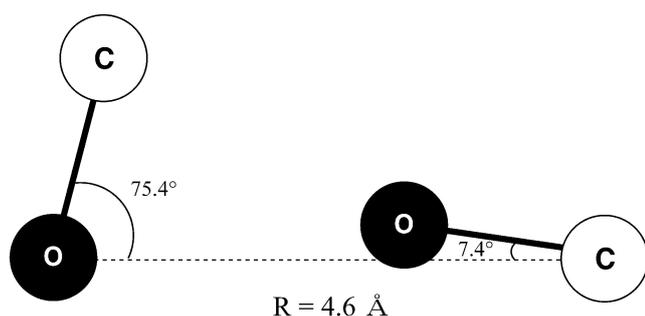


**Figure 1.** The coordinate system of  $(\text{CO})_2$ . Both monomers are in the same plane. The bond distance in the monomer is fixed at  $r_{\text{CO}} = 1.1282 \text{ \AA}$ .

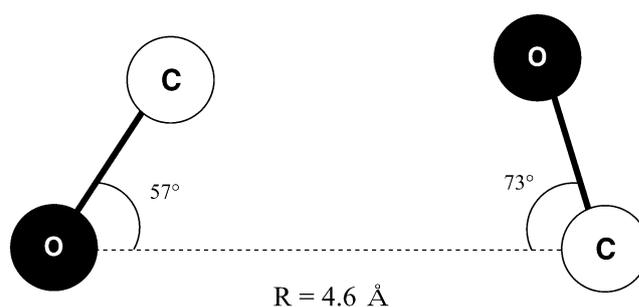
the experimental results in Table 1. All ab initio electronic computations were performed using Gaussian 98 program package.<sup>20</sup> In Figure 1 a schematic representation of  $(\text{CO})_2$  along with the optimized(scanned) variables ( $R, \alpha, \beta$ ) is shown.  $R$  represents the intermolecular distance connecting the oxygen atom in one monomer and carbon atom in the other monomer and angles ( $\alpha, \beta$ ) represent the angles between the  $R$  vector and each monomer's internuclear distance vector. Following the previous study,<sup>6</sup> monomers were assumed to be in the same plane. Initially, as the starting structures, we adopted the global and local minimum structures of  $(\text{CO})_2$  by Rode *et al.*<sup>6</sup> at the MP4 level which correspond to  $\alpha = 47^\circ$ ,  $\beta = 133^\circ$  (global) and  $\alpha = 137^\circ$ ,  $\beta = 43^\circ$  (local) configuration in Figure 1. As previous studies,<sup>6</sup> the monomer bond distance was fixed at its equilibrium distance ( $r_{\text{CO}} = 1.1282 \text{ \AA}$ ). At first, intermolecular bond distance  $R$  were fixed and two angles ( $\alpha, \beta$ ) were varied, which led to approximately T-shaped structures in both the global and local minima, although two structures were oriented in opposite direction as depicted in Figure 2 and Figure 3. Then, the PES was scanned extensively according to variation of the intermolecular distance  $R$ . In both cases of minima, the PES tends to go lower as  $R$  increases until it reaches near 4.6 or 4.7  $\text{\AA}$ . Therefore, at this point, simultaneous optimization of intermolecular distance ( $R$ ) and angles ( $\alpha, \beta$ ) was performed to locate the stationary structures corresponding to true minima of the PES. For local minimum search, the optimization was successful in yielding the O-bonded T-shaped structure shown in Figure 3



**Figure 2.** The equilibrium structure of  $(\text{CO})_2$ . The intermolecular distance between the centers of the mass of the monomers corresponds to 4.4  $\text{\AA}$  in this case.



**Figure 3.** The local minimum structure of  $(CO)_2$ . The intermolecular distance between the centers of the mass of the monomers corresponds to 3.9 Å in this case.

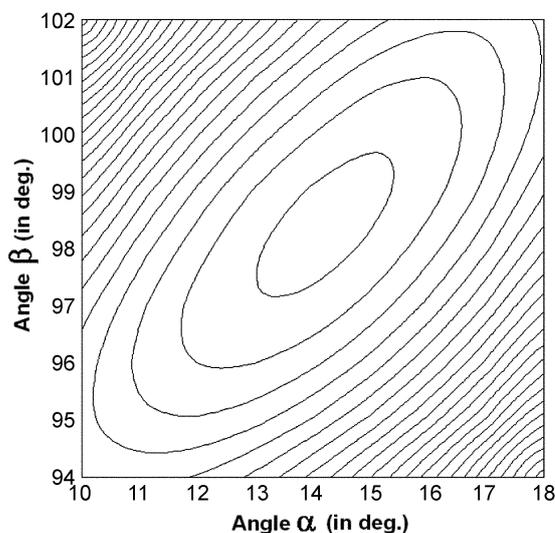


**Figure 4.** The saddle point structure of  $(CO)_2$ . The intermolecular distance between the centers of the mass of the monomers corresponds to 4.2 Å in this case.

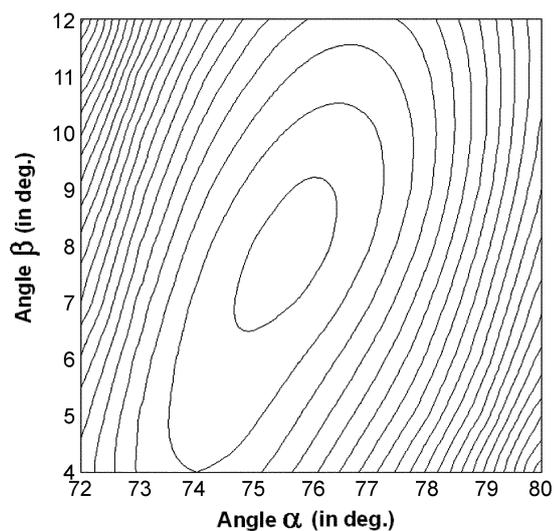
which was confirmed as the minimum through local scanning of the PES around this structure. For global minimum, however, conventional optimization procedure failed to yield the stationary structure as the PES appeared to be too floppy to locate the minimum. Therefore we scanned the PES with the interval of 1.0 Å for  $R$  and  $1.0^\circ$  for  $\alpha$  and  $\beta$  to locate the global minimum. This finally led to the global minimum structure shown in Figure 2, which is a T-shaped structure with C-bonded configuration. Interestingly, the intermolecular distances connecting the center of masses of the monomers for global and local minimum are found to be 4.4 and 3.9 Å, respectively, which are very close to the experimentally derived values (4.4 and 4.0 Å) by Brookes and McKellar.<sup>2</sup> Our results are also consistent with the previous studies in that while global minimum with longer intermolecular distance is in a C-bonded (headed) configuration, local minimum with shorter distance is in O-bonded (headed) configuration. Figure 5 shows the variation of the PES near global equilibrium structure according to variation of angles ( $\alpha, \beta$ ). Although the PES was found to change noticeably with intermolecular distance even at the equilibrium structure, its change with angles is hardly noticeable near equilibrium structure, exhibiting unusual floppiness around global minimum. It is remarkable to observe that variation of angles by about  $4^\circ$  in both direction would only increase the energy by  $\sim 5 \mu E_h$  (or  $1 \text{ cm}^{-1}$ ), which may be only found in purely van der Waals systems such as  $Ne_3$  or  $Ar_3$ .<sup>21,22</sup> Similar behavior is observed near local minimum in Figure 6, though the floppiness with angle  $\alpha$  near local minimum is less pronounced compared to global minimum.

To locate the saddle point connecting the two minimum structures, extensive scanning of the PES according to angles with intermolecular distance  $R$  fixed at  $R = 4.6$  and  $R = 4.7$  Å has been performed, which yielded the apparent saddle points at  $\alpha = 57^\circ, \beta = 74^\circ$  in the case of  $R = 4.6$  Å and  $\alpha = 54^\circ, \beta = 68^\circ$  in the case of  $R = 4.7$  Å, respectively. Among these two apparent saddle points, one with  $R = 4.6$  Å was determined as the true saddle point connecting the two minima as it corresponds to the lower one in energy than the one with  $R = 4.7$  Å. The intermolecular distance connecting the centers of masses of CO monomers in the saddle point structure in Figure 4 corresponds to 4.2 Å. In Figure 7 the

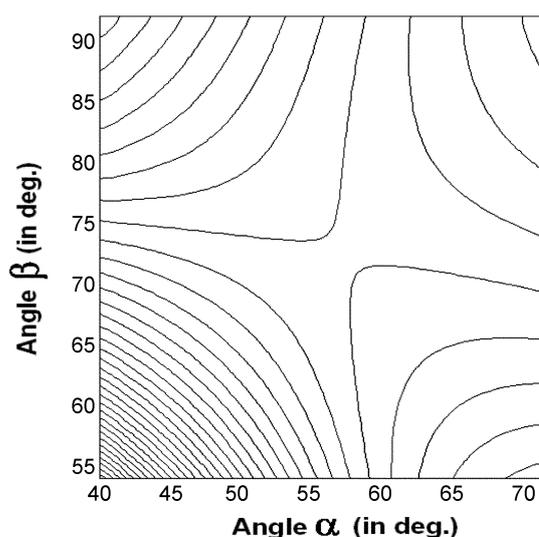
PES around the saddle point connecting the local and global minimum is shown which also exhibits floppiness near the saddle point along the reaction coordinate. Although optimization to locate the other stationary structures such as the ones with different intermolecular distances suggested by Roth *et al.*<sup>3</sup> has been tried, it did not succeed to locate a new stationary structure at the CCSD(T)/aug-cc-pVTZ level. Therefore, use of more sophisticated theoretical model, either in correlation treatment or basis set choice (or both), appears necessary to investigate the detailed shape of PES and identify the stationary structures in the higher energy region than examined in this study. While it appears quite formidable to investigate the PES of  $(CO)_2$  employing more sophisticated method than employed here at the present time, for the future work to be followed to understand the spectroscopic and dynamical properties of  $(CO)_2$ , the remaining important task at this point would be to elucidate the exact magnitude of the energy difference between the global and local minima as well as the binding energy at the equilibrium, which is examined in the next section.



**Figure 5.** The contour plot of the potential energy surface near equilibrium of  $(CO)_2$ . The interval between the contour lines is  $1.0 \mu E_h$ .



**Figure 6.** The contour plot of the potential energy surface near local minimum of  $(\text{CO})_2$ . The interval between the contour lines is  $1.0 \mu E_h$ .



**Figure 7.** The contour plot of the potential energy surface near the saddle point. The lowest energy path connecting the global and local minimum is clearly visible. The interval between the contour lines is  $25 \mu E_h$ .

### Relative Energies between Stationary Structures and Binding Energy of $(\text{CO})_2$

After characterizing the stationary points in the PES of  $(\text{CO})_2$ , the relative energies between stationary structures and electronic binding energies of  $(\text{CO})_2$  have been computed with basis set at the same CCSD(T) level but with larger basis sets including aug-cc-pVQZ and aug-cc-pV5Z sets, which are composed of [6s5p4d3f2g] and [7s6p5d4f3g2h], respectively. In Table 2 we present the total energies of global, local, and saddle point structure of  $(\text{CO})_2$  along with the relative energies as well as their correlation contributions between them with basis set. Although the relative energies and their correlation contributions between stationary structures converge with basis set in general, it is worth noting that they do not exhibit the monotonic convergence pattern with basis set in some cases and do not appear to fully converge to the basis set limits even with the basis set as large as aug-cc-pV5Z. This appears especially true in case of computing the energy differences between the

saddle point and the minima. Therefore, to accurately predict the relative energies between stationary structures, the complete basis set (CBS) limit values for relative energies were estimated using aug-cc-pVQZ and aug-cc-pV5Z basis set correlation results employing the various two-point extrapolation methods, which are also shown in Table 2. For consistency, all Hartree-Fock(HF) contributions in the CBS limit results in Table 2 were taken from the computed HF results with aug-cc-pV6Z basis set which could be considered as the basis set limits at the HF level in actuality. The CBS limit estimates in Table 2, CBS1 and CBS2, denote the basis set limit values obtained through extrapolation of the correlation contributions with aug-cc-pVQZ and aug-cc-pV5Z basis sets by  $X^{-3}$  ( $X=4,5$ )<sup>23</sup> and  $(X-1/2)^{-3}$ ,<sup>24</sup> respectively, to deduce the correlation limits. Inclusion of  $-1/2$  in the latter extrapolation formula could be attributed to the incomplete convergence to the CBS limit with these basis sets. Although the CBS limit estimates for relative energies change somewhat depending on the extrapolation

**Table 2.** Total (E) and relative ( $\Delta E$ ) energies<sup>a</sup> between stationary structures of  $(\text{CO})_2$

Basis set	$E_{\text{global}} (\infty)$	$E_{\text{local}} (\infty)$	$E_{\text{saddle}} (\infty)$	$\Delta E_1^b$	$\Delta E_2^c$	$\Delta E_3^d$	
aug-cc-pVDZ	-226.1475096	-226.1474217	-226.1469919	0.518(0.226)	0.430(0.007)	0.088(0.219)	
aug-cc-pVTZ	-226.3249213	-226.3248713	-226.3244742	0.447(0.203)	0.397(0.027)	0.050(0.176)	
aug-cc-pVQZ	-226.3813678	-226.3813163	-226.3809706	0.397(0.189)	0.346(0.038)	0.052(0.151)	
aug-cc-pV5Z	-226.3991394	-226.3990885	-226.3987723	0.367(0.164)	0.316(0.008)	0.051(0.156)	
CBS limit							
estimates	CBS1 <sup>e</sup>	-226.4147835 <sup>g</sup>	-226.4147279 <sup>g</sup>	-226.4144437 <sup>g</sup>	0.340(0.138)	0.284(-0.024)	0.056(0.162)
	CBS2 <sup>f</sup>	-226.4124470 <sup>g</sup>	-226.4123921 <sup>g</sup>	-226.4121032 <sup>g</sup>	0.344(0.142)	0.289(-0.019)	0.055(0.161)

<sup>a</sup>All energies at the frozen-core CCSD(T) level in units of  $E_h$  and  $mE_h$  for total and relative energies, respectively. The values in parentheses correspond to the correlation contributions. <sup>b</sup> $\Delta E_1 = E_{\text{saddle}} - E_{\text{global}}$ . <sup>c</sup> $\Delta E_2 = E_{\text{saddle}} - E_{\text{local}}$ . <sup>d</sup> $\Delta E_3 = E_{\text{local}} - E_{\text{global}}$ . <sup>e</sup>The CBS limit correlation energies (and contributions to the relative energies) were estimated by the  $X^{-3}$  ( $X=4,5$ ) extrapolation of correlation energies with aug-cc-pVQZ and aug-cc-pV5Z basis sets. <sup>f</sup>The CBS limit correlation energies (and contributions to the relative energies) were estimated by the  $(X-0.5)^{-3}$  ( $X=4,5$ ) extrapolation of correlation energies with aug-cc-pVQZ and aug-cc-pV5Z basis sets. <sup>g</sup>The CBS limit total energies represent the sum of the estimated (extrapolated) CBS limit correlation energies and HF energies with aug-cc-pV6Z basis set

**Table 3.** Total (E) and binding ( $\Delta E$ ) energies<sup>a</sup> of (CO)<sub>2</sub>

Basis set		$E_{AB}^b$	$E_A^b$	$E_B^b$	$\Delta E$
aug-cc-pVDZ		-226.1475096	-113.0734762	-113.0735705	0.463(0.723)
aug-cc-pVTZ		-226.3249213	-113.1621409	-113.1622446	0.536(0.807)
aug-cc-pVQZ		-226.3813678	-113.1903868	-113.1904084	0.573(0.839)
aug-cc-pV5Z		-226.3991394	-113.1992738	-113.1992777	0.588(0.853)
CBS limit	CBS1 <sup>c</sup>	-226.4144058 <sup>e</sup>	-113.2069052 <sup>e</sup>	-113.2068988 <sup>e</sup>	0.602(0.866)
estimates	CBS2 <sup>d</sup>	-226.4120693 <sup>e</sup>	-113.2057372 <sup>e</sup>	-113.2057324 <sup>e</sup>	0.600(0.864)

<sup>a</sup>All energies at the frozen-core CCSD(T) level in units of  $E_h$  and  $mE_h$  for total and binding energies, respectively. The values in parentheses correspond to the correlation contributions. <sup>b</sup> $E_{AB}$ ,  $E_A$  and  $E_B$  represent the total energies of the complex AB, monomer A and monomer B, respectively. The monomer energies are computed with the basis set of the complex. <sup>c</sup>The correlation contributions to the binding energies were estimated by the  $X^{-3}$  ( $X=4,5$ ) extrapolation of correlation energies with aug-cc-pVQZ and aug-cc-pV5Z basis sets. <sup>d</sup>The correlation contributions to the binding energies were estimated by the  $(X-0.5)^{-3}$  ( $X=4,5$ ) extrapolation of correlation energies with aug-cc-pVQZ and aug-cc-pV5Z basis sets. <sup>e</sup>The CBS limit total energies represent the sum of the estimated (extrapolated) CBS limit correlation energies and HF energies with aug-cc-pV5Z basis set

method employed, they are not different by more than  $5 \mu E_h$  in case of  $\Delta E_1$  and  $\Delta E_2$ , and not different by more than  $1 \mu E_h$  in case of  $\Delta E_3$ . Therefore, the CBS limit estimates reported in Table 2 appear to be reliable estimates to the exact CBS limit values. The CCSD(T) CBS limit result for the relative energy between the global and local minimum of about  $55\text{--}56 \mu E_h$  ( $\sim 12 \text{ cm}^{-1}$ ) is in accord with the results from the analysis of the infrared spectrum on this dimer by Brooke and McKellar.<sup>2</sup>

In Table 3 we present the counterpoise (CP) corrected<sup>25</sup> binding energies of (CO)<sub>2</sub> at the equilibrium structure. Compared to the energy differences between the stationary structures, the binding energy converges more smoothly toward the basis set limits. This could be expected considering that unlike the case of computing the energy difference between the stationary points which correspond to the different geometries of the dimer (Fig. 2 and Fig. 3), same dimer basis sets with the same geometries are employed for computing the energies of the monomer and dimer in the case of the CP corrected binding energies. The CBS limit estimates for the binding energy from the same extrapolation methods used to estimate the CBS limit relative energies in Table 2 agree one another which again suggests the reliability of the estimated results. (In both cases of relative and binding energies, the core-correlation effect caused by activating the all electrons including the core orbitals in the correlation treatment was found negligible. For all electron correlation calculation at the CCSD(T) level with aug-cc-pCVTZ basis sets<sup>23</sup> which contain the tight core-correlating functions in addition to the aug-cc-pVTZ set, the correlation contributions to the relative ( $\Delta E_3$  in Table 2) and binding energies change by 7 and  $3 \mu E_h$ , respectively, from the frozen-core results with aug-cc-pVTZ basis set).

The estimated CBS limit electronic binding energies of about  $600\text{--}602 \mu E_h$  ( $132 \text{ cm}^{-1}$ ) suggests that the (CO)<sub>2</sub> is much weakly bound cluster compared to (NO)<sub>2</sub> (binding energy of  $700 \text{ cm}^{-1}$ ) or (O<sub>2</sub>)<sub>2</sub> (binding energy of  $300 \text{ cm}^{-1}$ ). Furthermore, it appears that the vibrational zero point correction to the electronic binding energy could further reduce the binding of this dimer. Our estimate of the zero point correction at the MP2/aug-cc-pVTZ level amounts to

$336 \mu E_h$ , yielding actual binding energies of  $264\text{--}266 \mu E_h$  for this dimer. This appears to be related to the unusually low boiling point of CO in the bulk phase.

## Conclusion

Despite the recent experimental progress made on the spectroscopic properties of (CO)<sub>2</sub>, the determination of the accurate structure and binding energy of this dimer has been very elusive due to its unusually weak interactions between the monomers in the system. By employing highly correlated CCSD(T) method in combination with the aug-cc-pVTZ basis set which includes the appropriate polarization and diffuse functions and exploiting the extensive use of optimization procedure and scanning of the PES of this dimer, we were able to characterize the T-shaped minimum structures of intermolecular distances of 4.4 (global minimum) and 3.9 Å (local minimum) with the energy difference of  $\sim 10 \text{ cm}^{-1}$  between the minima. This is in good agreement with the results of the previous experimental study on the infrared spectrum of this dimer which predicted the intermolecular distances of 4.4 and 4.0 Å for the global and local minimum structure. We also located the saddle point structure approximately  $70 \text{ cm}^{-1}$  above the global minimum which appears to connect the global and local minima. The CBS limit electronic binding energies of (CO)<sub>2</sub> at the CCSD(T) level is estimated to be  $132 \text{ cm}^{-1}$ , which signifies the unusually weak interactions present in this dimer. This value of binding energy is much smaller than the binding energy of near-isoelectronic (NO)<sub>2</sub> and appears to be related to the lower boiling point of CO compared to NO or even O<sub>2</sub>. The next step would be to characterize other stationary points in the higher energy region than examined here, which probably would require more sophisticated theoretical model than employed here, especially in terms of basis set choice.

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