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## Ab initio and DFT study of carbon monoxide cyclic oligomers, (CO)<sub>2</sub> to (CO)<sub>6</sub>

Hassan Sabzyan\*, Mohammad Reza Noorbala

*Department of Chemistry, University of Isfahan, Isfahan 81746-73441, Islamic Republic of Iran*

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### Abstract

Structural, thermochemical stability, electrical and molecular orbital properties of (CO)<sub>n</sub> cyclic oligomers of CO (oxocarbons) have been calculated using RHF and DFT-B3LYP levels of theory with 6-31G\* basis set. Contributions of these compounds in the macroscopic properties of solid CO have been investigated. Atoms in molecule (AIM) and NBO analyses have been carried out to study in detail the nature of the C–C bonds in these molecules. Population analysis has been used to search for any possible aromaticity in the rings of these cyclic oxocarbons. AIM and population analysis showed that ring bonds in the (CO)<sub>3</sub> molecule have an aromatic character significantly more than those in other molecules do. The results of this study showed that (CO)<sub>n</sub> cyclic oligomers do not contribute significantly to the physicochemical properties of CO in the solid phase due to being thermodynamically instable at standard pressure and temperature.

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**Keywords:** Ab initio; DFT-B3LYP; Carbon monoxide; Cyclic oligomer; Oxocarbons

### 1. Introduction

The high-level ab initio calculations expanded into most areas of science during the past few years, playing a major role in many areas such as chemistry, biochemistry, drug design and physics [1–10]. As well as ab initio calculations, approximate density functional theory (DFT) has over the past decade emerged as a tangible and versatile computational method. It has been employed successfully to obtain

thermochemical data, molecular structures, force fields and frequencies, assignments of NMR, photoelectron, ESR, and UV spectra, transition-state structures, as well as activation barriers, dipole moments, and other one-electron properties [11–19]. Thus, approximate DFT is now applied to many problems previously covered exclusively by ab initio Hartree–Fock (HF) and post-HF (CI, CC and MPPT) methods [7–10]. The recent success and credit of DFT and ab initio quantum chemistry have been reflected by the 1998 Nobel Prize awarded to Pople and Kohn [20].

Low temperature behavior, especially superconductivity of compounds is of great interests to

\* Corresponding author. Tel.: 98-311-793-2749; fax: 98-311-668-9732.

E-mail address: [sabzyan@sci.ui.ac.ir](mailto:sabzyan@sci.ui.ac.ir) (H. Sabzyan).

chemists and physicists. Theoretically, many compounds can show superconductivity at very low temperatures due to their perfect lattice molecular orbitals alignments [21–24]. Of course, the only way nonmetallic molecular solids can show superconductivity is to form actual intermolecular chemical bonds spanning over the entire lattice, or in other words, to form a conductive polymer [25–30]. This means that the molecular nature of the lattice should be changed into a crystal nature. This state is possible only for molecules with nonbonding and  $\pi$ -electrons such as CO, NO and  $N_2$ .

Although the majority of CO molecules in the solid phase cluster in linear chains with a variety of sequences, there is still a certain possibility for the formation of cyclic clusters or oligomers which existence probability is being studied in this research. These cyclic CO oligomers can be considered either as impurity clusters, primary nucleation centers or, least likely, the unit cells of the solid CO lattice, thus, possibly contributing to the electrical and thermochemical properties of the CO solid lattice.

In some previous studies researchers had hoped to work on different aspects of CO ice [31]. The present study addresses some questions posed about molecular properties of CO and CO clusters in the solid phase.

The term *oxocarbon*, first suggested by West in 1963 [32], designates compounds in which all carbon atoms are bonded to carbonyl or enolic oxygens, and their hydrated or deprotonated equivalents. Due to their highly functionalized and interesting structures, the cyclic oxocarbon acids ( $C_nO_nH_2$ ) and their conjugated bases, the oxocarbon dianions ( $C_nO_n$ )<sup>2-</sup>, have been widely investigated both theoretically and experimentally [33–37]. In the oxocarbon dianions ( $C_nO_n$ )<sup>2-</sup>, all carbon–oxygen  $\pi$ -bonds are conjugated [38]. This conjugation contributes considerably to their thermochemical stability. However, this conjugation is not so large to create significant aromaticity in these compounds. A Hückel molecular orbital theory study on  $C_nO_n$  neutral molecules shows no conjugation in these compounds. The  $C_3O_3$  is an exception [39]. To our knowledge, so far, ab initio study on carbon monoxide oligomers has been reported only for  $C_2O_2$ , yet on its intermolecular

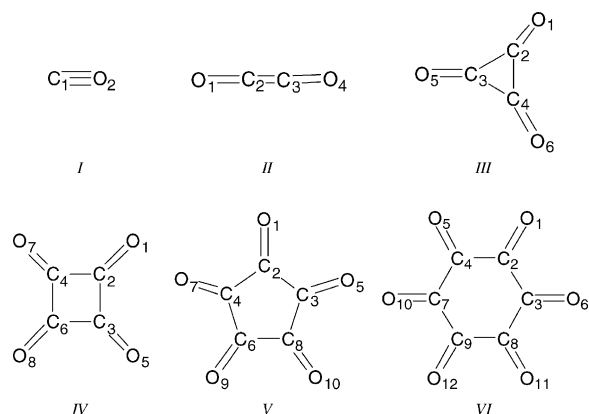
potential energy surface [40] and its FT–IR spectrum [41] only.

In this work, we have studied (CO)<sub>1</sub> to (CO)<sub>n</sub> cyclic oligomers with the focus on their thermochemical stability, molecular structure, bonding and electrical properties including electric polarizability. A thorough computational study on the linear oligomers of CO is underway which result will be reported upon completion. Here, results of our study on the cyclic CO oligomers are reported.

## 2. Computational techniques

The computational procedures started with geometry optimization of these oligomers at RHF and DFT-B3LYP [42–45] levels of theory with 6-31G\* basis set using semiempirical PM3 optimized structures as initial guesses. To be able to carry out a comparative study on the success of different levels of theory, MP2/6-31G\* method has been tried also, but its computations was successful only for oligomers up to (CO)<sub>4</sub>. Optimization of the (CO)<sub>5</sub> geometry at MP2 level of theory have been carried out but vibrational analysis on this oligomer was not successful due to convergence failure. For (CO)<sub>6</sub> cyclic oligomer, MP2 computations was not successful even at the geometry optimization step. We have used several SCF and geometry optimization convergence criteria and a variety of initial guess geometries to overcome this problem, but we were not successful. In addition, we have used several available hardware configurations. However, we end up with the same problem in the convergence. We do not have any idea about the source of this problem.

Vibrational, thermochemical stability and population analysis have been carried out for the optimized structures using the same level of theory and basis set. In the calculation of vibrational frequencies, a scaling factor of 0.8929 has been used for all compounds. Vibrational analysis characterized optimized structures as stationary points on the corresponding molecular potential energy surface, except for RHF (CO)<sub>2</sub> and (CO)<sub>4</sub> and B3LYP (CO)<sub>2</sub> optimized structures which all show a single relatively large negative mode



Scheme 1. Structures of  $(\text{CO})_1$  to  $(\text{CO})_6$  oligomers studied in this work. Except for the  $(\text{CO})_1$  and  $(\text{CO})_2$  which are linear, the optimized structures for all oligomers are planar.

with, 400.6, 398.9 and  $530.7 \text{ cm}^{-1}$  imaginary frequencies, respectively.

Bond order analysis has been carried out to investigate possible aromaticity in these cyclic oligomers, which have sufficiently high number of  $\pi$ -electrons, using both natural bond orbital (NBO) and population analysis as well as atoms in molecule (AIM) theory calculations. Electric polarizability and HOMO–LUMO energy gaps have also been calculated for these compounds as measures of their contribution to the macroscopic electrical conductivity of the solid CO. For all computations, GAUSSIAN 98W software package has been used [46]. The initial guess structures and the graphical presentation of the molecular wavefunctions have been obtained using HyperChem program suite [47].

### 3. Results and discussion

#### 3.1. Structural analysis

The results of DFT and RHF optimizations show that all oligomers have planar (linear for  $(\text{CO})_2$ ) structure. The optimized structures are depicted in Scheme 1.

The optimized planar structure and its  $C_n$  symmetry requires that the C–C–C bond angles to be  $2[1/2(180 - 360/n)] = 180[(n - 2)/n]$ , which is 60.0, 90.0, 108.0 and 120.0 degrees for  $(\text{CO})_3$  to  $(\text{CO})_6$ , respectively. The corresponding values of the C–C–O bond angles are therefore, 180.0, 150.0, 135.0, 126.0 and 120.0 degrees for  $(\text{CO})_2$  to  $(\text{CO})_6$ , respectively. The optimized bond lengths are reported in Table 1. Note that because of planar structure and  $C_n$  symmetry, all C–O and C–C bond lengths for each compound are identical. As can be seen from Table 1, RHF method predicts that the C–O bond length follows the increasing order of  $(\text{CO})_1 < (\text{CO})_4 < (\text{CO})_3 < (\text{CO})_2 < (\text{CO})_5 \sim (\text{CO})_6$ , while, the calculated C–O bond length at B3LYP level of theory follows the trend  $(\text{CO})_1 < (\text{CO})_3 \sim (\text{CO})_4 < (\text{CO})_2 < (\text{CO})_5 \sim (\text{CO})_6$ . These, however small, differences in the C–O bond lengths, compared to that of the free CO molecule, suggest the existence of a weak direct C–C chemical bond that essentially leads to weaker C–O bond in these compounds. The C–C bond length for  $(\text{CO})_2$  shows that it is exceptionally shorter and is on the order of direct C–C bond lengths observed in stable organic compounds. The C–C bond length order for

Table 1

The RHF and B3LYP optimized structural properties for carbon monoxide cyclic oligomers  $(\text{CO})_n$  using 6-31G\* basis set; bond lengths and AIM critical points in angstrom, and molecular volume  $\bar{v}$  in  $\text{bohr}^3 \text{ mol}^{-1}$ . Because of symmetry, all C–C and all C–O bonds are identical and the optimized values of the C–C–C bond angle are given by  $2[1/2(180-360/n)] = 180[(n-2)/n]$  for  $(\text{CO})_n$  cyclic oligomers

<i>n</i>	RHF					B3LYP				
	C–C	C–O	C–P <sup>a</sup>	<i>r</i> <sup>b</sup>	$\bar{v}$	C–C	C–O	C–P <sup>a</sup>	<i>r</i> <sup>b</sup>	$\bar{v}$
1	–	1.113	0.368	33.06	246.1	–	1.138	0.376	33.04	215.2
2	1.280	1.167	0.384	32.90	457.8	1.291	1.196	0.397	33.19	393.8
3	1.570	1.163	0.381	32.76	615.6	1.612	1.188	0.392	33.00	528.4
4	1.571	1.151	0.379	32.93	725.6	1.544	1.190	0.394	33.11	708.0
5	1.540	1.177	0.384	32.63	950.8	1.553	1.204	0.397	32.97	763.6
6	1.540	1.177	0.384	32.63	977.4	1.554	1.205	0.397	32.95	993.1

<sup>a</sup> C–P is the distance between the critical point P and the C attractor along the C–O bond.

<sup>b</sup> *r* is the fractional relative position of the critical point along the C–O bond defined as  $[(\text{C–P})/(\text{C–O})] \times 100$ .

(CO)<sub>n</sub> oligomers other than (CO)<sub>2</sub> is consistent with that obtained for the C–O bond lengths.

Table 1 also contains molecular volumes,  $\bar{v}$ , calculated for these oxocarbon oligomers. The molecular volume is defined as the volume over which the total electron density of the molecule is distributed within a predefined criterion. In the calculation of these molecular volumes, an electron density criterion of 99.99% has been used.

### 3.2. Thermochemistry

Thermochemical analysis has been carried out to investigate thermal stabilities of these oligomers. Some calculated thermochemical properties have been tabulated in Table 2. Thermochemical quantities reported in this table are defined for the gas phase formation reaction (1) at 298.15 K and 1 atm for one mole of carbon monoxide cyclic oligomer (CO)<sub>n</sub> according to Eq. (2).



$$\Delta Y = Y[(\text{CO})_n] - nY[(\text{CO})] \quad (2)$$

$$Y = E, H, G \text{ and } S$$

It can be seen from  $\Delta G$  values listed in Table 2 that formation of all of these oligomers from CO molecules is thermodynamically nonspontaneous at standard conditions of temperature and pressure. RHF method predicts that the maximum and minimum values of  $\Delta G$  belong to (CO)<sub>4</sub> and (CO)<sub>5</sub>, respectively. While, B3LYP method predicts that the  $\Delta G$  value for (CO)<sub>3</sub> and (CO)<sub>5</sub> are the maximum and minimum, respectively. At MP2 level of theory,  $\Delta G$  for (CO)<sub>3</sub> has the lowest positive value and a population analysis on the bonding of this oligomer at the same level of theory reveals that the CO bond order is 97.48% of that of isolated CO molecule. This implies that the three constituting CO molecules of (CO)<sub>3</sub> are not engaged in a normal chemical bond (Scheme 2), so explaining its minimum value of formation  $\Delta G$ .

### 3.3. Vibrational analysis

Vibrational analysis on (CO)<sub>2</sub> to (CO)<sub>6</sub> cyclic oligomers have been carried out to characterize stable states of the optimized structures. The vibrational

frequencies calculated at the same level of theory with the same basis set showed no imaginary frequency approving the (quantum mechanically) stable nature of the optimized structures on the molecular potential energy surface for these CO cyclic oligomers, except for (CO)<sub>4</sub> at RHF and (CO)<sub>2</sub> at both levels of theory which have a negative mode. We could not interpret the existence of the negative vibrational mode obtained for (CO)<sub>2</sub> and (CO)<sub>4</sub>, in spite of full optimization with various initial guesses and the use of different appropriate SCF criteria.

Frequencies, IR(Raman) intensities, and degeneracies of the vibrational modes of these oligomers calculated at RHF and B3LYP levels of theory are listed in Table 3. Results listed in this table show that the vibrational frequency of the breathing mode for (CO)<sub>n</sub> cyclic oligomers labeled by # follows the order (CO)<sub>3</sub> < (CO)<sub>6</sub> < (CO)<sub>5</sub> < (CO)<sub>4</sub> < (CO)<sub>2</sub>. No chemical interpretation could be presented for this trend. Vibrational study on these compounds shows (Fig. 1) also that the highest frequency mode has a red-shift with increasing  $n$  (number of CO groups). The same trend has been observed for the lowest frequency mode.

Fig. 1 visualizes that the (gas phase) isolated (CO)<sub>n</sub> cyclic oligomers would be distinguishable in an experimental vibrational study, especially in the finger print region. However, due to the matrix effects and averaging of various time-dependent interactions and fluctuations in the force field acting on a surrounded molecule in the liquid or solid phase, the peak assignment might be very complicated. This difficulty is enhanced if the very low concentration of these oligomers is taken into account.

### 3.4. Population analysis

In addition to stabilization energy [48,49], structural criteria [50], magnetic properties [51], and nuclear spin (NMR) chemical shifts [52], population analysis can be used to investigate the conjugation of  $\pi$ -systems and aromaticity of compounds, theoretically. Contributions of the basis set functions to the HOMO and LUMO molecular orbitals of (CO)<sub>2</sub> and (CO)<sub>6</sub> have been calculated and listed in Tables 4–6.

The results of the same analysis on (CO)<sub>3</sub>, (CO)<sub>4</sub> and (CO)<sub>5</sub> have been given in Tables A1–A3 in Appendix A.

Table 2

Thermochemical properties calculated at RHF, DFT-B3LYP and MP2 levels of theory using 6-31G\* basis set for the fully optimized structures of (CO)<sub>n</sub> oligomers. Note that the MP2/6-31G\* calculations were not successful for (CO)<sub>5</sub> and (CO)<sub>6</sub> cyclic oligomers

Method	Property	(CO) <sub>1</sub>	(CO) <sub>2</sub>	(CO) <sub>3</sub>	(CO) <sub>4</sub>	(CO) <sub>5</sub>	(CO) <sub>6</sub>
RHF	<i>C<sub>v</sub></i>	20.8	35.9	74.2	80.7	111.5	135.8
	<i>S</i>	197.5	190.0	306.3	311.7	371.5	444.3
	$\overline{\text{ZPE}}$	14.6	5.9	5.4	4.6	5.4	5.4
	$\Delta E$	0.0	398.3	486.6	655.2	391.2	467.8
	$\Delta H$	0.0	395.8	481.6	647.7	381.2	455.6
	$T\Delta S$	0.0	−61.0	−85.2	−142.3	−183.4	−220.4
	$\Delta G$	0.0	456.9	566.9	789.9	564.8	676.1
	<i>m/v</i>	0.114	0.122	0.136	0.154	0.147	0.172
B3LYP	<i>C<sub>v</sub></i>	20.8	38.2	63.6	98.4	121.3	129.2
	<i>S</i>	197.5	164.4	299.2	333.0	366.9	398.3
	$\overline{\text{ZPE}}$	13.4	5.0	4.6	4.6	5.0	4.6
	$\Delta E$	0.0	240.2	251.5	123.4	73.2	82.0
	$\Delta H$	0.0	237.7	246.4	115.9	63.2	69.5
	$T\Delta S$	0.0	−68.7	−87.6	−136.5	−185.2	−234.8
	$\Delta G$	0.0	306.7	333.9	252.3	248.5	304.2
	<i>m/v</i>	0.130	0.142	0.159	0.158	0.183	0.169
MP2	<i>C<sub>v</sub></i>	18.8	40.6	49.8	93.7	—	—
	<i>S</i>	197.9	242.3	342.3	344.8	—	—
	$\overline{\text{ZPE}}$	12.6	5.4	3.3	5.0	—	—
	$\Delta E$	0.0	311.7	−5.9	237.7	—	—
	$\Delta H$	0.0	309.2	−10.9	230.1	—	—
	$T\Delta S$	0.0	−45.8	−75.0	−133.1	—	—
	$\Delta G$	0.0	355.2	64.0	363.2	—	—

$\Delta E$ ,  $\Delta H$ ,  $T\Delta S$  and  $\Delta G$  are given in kJ mol<sup>−1</sup> and *C<sub>v</sub>* and *S* are given in J mol<sup>−1</sup> K<sup>−1</sup>.  $\overline{\text{ZPE}}$  is the average value of zero point energy per one vibrational mode in kJ mol<sup>−1</sup> and *m/v* is the molecular mass density in atomic unit.

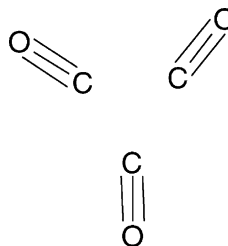
Mutual contributions from 2P<sub>Z</sub> and 3P<sub>Z</sub> basis functions of the atoms not connected directly in the LUMO 43 (Tables 5 and 6), approves existence of, however small, aromaticity in (CO)<sub>6</sub> oligomer. Existence of a molecular orbital constituted from 2P<sub>Z</sub> and 3P<sub>Z</sub> basis function of all atoms in (CO)<sub>2</sub> oligomer (Table 4) even more clearly shows conjugation of the  $\pi$ -electrons in this compound. The same results, however, with different extents, are obtained for other (CO)<sub>n</sub> compounds based on this population analysis.

### 3.5. The HOMO–LUMO energy gaps

It is already known that orbital energy gaps from Koopman's theorem are overestimated since electron correlation is not included in the Hartree–Fock formalism and, furthermore, the electron density relaxation following to the excitation is not taken

into account. Even though several disadvantages can be pointed out in getting energy gaps from Koopman's theorem, its simplicity and no additional computational cost make it very attractive and an interesting approach to study larger and complex systems.

Ionization potential (IP) and electron affinity (EA) are properties that are well-defined in DFT. Janak's theorem [53] establishes that the HOMO and LUMO



Scheme 2. The optimized bonding structure of (CO)<sub>3</sub> at MP2 level of theory.

Table 3

Wavenumbers ( $\tilde{\nu}$ ), IR(*Raman*) intensities and degeneracies (*g*) of vibrational modes for the (CO)<sub>*n*</sub> cyclic oligomers calculated at RHF and B3LYP levels of theory using 6-31G\* basis set

RHF $\tilde{\nu}$ (cm <sup>-1</sup> )	IR( <i>Raman</i> ) intensity	<i>g</i>	B3LYP $\tilde{\nu}$ (cm <sup>-1</sup> )	IR( <i>Raman</i> ) intensity	<i>g</i>
CO					
2439.0	137.9(11.8)	1	2208.6	67.9(12.1)	1
(CO) <sub>2</sub>					
– 400.6	8.8(8.4)	1	– 530.7	0.0(8.6)	1
376.7	16.6(0.0)	1	322.7	6.2(0.0)	1
752.6	0.1(1.6)	1	579.0	6.3(0.3)	1
1033.0	0.0(23.4)	1	946.8	0.0(21.1)	1
1993.4	726.0(0.0)	1	1816.2	356.8(0.0)	1
2637.9 <sup>a</sup>	0.0(32.7)	1	2396.0 <sup>a</sup>	0.0(24.3)	1
(CO) <sub>3</sub>					
216.8	35.5(0.0)	1	116.6	15.3(0.0)	1
265.1	2.6(3.9)	2	192.7	0.4(4.4)	2
595.4	0.0(4.2)	1	427.2	0.0(4.4)	1
1023.4	188.3(0.5)	2	903.5	117.5(0.5)	2
2027.9 <sup>a</sup>	0.0(74.7)	1	1761.9 <sup>a</sup>	0.0(63.1)	1
2140.0	163.6(29.2)	2	1907.4	109.3(24.8)	2
(CO) <sub>4</sub>					
– 398.9	616.5(0.0)	2	256.4	17.3(0.0)	1
291.2	32.8(0.0)	1	292.3	0.0(8.2)	1
305.0	0.0(8.9)	1	296.5	2.1(0.0)	2
316.8	24.7(0.0)	2	549.7	0.0(12.0)	1
572.0	0.0(10.4)	1	617.9	0.0(0.2)	2
646.8	0.0(20.9)	1	630.8	111.6(0.0)	2
677.8	0.0(1.0)	2	644.6	0.0(16.9)	1
1160.5	0.0(3.6)	1	1767.9	884.3(0.0)	2
1938.7	2353.2(0.0)	2	1931.6 <sup>a</sup>	0.0(102.3)	1
2181.7	0.0(135.1)	1	1939.0	0.0(76.9)	1
2214.6 <sup>a</sup>	0.0(102.2)	1			
(CO) <sub>5</sub>					
253.2	68.9(0.0)	1	217.0	43.3(0.0)	1
321.4	0.0(2.6)	2	287.4	0.0(2.5)	2
362.1	20.0(0.0)	2	320.6	12.3(0.0)	2
429.4	0.0(3.2)	2	363.3	0.0(1.3)	2
548.6	0.0(2.7)	2	493.6	0.0(3.4)	2
590.5	0.0(11.8)	1	520.4	0.0(11.3)	1
1159.6	247.6(0.0)	2	1044.7	147.3(0.0)	2
1231.9	0.0(1.0)	2	1068.4	0.0(2.5)	2
2074.2	160.4(0.0)	2	1819.4	104.7(0.0)	2
2095.8	0.0(25.0)	2	1828.0 <sup>a</sup>	0.0(101.2)	1
2096.8 <sup>a</sup>	0.0(93.9)	1	1869.5	0.0(10.3)	2
(CO) <sub>6</sub>					
259.6	78.3(0.0)	1	224.6	50.3(0.0)	1
386.4	21.6(0.0)	2	343.6	14.2(0.0)	2
407.1	0.0(3.7)	2	355.6	0.0(1.8)	2
438.8	0.0(6.1)	2	393.8	0.0(7.4)	2
516.2	0.0(15.9)	1	454.5	0.0(15.9)	1
1126.2	294.3(0.0)	2	1018.2	188.7(0.0)	2

Table 3 (continued)

RHF $\bar{\nu}$ (cm <sup>-1</sup> )	IR(Raman) intensity	g	B3LYP $\bar{\nu}$ (cm <sup>-1</sup> )	IR(Raman) intensity	g
1280.2	0.0(0.1)	2	1125.8	0.0(1.0)	2
2051.2	187.5(0.0)	2	1799.7	129.2(0.0)	2
2057.6	0.0(22.4)	2	1808.4 <sup>a</sup>	0.0(89.4)	1
2069.5 <sup>a</sup>	0.0(75.9)	1	1825.8	0.0(5.4)	2

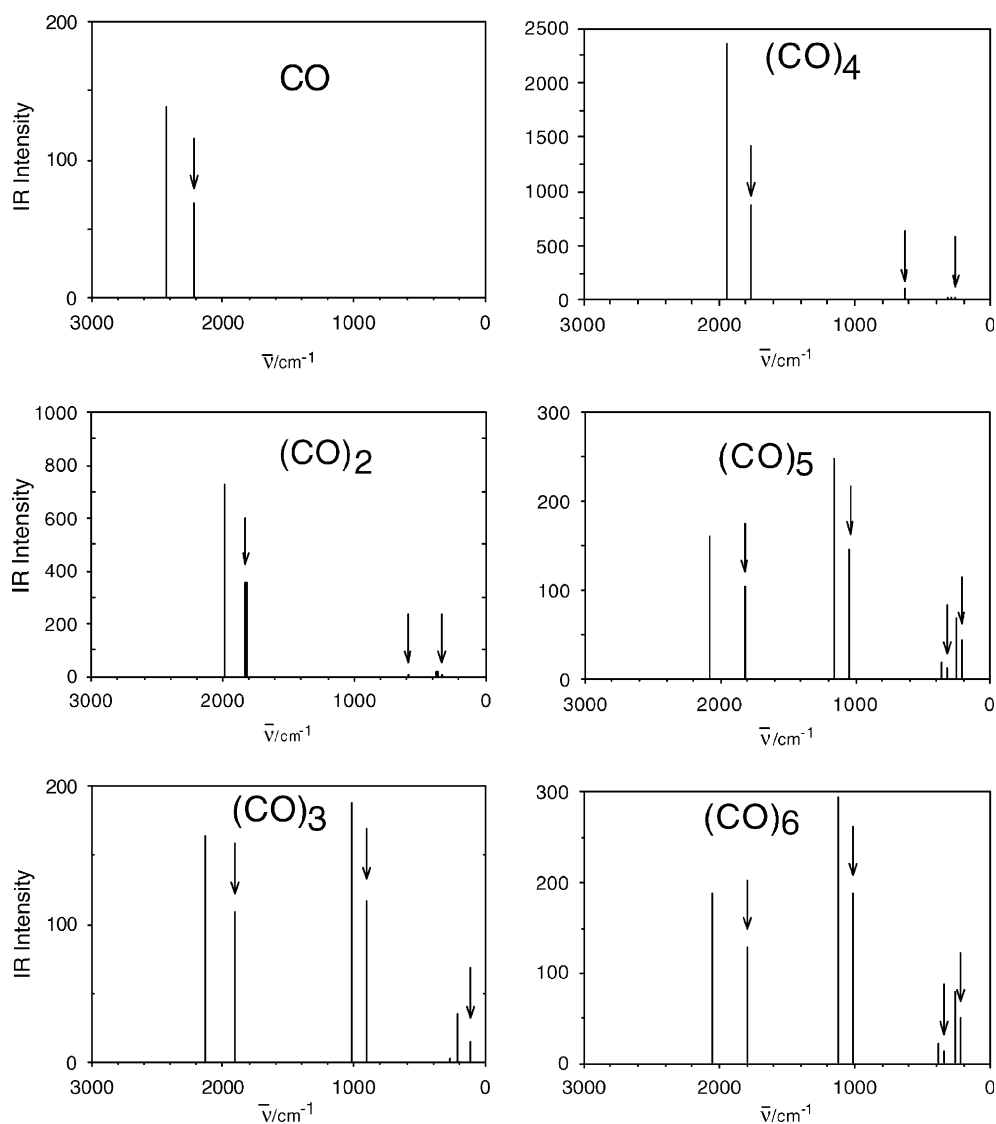
<sup>a</sup> The breathing mode of vibration.

Fig. 1. The calculated IR spectrum for the optimized structures of carbon monoxide (CO)<sub>n</sub> oligomers using RHF/6-31G\* and B3LYP/6-31G\* methods. The arrows show the peaks calculated at B3LYP level of theory.



Table 4

Relative contributions of some atomic basis functions (BF) to a few molecular orbitals including the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO) for (CO)<sub>2</sub> oligomer

BF	RHF				B3LYP			
	O1 <sup>a</sup>	C2	C3	O4	O1	C2	C3	O4
HOMO 14( <i>e</i> = −9.462 eV)					HOMO 14( <i>e</i> = −5.995 eV)			
2P <sub>X</sub>	0	0	0	0	17	14	14	17
2P <sub>Y</sub>	14	14	14	14	0	0	0	0
3P <sub>X</sub>	0	0	0	0	12	7	7	12
3P <sub>Y</sub>	13	9	9	13	0	0	0	0
LUMO 15( <i>e</i> = −0.048 eV)					LUMO 15( <i>e</i> = −4.542 eV)			
2P <sub>Z</sub>	13	13	10	12	16	13	13	16
3P <sub>Z</sub>	15	12	12	15	13	8	8	13

<sup>a</sup> For numbering scheme see structure II in Scheme 1.

energies are, respectively, the IP and EA (with a minus sign) for a given molecular system. Furthermore, recently, Levy and Nagy [54] developed a DFT version of Koopman's theorem, showing that the energy gap can be estimated directly from the eigenvalues of the Kohn–Sham equations. Consequently, the energy gap can be estimated directly from the HOMO/LUMO energy difference, in a similar way, as it is estimated from ab initio calculations using Koopman's theorem.

In a first approximation, the barrier for electron transfer is proportional to HLG (HOMO–LUMO energy gap) value. Therefore, from the calculated HLG values reported in Table 7, one can conclude that the molar contributions of these cyclic CO oligomers to the bulk electric conductance of the solid CO follow the trend (CO)<sub>3</sub> < (CO)<sub>5</sub> < (CO)<sub>6</sub> < (CO)<sub>2</sub> < (CO)<sub>4</sub>.

Table 5

Relative contributions of some atomic basis functions (BF) to a few molecular orbitals including three highest occupied molecular orbitals MO 40, MO 41 and HOMO and the lowest unoccupied molecular orbital (LUMO) for (CO)<sub>6</sub> oligomer calculated using RHF/6-31G\* method

BF	O1 <sup>a</sup>	C2	C3	C4	O5	O6	C7	C8	C9	O10	O11	O12
Occupied MO 40 ( <i>e</i> = −13.901 eV)												
2S	0	0	1	0	1	0	0	0	1	1	0	0
2P <sub>X</sub>	2	2	2	2	2	2	10	2	2	2	10	2
2P <sub>Y</sub>	1	1	0	0	0	1	0	0	0	0	0	1
3S	0	0	6	0	6	0	0	0	6	6	0	0
3P <sub>X</sub>	1	1	2	1	1	1	6	1	1	2	6	1
3P <sub>Y</sub>	1	1	0	0	0	1	0	0	0	0	0	1
Occupied MO 41 ( <i>e</i> = −13.901 eV)												
2S	0	0	0	1	0	0	0	1	0	0	0	0
2P <sub>X</sub>	1	1	0	0	0	1	0	0	0	0	0	1
2P <sub>Y</sub>	8	8	2	2	2	8	1	2	2	2	1	8
3S	0	0	2	8	2	0	0	8	2	2	0	0
3P <sub>X</sub>	1	1	0	0	0	1	0	0	0	0	0	1
3P <sub>Y</sub>	4	4	0	2	0	4	0	2	0	0	0	4
HOMO 42 ( <i>e</i> = −11.600 eV)												
2P <sub>X</sub>	1	1	6	1	1	6	6	1	1	6	1	1
2P <sub>Y</sub>	4	4	0	4	4	0	0	4	4	0	4	4
3P <sub>X</sub>	1	0	1	0	1	5	1	0	0	5	1	1
3P <sub>Y</sub>	4	1	0	1	4	0	0	1	1	0	4	4
LUMO 43 ( <i>e</i> = −1.565 eV)												
2P <sub>Z</sub>	5	2	2	2	5	5	2	2	2	5	5	5
3P <sub>Z</sub>	6	4	4	4	6	6	4	4	4	6	6	6

<sup>a</sup> For numbering scheme see structure VI in Scheme 1.

Table 6

Relative contributions of some atomic basis functions (BF) to a few K–S molecular orbitals including the highest occupied and the lowest unoccupied K–S molecular orbitals (HOMO and LUMO) for (CO)<sub>6</sub> oligomer calculated using B3LYP/6-31G\* method

BF	O1 <sup>a</sup>	C2	C3	C4	O5	O6	C7	C8	C9	O10	O11	O12
Occupied MO 40 ( $e = -9.047$ eV)												
2S	0	0	1	1	0	0	1	1	0	0	0	0
2P <sub>X</sub>	10	1	2	2	2	2	2	2	1	2	2	10
2P <sub>Y</sub>	0	0	0	0	2	2	0	0	0	2	2	0
3S	0	0	7	7	0	0	7	7	0	0	0	0
3P <sub>X</sub>	5	0	1	1	1	1	1	1	0	1	1	5
3P <sub>Y</sub>	0	0	0	0	1	1	0	0	0	1	1	0
Occupied MO 41 ( $e = -9.047$ eV)												
2S	0	1	0	0	0	0	0	0	1	0	0	0
2P <sub>X</sub>	0	0	0	0	2	2	0	0	0	2	2	0
2P <sub>Y</sub>	1	2	2	2	7	7	2	2	2	7	7	1
3S	0	10	2	2	0	0	2	2	10	0	0	0
3P <sub>X</sub>	0	0	0	0	1	1	0	0	0	1	1	0
3P <sub>Y</sub>	0	2	0	0	3	3	0	0	2	3	3	0
HOMO 42 ( $e = -7.424$ eV)												
2S	0	0	0	0	0	0	0	0	0	2	0	0
2P <sub>X</sub>	7	5	2	2	2	2	2	2	5	5	2	7
2P <sub>Y</sub>	0	0	3	3	5	5	3	3	0	0	5	0
3S	0	0	0	0	0	0	0	0	0	1	0	0
3P <sub>X</sub>	5	1	0	0	1	1	0	0	1	3	1	5
3P <sub>Y</sub>	0	0	0	0	3	3	0	0	0	0	3	0
LUMO 43 ( $e = -5.524$ eV)												
2P <sub>Z</sub>	6	2	2	2	6	6	2	2	2	6	6	6
3P <sub>Z</sub>	6	2	2	2	6	6	2	2	2	6	6	6

<sup>a</sup> For numbering scheme see structure VI in Scheme 1.

### 3.6. Atomic point charges, bond dipole moments and electric polarizabilities

Electric charges on carbon atoms calculated for the optimized geometries of (CO)<sub>n</sub> cyclic oligomers

have been tabulated in Table 7. Because of  $C_n$  symmetry, in each compound all carbon atoms and all oxygen atoms have exactly the same electric charges. The negative charge on the oxygen atom is exactly equal to the positive charge on the carbon

Table 7

Polarizability tensor elements, atomic charges and HLG values calculated at RHF and DFT-B3LYP levels of theory using 6-31G\* basis set. In this table  $q_C$  is the electric charge on the carbon atom and HLG is in eV

$n$	RHF						B3LYP					
	$a_{xx}$	$a_{yy}$	$a_{zz}$	$a_{iso}$	$q_C^a$	HLG	$a_{xx}$	$a_{yy}$	$a_{zz}$	$a_{iso}$	$q_C^a$	HLG
1	7.7	7.7	12.0	9.1	0.268	19.43	8.0	8.0	12.6	9.5	0.174	9.52
2	10.9	10.9	44.3	22.0	0.399	9.41	11.3	11.1	45.6	22.6	0.351	1.45
3	40.2	40.2	16.6	32.4	0.372	11.15	43.8	43.8	17.4	35.0	0.304	2.97
4	78.4	78.4	21.0	59.3	0.387	6.21	77.6	77.6	21.3	58.9	0.336	1.23
5	63.1	63.1	26.6	50.9	0.400	10.42	68.7	68.7	27.0	54.8	0.350	2.13
6	75.2	75.2	31.8	60.8	0.386	10.04	82.5	82.5	32.3	65.7	0.340	1.90

<sup>a</sup> Electric charge on oxygen atom,  $q_O$ , is equal to  $-q_C$ .

Table 8

Density Laplacian, ellipticity, buckling parameter, ring total density ( $\rho_{\text{ring}}$ ) and the electric charge on carbon atom calculated for  $(\text{CO})_n$  compounds within AIM at RHF and B3LYP levels of theory using 6-31G\* basis set

$n$	Density Laplacian		Ellipticity		Buckling	$\rho_{\text{ring}}$	Charge
	C–C	C–O	C–C	C–O	C–C		
<i>RHF</i>							
1	–	1.727	–	0.000	–	–	1.403
2	– 1.0610	0.9885	1.3550	0.0346	0.0001	–	1.235
3	– 0.5482	1.0360	0.0305	0.1169	0.1916	0.1487	1.261
4	– 0.3752	0.9944	0.2616	0.0170	0.0282	0.0651	1.291
5	– 0.7693	0.9234	0.0653	0.1180	0.0029	0.0281	1.207
6	– 0.7476	0.9364	0.0690	0.1239	0.0436	0.0110	–
<i>B3LYP</i>							
1	–	1.354	–	0.0000	–	–	1.222
2	– 0.8922	0.6211	0.9783	0.0588	0.0000	–	1.010
3	– 0.3323	0.6803	0.0286	0.0463	0.1738	0.1333	1.076
4	– 0.3861	0.5495	0.2286	0.0553	0.0115	0.0711	1.052
5	– 0.5774	0.4707	0.0661	0.0558	0.0067	0.0275	1.030
6	– 0.5615	0.4721	0.0666	0.0622	0.0348	0.0109	1.023

atom. Compared to the RHF calculations, B3LYP predict less positive charges on carbon atoms. The order of positive charges on carbon atoms calculated at both levels of theory in these oligomers follows the trend  $(\text{CO})_1 < (\text{CO})_3 < (\text{CO})_4 \sim (\text{CO})_6 < (\text{CO})_2 \sim (\text{CO})_5$ .

The state of having positive charges on all interconnected carbon atoms can explain the thermochemical instability of these compounds compared to that of the isolated constituting CO molecules.

Values of electric dipole moment of the C–O bond in the  $(\text{CO})_n$  oligomers,  $\mu_n$  with  $n$  the number of monomers in oligomer, is calculated for all oligomers using C–O bond lengths listed in Table 1 based only on the atomic point charges given in Table 7 using Eq. (3).

$$\mu_n = (q_{\text{C}} \cdot r_{\text{CO}})_n \quad (3)$$

In this equation,  $q_{\text{C}}$  and  $r_{\text{CO}}$  represent, respectively, the electric point charge on the carbon atom and the carbon-oxygen bond length in the  $(\text{CO})_n$  oligomer. The calculated values of the C–O bond dipole moments  $\mu_n$  for the  $(\text{CO})_n$  oligomers obtained from RHF and B3LYP computations are slightly different, however, both set of bond dipole moments follow the same trend  $\mu_1 < \mu_3 < \mu_4 < \mu_6 < \mu_2 < \mu_5$ . This

Table 9

Hybrids of natural bond orbitals calculated by NBO analysis at RHF and DFT-B3LYP levels of theory using 6-31G\* basis set for carbon monoxide cyclic oligomers

$n$	BD (1) C–O		BD (2) C–O		BD (3) C–O		BD (1) C–C	
	C	O	C	O	C	O	C	C
<i>RHF</i>								
1	sp <sup>2.67a</sup>	sp <sup>1.01a</sup>	p	p	p	–	–	–
2	sp <sup>1.25</sup>	sp <sup>1.35b</sup>	p	p	–	–	sp <sup>0.80</sup>	sp <sup>0.80</sup>
3	sp <sup>1.10b</sup>	sp <sup>1.60b</sup>	p	p <sup>b</sup>	–	–	sp <sup>2.21b</sup>	sp <sup>2.21b</sup>
4	sp <sup>2.10b</sup>	sp <sup>0.99b</sup>	p <sup>b</sup>	p	p	p	–	–
5	sp <sup>1.95b</sup>	sp <sup>1.14b</sup>	p	p	–	–	sp <sup>2.03b</sup>	sp <sup>2.03b</sup>
6	sp <sup>2.06b</sup>	sp <sup>1.15b</sup>	p	p	–	–	sp <sup>1.97</sup>	sp <sup>1.97</sup>
<i>B3LYP</i>								
1	sp <sup>3.02b</sup>	sp <sup>1.18a</sup>	p <sup>b</sup>	p	p <sup>b</sup>	p	–	–
2	sp <sup>1.26</sup>	sp <sup>1.59b</sup>	p	p	–	–	sp <sup>0.80</sup>	sp <sup>0.80</sup>
3	sp <sup>1.62</sup>	sp <sup>1.27b</sup>	p	p	–	–	sp <sup>2.22</sup>	sp <sup>2.22</sup>
4	sp <sup>1.81</sup>	sp <sup>1.24b</sup>	p	p	pd <sup>0.59</sup>	p	sp <sup>1.21</sup> d <sup>0.89</sup>	sp <sup>1.21</sup> d <sup>0.89</sup>
5	sp <sup>1.99</sup>	sp <sup>1.33b</sup>	p	p	–	–	sp <sup>2.01</sup>	sp <sup>2.01</sup>
6	sp <sup>2.12</sup>	sp <sup>1.34b</sup>	p	p	–	–	sp <sup>1.95</sup>	sp <sup>1.95</sup>

<sup>a</sup> These orbitals have d<sup>0.02</sup> contribution.

<sup>b</sup> These orbitals have d<sup>0.01</sup> impurity.

trend shows that the C–O bond dipole moment is altered significantly by the interactions between monomers in the  $(\text{CO})_n$  compounds. It is obvious that because of  $C_n$  symmetry for each oligomer, all C–O bond dipole moments are equal. This means that each  $(\text{CO})_n$  oligomer can be characterized with a single value of bond dipole moment  $\mu_n$  only. Furthermore, the calculated dipole moments in this fashion are not quantum mechanically accurate to be regarded as quantitative local bond characteristics. However, they are accurate enough for qualitative analysis, especially on a comparative basis.

Polarizability is a measure of ability of a molecule to respond to an external electric field. When electrons of the molecules are subjected to an electric field, they acquire enough energy and can move along the direction of the applied field, thus, electric conductivity will take place. In order to study contributions of these oligomers to the electric conductivity of the solid CO, diagonal elements of electric polarizability tensor ( $a_{xx}$ ,  $a_{yy}$ ,  $a_{zz}$ ) and its isotropic component ( $a_{\text{iso}}$ ) have been calculated and reported in Table 7. It can be seen from this table that values of polarizability increases when  $n$  (the number of CO groups of the oligomer) increases, with the exception of  $(\text{CO})_4$  that has higher polarizability than that  $(\text{CO})_5$  does. Due to the unidirectional correlation between macroscopic electric conductivity and molecular electric polarizability, this implies that the contribution of  $(\text{CO})_n$  oligomer to the electric conductivity of solid CO increases when  $n$  increases.

### 3.7. AIM analysis of bond strength

The nature of the chemical bonds in these cyclic oligomers has been studied also by means of the Bader's theory of AIM [55,56]. The AIM method was extended and implemented within GAUSSIAN 98W program by Cioslowski [57–60]. Such analysis was performed since it is known that the electronic density at the bond critical point (BCP) may be very useful parameters for the estimation of the relative strength of the chemical bonding [61]. The distance between the BCP and C attractor along the C–O bond at RHF/6-31G\* and DFT-B3LYP/6-31G\* levels of theory are listed in Table 1.

The AIM calculated relative position,  $r$  of the BCP of the C–O bond defined as  $r = [(C-P)/(C-O)] \times 100$ , for the B3LYP optimized structures of

$(\text{CO})_n$  compounds show that the largest value of  $r$  belongs to  $(\text{CO})_2$ , i.e. the critical points is moved towards oxygen atoms compared to that of other  $(\text{CO})_n$  oligomers. This is an indication of the reduced ionic character of the C–O bonds implying larger removal of the  $\pi$ -electrons from C–O bonds of the molecule. Since electron correlations are ignored in the RHF calculations, no specific and interpretable results are expected from the calculations at this level of theory.

The C–C bond density Laplacian calculated at B3LYP level of theory listed in Table 8, shows that  $\text{C}_2\text{O}_2$  has the most strong carbon–carbon bond while,  $\text{C}_3\text{O}_3$  has the weakest carbon–carbon bond. The results of the same analysis at RHF level of theory also indicate that  $\text{C}_2\text{O}_2$  has the most strong carbon–carbon bond while,  $\text{C}_4\text{O}_4$  has the weakest carbon–carbon bond. Accordingly, the carbon–oxygen bond strength has the reverse order of that of carbon–carbon bond. The relatively strongest C–C bond for the  $\text{C}_2\text{O}_2$  molecule calculated from the density laplacian is consistent with what obtained from BCPs.

Buckling parameter showing the extent of aromaticity on a ring compound, has been calculated within AIM for  $(\text{CO})_n$  compounds and are listed in Table 8. The buckling parameters show interestingly that, although C–C bond in  $(\text{CO})_3$  is very weak, the ring (C–C) bonding structure of this compound as the highest aromaticity among  $(\text{CO})_n$  compounds. In addition, the fact that HOMO for  $(\text{CO})_3$  oligomer is doubly degenerate, increases the possibility of aromaticity in this compound. This is in complete agreement with what previously reported by Aihara [39].

The chemical bonding characteristics have also been studied via natural bond orbital (NBO) analysis that extended and implemented within GAUSSIAN 98W program [62–68]. The calculated results have been tabulated in Table 9. The NBO analysis has not been successful in characterizing chemical bonds in  $(\text{CO})_3$  and  $(\text{CO})_4$  probably due to their high angular strain. However, NBO predicts that a perfect C–C bond is formed between CO monomers in other  $(\text{CO})_n$  cyclic oligomers.

### 3.8. Molecular orbital and charge density analysis

The RHF/6-31G\* and DFT-B3LYP/6-31G\* iso-surface maps of the HF and KS HOMO and

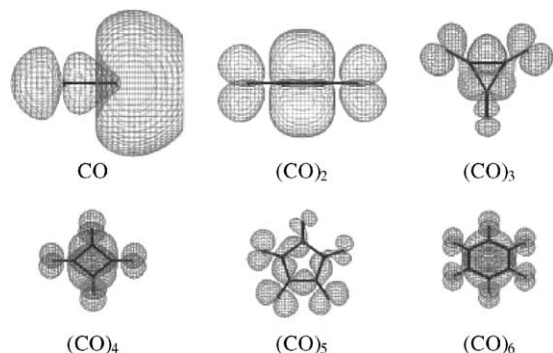


Fig. 2. The HF (and identically K–S) HOMO isosurfaces for the first six carbon monoxide cyclic oligomers calculated at RHF and B3LYP levels of theory using 6-31G\* basis set. The HOMO for (CO)<sub>3</sub> is doubly degenerate.

LUMO of these cyclic oligomers have been calculated. Since molecular orbitals and total charge density isosurfaces obtained for the HOMO and LUMO of (CO)<sub>n</sub> oligomers at the two RHF and B3LYP levels of theory are more and less identical, only one set of the results are demonstrated in Figs. 2–4. In spite of their different eigenvalues, similarities of the corresponding HF and KS molecular orbital isosurfaces and, especially, of the total charge densities isosurfaces obtained for each molecule at RHF and B3LYP levels of theory are in complete agreement with what reported by Levy and Nagy [54]. The HOMO isosurfaces calculated at both RHF and DFT levels of theory indicate that p-electrons on the carbon atoms in all (CO)<sub>n</sub> compounds are partially

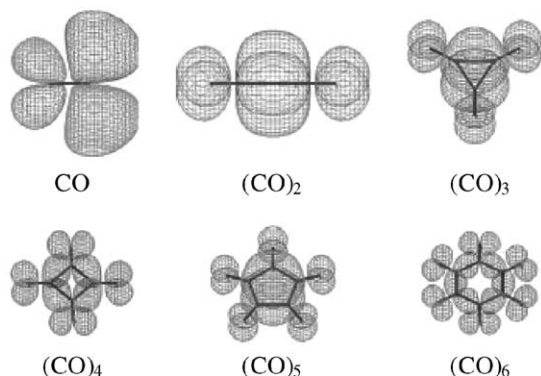


Fig. 3. The HF (and identically K–S) LUMO isosurfaces for the first six carbon monoxide cyclic oligomers calculated at RHF and B3LYP levels of theory using 6-31G\* basis set.

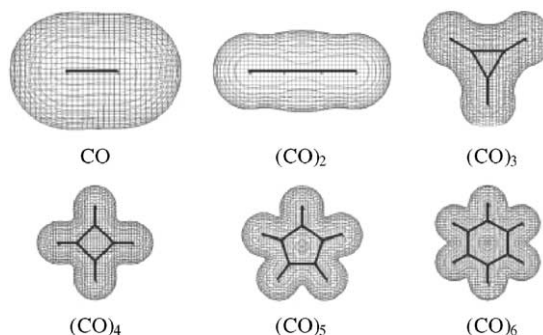


Fig. 4. Isosurfaces of the total charge density for the first six carbon monoxide cyclic oligomers calculated at RHF level of theory using 6-31G\* basis set. The calculated isosurfaces at B3LYP level of theory are indistinguishably similar to those obtained at RHF level of theory.

delocalized over the entire ring in this molecular orbital. The HOMO for (CO)<sub>3</sub> is exceptional in the sense that it is doubly degenerate. This further facilitates the delocalization of  $\pi$ -electrons over the three-member ring atoms of this molecule and enhances its aromaticity. The isosurfaces calculated for the LUMO of (CO)<sub>n</sub> oligomers show larger number of nodal planes reflecting its more antibonding nature. Since the HOMO and LUMO contribute largely, in some systems exclusively, to the response properties of a molecule, the delocalization of  $\pi$ -electrons deduced from these isosurfaces, is expected to be observable in, for example, electric polarization of these molecules.

#### 4. Conclusions

The (CO)<sub>n</sub> oxocarbons which are the cyclic oligomers of CO are quantum mechanically stable molecules. However, formation of neither of these molecules from isolated CO molecules at standard conditions of temperature and pressure is spontaneous within prediction of RHF and DFT-B3LYP levels of theory. The B3LYP calculation results predict less thermochemical stabilities for this series of oxocarbons. It can therefore be concluded that these CO oligomers statistically do not contribute significantly to the physical and chemical properties of the solid CO. Formation of these compounds leads to higher density for the solid CO, see Table 2.

Table A1

Relative contributions of some atomic basis functions (BF) to a few molecular orbitals including the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO) for (CO)<sub>3</sub> oligomer

BF	RHF						B3LYP					
	O1 <sup>a</sup>	C2	C3	C4	O5	O6	O1	C2	C3	C4	O5	O6
HOMO 21( $e = -12.080$ eV)							HOMO 21( $e = -7.914$ eV)					
1S	0	1	0	0	0	0	0	0	0	0	0	0
2S	0	2	0	0	0	0	0	0	2	2	0	0
2P <sub>x</sub>	0	0	5	5	5	5	16	5	2	2	0	0
2P <sub>y</sub>	2	5	2	2	6	6	0	0	3	3	6	2
3S	0	25	6	6	0	0	0	0	18	18	0	0
3P <sub>x</sub>	0	0	1	1	3	3	9	0	1	1	0	0
3P <sub>y</sub>	1	4	0	0	4	4	0	0	1	1	3	1
LUMO 22 ( $e = -0.928$ eV)							LUMO 22 ( $e = -4.943$ eV)					
2P <sub>z</sub>	9	5	5	5	9	9	12	7	7	7	12	12
3P <sub>z</sub>	12	8	8	8	12	12	9	5	5	5	9	9

<sup>a</sup> Refer to structure III in Scheme 1 for numbering of atoms.

Population analysis shows that the  $\pi$ -electrons of the individual CO bonds are delocalized partially over the ring atoms of the molecule, thus, contributing to higher polarizability and hence higher contributions to the electric conductance of the solid CO. The delocalization of the  $\pi$ -electrons over the ring atoms for the (CO)<sub>3</sub> is so large that it can be considered as a weak aromaticity. The AIM calculated BCPs, density Laplacian and buckling parameters are consistent with the results obtained from population analysis.

The RHF and B3LYP vibrational analysis shows that the highest and lowest frequency modes for the (CO)<sub>n</sub> cyclic oligomers show red-shift with increasing  $n$ . An experimental vibrational study, IR or Raman, on these compounds seems to be successful in the gas phase only. The C–O and C–C bond lengths depend on the geometry of the compound and do not show any well-behaved trend with  $n$ . The lack of well-behaved trends with  $n$  in most of the molecular properties of these compounds indicates that the chemical natures of the C–C bonds in this series of oxocarbons are significantly different. Therefore, it might be suitable to name these compounds as clusters rather than oligomers. The C–C bond in (CO)<sub>2</sub> molecule is, however, a true chemical bond.

Table A2

Relative contributions of some atomic basis functions (BF) to a few molecular orbitals including the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO) for (CO)<sub>4</sub> oligomer

BF	O1 <sup>a</sup>	C2	C3	C4	O5	C6	O7	O8
<i>RHF</i>								
HOMO 28( $e = -8.829$ eV)								
2P <sub>z</sub>	8	4	4	4	8	4	8	8
3P <sub>z</sub>	8	5	5	5	8	5	8	8
LUMO 29( $e = -2.620$ eV)								
2P <sub>x</sub>	8	7	0	0	0	7	0	8
2P <sub>y</sub>	0	0	7	7	8	0	8	0
3P <sub>x</sub>	8	2	0	0	0	2	0	8
3P <sub>y</sub>	0	0	2	2	8	0	8	0
<i>B3LYP</i>								
HOMO 28 ( $e = -6.904$ eV)								
2P <sub>z</sub>	10	4	4	4	10	4	10	10
3P <sub>z</sub>	7	4	4	4	7	4	7	7
LUMO 29 ( $e = -5.676$ eV)								
2P <sub>x</sub>	10	7	0	0	0	7	0	10
2P <sub>y</sub>	0	0	7	7	10	0	10	0
3P <sub>x</sub>	7	1	0	0	0	1	0	7
3P <sub>y</sub>	0	0	1	1	7	0	7	0

<sup>a</sup> See structure IV in Scheme 1 for numbering of atoms.

Based on the results of this study, it seems to be interesting to carry out similar investigations on NO and N<sub>2</sub> cyclic oligomers.

supports. We gratefully acknowledge Professors A.C. and M.J. for providing there hardware and software facilities to carry out computations on GAUSSIAN 98W program via telnetting over the internet.

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## Appendix A

Tables A1–A3.

Table A3

Relative contributions of some atomic basis functions (BF) to a few molecular orbitals including the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO) for (CO)<sub>5</sub> oligomer

BF	O1 <sup>a</sup>	C2	C3	C4	O5	C6	C7	C8	O9	O10
<i>RHF</i>										
HOMO 34( $e = -12.113$ eV)										
2P <sub>x</sub>	0	0	2	0	2	2	2	5	2	9
2P <sub>y</sub>	0	2	2	2	3	4	2	0	7	0
3S	0	10	6	7	0	1	0	1	0	0
3P <sub>x</sub>	0	1	3	0	1	1	1	1	1	6
3P <sub>y</sub>	0	3	0	3	2	0	1	0	5	0
HOMO 35 ( $e = -12.113$ eV)										
2P <sub>x</sub>	6	4	0	4	0	0	0	0	0	6
2P <sub>y</sub>	3	2	4	0	6	2	2	2	2	3
3S	0	0	4	3	0	9	9	10	0	0
3P <sub>x</sub>	5	1	1	1	0	3	3	0	0	5
3P <sub>y</sub>	2	0	1	0	4	1	1	4	1	2
LUMO 36( $e = -1.696$ eV)										
2P <sub>z</sub>	6	2	2	2	6	2	6	2	6	6
3P <sub>z</sub>	8	4	4	4	8	4	8	4	8	8
<i>B3LYP</i>										
HOMO 34( $e = -7.758$ eV)										
2S	0	0	0	0	0	1	0	1	0	0
2P <sub>x</sub>	12	5	1	1	2	0	2	0	0	0
2P <sub>y</sub>	0	0	2	2	6	1	6	1	1	1
3S	0	0	4	4	0	10	0	10	0	0
3P <sub>x</sub>	7	0	1	1	1	1	1	1	0	0
3P <sub>y</sub>	0	0	0	0	4	2	4	2	1	1
HOMO 35( $e = -7.758$ eV)										
2S	0	2	0	0	0	0	0	0	0	0
2P <sub>x</sub>	0	0	0	0	0	4	0	4	7	7
2P <sub>y</sub>	1	1	2	2	4	1	4	1	4	4
3S	0	11	7	7	0	1	0	1	0	0
3P <sub>x</sub>	0	0	2	2	0	0	0	0	4	4
3P <sub>y</sub>	0	3	1	1	2	0	2	0	2	2
LUMO 36( $e = -5.623$ eV)										
2P <sub>z</sub>	8	2	2	2	8	2	8	8	8	8
3P <sub>z</sub>	6	2	2	2	6	2	6	6	6	6

<sup>a</sup> Refer to structure V in Scheme 1 for numbering of atoms.



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