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# $(QCO)^+$ as the model for bonding in non-classical carbonyls: a force approach study

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#### Abstract

As a model for non-classical metal carbonyls, we investigate CO in presence of a unit positive charge placed at different distances along the bond axis. We use the force approach, to look into the nature of the individual molecular orbitals. We find that in free CO the HOMO ( $\sigma(3)$ ) is antibinding. As the positive charge approaches form carbon side,  $\sigma(1)$  and degenerate  $\pi$  orbitals become more binding, while  $\sigma(2)$ and  $\sigma(3)$  become more antibinding. The overall effect is more binding resulting in a shorter C–O bond. If the charge approaches from oxygen side, then  $\sigma(1)$ ,  $\sigma(3)$  and degenerate  $\pi$  orbitals become less binding, while  $\sigma(2)$  becomes slightly more binding, resulting in a lengthening of C-O bond.

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Keywords: Non-classical carbonyl; Force approach; Binding; Antibinding; Non-binding

#### 1. Introduction

Recently there is much interest in studying the nature of bonding in 'non-classical' carbonyls [1]. In contrast to the classical metal carbonyl complexes, most of which are neutral or anionic, the non-classical metal carbonyls have a net positive charge or are neutral compounds in which there is a high degree of positive charge density on the metal ion. This results in a very limited  $\pi$  backbonding in these systems.  $(QCO)^+$  (where  $Q^+$  is a unit positive charge) is a system which resembles the cationic 'non-classical' metal carbonyls due to the absence of  $\pi$  backbonding. So (QCO)<sup>+</sup> has been used as a successful model to study theoretically the bonding in non-classical metal carbonyls [1-3]. We report here a comparative force approach study of the nature of 'binding' in CO,  $(QCO)^+$  and  $(COQ)^+$ .

Quite a number of discussions are available on the nature

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of bonding in classical and non-classical metal carbonyls [1, 2,4]. The most striking features of non-classical carbonyls are known to be shorter bond-lengths, greater vibrational frequencies and higher force constant values associated with C–O bond, compared to the free CO molecule ( $r_{C-O}$ =  $1.1282 \text{ Å}, \nu_{C-O} = 2143 \text{ cm}^{-1}$ , force-constant 18.56 mdyn/Å for free CO). Here, we attempt to obtain an insight into the nature of binding in such non-classical carbonyls by considering  $(QCO)^+$  and  $(COQ)^+$ , in which we allow a unit positive charge (with no orbitals on it) to approach CO molecule from either side. This is a simple system which resembles the non-classical carbonyls, lacking  $\pi$  back-bonding totally. Further, as the Q<sup>+</sup> has no orbitals, its effect is purely electrostatic. It is to be noted that this 'point charge plus CO' system is a simplified model for the metal cation CO bond in these carbonyls. It captures the dominant effect at large distances, which is the coulombic interaction. At shorter distances, orbital interactions would become more and more important and the model does not account for these interactions. The model has the advantage that it allows one to study effects that are purely electrostatic. Because of this reason, the model has been used earlier [2, 3], and interesting information has been obtained from such studies. We continue along the same line and ask the following questions: 

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113 1. What is the nature of the molecular orbitals (MOs) in114 free CO?

- 115 2. When the positive charge approaches CO molecule116 which are the orbitals that become more binding/117 antibinding?
- 118 We have used the Hellmann–Feynman force approach to 119 answer these questions. This electrostatic force approach is 120 conceptually a very simple method, where electronic charge 121 density plays the key role in determining the nature of 122 'binding' [5]. An important point to note here is that the 123 concept of 'binding', is not the same as 'bonding' as is 124 generally used in chemistry [5]. The term bonding is used in 125 the more popular energy-based concepts in chemistry, 126 whereas, the word binding is used in the force based 127 approaches. Force approach calculates the force exerted on 128 a given nucleus due to the electron density of any given 129 molecular orbital. The magnitude and the direction of the 130 force on each individual nucleus gives us a physical picture 131 of the binding in the molecule concerned. Most importantly, 132 it is possible to have a quantitative idea on the binding/ 133 antibinding nature of each MO. 134

Also, we wish to comment on the use of the force 135 approach. The electrostatic force approach is valid for the 136 Hartree-Fock wave functions. However, questions have 137 been raised regarding its utility, when one makes use of 138 limited basis sets. These questions have been addressed by 139 Nakatsuji et al. [27-29] who showed that if one includes 140 derivatives of basis sets to all orders, then the theorem is 141 satisfied. Further their calculations showed that results 142 obtained with basis sets containing only the first derivatives 143 lead to excellent results. Therefore, in the calculations 144 reported in the paper, we have used a basis set which 145 includes first derivatives and hence the conclusions that we 146 draw from the calculations, we believe, are quite 147 dependable. 148

# 151 2. Earlier studies on 'non-classical' carbonyl complexes152

Despite the recent activity in the area of non-classical 153 metal carbonyls [4,6–10] this kind of metal carbonyls have 154 been known almost since the inception of metal carbonyl 155 chemistry. Interestingly, the compound Au(CO)Cl, with  $\nu_{C-}$ 156  $_{0} \simeq 2162 \text{ cm}^{-1}$  was first described in literature in 1925 [14]. 157 Previous workers noted the strange nature of metal 158 carbonyls of late d-block metal ions and suggested that 159 many such compounds have little or no  $\pi$  backbonding [11– 160 161 13].

162 The most popular understanding for the decrease C–O 163 bond-length in non-classical carbonyls is the lack of 164  $\pi$ -backbonding. Why the diminished  $\pi$ -backbonding should 165 lead to a bond-length shorter than free CO is a question yet 166 to be understood fully. A plausible explanation was given by 167 Fenske and co-workers in 1971 [15]. They reported that the 168 Mulliken overlap population of the highest occupied molecular orbital (HOMO,  $\sigma(3)$  orbital) of CO has a 169 negative value, which suggests that this orbital has 170 antibonding character. The reduction of electron density 171 from the antibonding HOMO by  $M \leftarrow CO \sigma$  donation is a 172 probable explanation of C-O bond shortening and higher 173  $\nu_{\rm C-O}$  values in non-classical carbonyl complexes [16,17]. It 174 has also been shown that the highest lying Khon-Sham 175 orbitals have negative Mulliken overlap populations for N<sub>2</sub>, 176 CO, BF, BO<sup>-</sup> [18,19]. There is however a debate regarding 177 the nature of the  $\sigma(3)$  orbital of CO. It has been pointed out 178 that the HOMO of CO has no node between the atoms [20] 179 (in this regard, see our plot for this MO in Fig. 10), thus 180 leading to suspicion that it has a bonding nature. 181

Lupinetti, Fau, Frenking and Strauss [2] studied the 182 change in  $r_{C-O}$  distance when a proton or a point charge Q<sup>+</sup> 183 approached CO from the carbon or from the oxygen side of 184 the molecule. According to their study, for  $(HCO)^+$  and 185  $(QCO)^+$  the decrease in the equilibrium  $r_{C-O}$  distance 186 relative to free CO is caused by electrostatic effects only, 187 since  $r_{C-O}$  values for (HCO)<sup>+</sup> and (QCO)<sup>+</sup> are virtually 188 same. Their paper says: the finding that  $r_{C-O}$  is lengthened 189 when  $H^+$  and  $Q^+$  are bonded to the oxygen atom of CO 190 demonstrates that the HOMO of CO is not antibonding, 191 because, if it were, the C–O bond-length in (COH)<sup>+</sup>, like 192 (HCO)<sup>+</sup> would be shorter than in free CO. From their 193 studies they conclude that 'it is the change in the covalent 194 contribution to the C-O bond which leads to a shorter or 195 longer bond in the C and O protonated isomers'. The 196 bonding orbitals of free CO are polarized towards the more 197 electronegative O atom. Thus, when a proton or a positive 198 charge is placed in the C-side, it attracts the electron density 199 from the oxygen atom, to the carbon atom, resulting in a less 200 polarized  $\sigma$  and  $\pi$  bonds, leading to a more covalent C–O 201 bond. 202

An independent study performed by Goldman and 203 Krogh–Jespersen [3] almost at the same time, attributed 204 the high stretching frequency and lower bond-length of 205 cationic carbon monoxide complexes to electrostatic effects 206 and not to the effect of withdrawal of electron density from 207 the HOMO ( $\sigma(3)$ ). They performed ab initio calculations on 208 CO in presence of a positive charge (located on the C-side 209 along the bond axis) and found that a simple Coulombic 210 field increases the C-O stretching force constant and 211 decreases the bond-length. They mention that the electron 212 donation from the  $\sigma(3)$  has no intrinsic positive effect on the 213 force constant of C-O. An electric field induced increase in 214 the force constant was thought as the effect of the field, 215 which reduces the polarization of the bonding orbitals in 216 CO, increasing the covalent character. They further propose 217 that the nature of  $\sigma(3)$  orbital of CO is mainly non-bonding. 218

We now comment briefly the shortcomings of the earlier 219 approaches and on the current status of the problem. In the 220 NBO analysis of CO molecule by Fenske et al. [15] the 221 electrostatic effects were not taken into account. Also, it is a 222 known fact that NBO analysis or the analysis of Mulliken 223 populations are somewhat arbitrary and can lead to 224

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Fig. 1. The coordinates of electron and nuclei in a molecule AB. The charge 234 of the two nuclei are  $Z_A$  and  $Z_B$ , respectively, the electron is denoted by e. A–B bond distance is given by R, the distance of the electron from nucleus 235 A is  $r_A$  and the distance of the electron from nucleus B is  $r_B$ . 236

237 confusing results. In the study of CO by Goldman and 238 Krogh–Jespersen [3] it was said that there is no correlation 239 between the extent of  $\sigma$ -bonding and the force constant of 240 CO, which essentially means that there is no effect of 241 depopulation from the HOMO. As described in previous 242 section, it is presently not clear whether the HOMO of free 243 CO is antibonding/non-bonding. Further, it is also not clear 244 what happens to its nature when a positive charge is brought 245 near it. In this paper, we use the force approach to 246 understand the nature of molecular orbitals in free CO, 247  $(QCO)^+$  and  $(COQ)^+$ . 248

#### 3. The force approach

The idea is based on the famous Hellmann–Feynman [21, 22] theorem. According to the theorem, the force on any nucleus in a molecule, can be calculated simply using classical electrostatics, if the electron density is obtained from quantum chemical calculations. For a diatomic molecule, the force between the two nuclei (for notations see Fig. 1) can be written as [5]:

$$F = \frac{Z_{\rm A} Z_{\rm B}}{R^2} - \frac{1}{2} \int f \rho(\mathbf{r}) d\mathbf{r}$$
<sup>(1)</sup>

where

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$$f = \frac{Z_{\rm A} \cos \theta_{\rm A}}{r_{\rm A}^2} + \frac{Z_{\rm B} \cos \theta_{\rm B}}{r_{\rm B}^2}$$
(2)

When F is negative, the force from the electron cloud prevents the nuclei from flying apart, i.e. prevents R from increasing. When F is positive, the nuclear repulsive force prevents R from decreasing. The equilibrium value of R in any diatomic molecule is to be determined by F=0. The force acting on nucleus A may be written as,

$$f_{\rm A} = Z_{\rm A} \left[ \frac{Z_{\rm B}}{R^2} - \int \frac{\cos \theta_{\rm A}}{r_{\rm A}^2} \rho(\mathbf{r}) \mathrm{d}\mathbf{r} \right].$$
(3)

At equilibrium, the force is zero implying that

$$Z_{78}^{277} \qquad Z_{\rm B} = R^2 \int \frac{\cos \theta_{\rm A}}{r_{\rm A}^2} \rho(\mathbf{r}) \mathrm{d}\mathbf{r}$$

$$(4)$$

The right hand side of Eq. (4), is known as the charge

equivalent of force and is denoted by  $F^{A}$ . Similarly,

$$Z_{\rm A} = R^2 \int \frac{\cos \theta_{\rm B}}{r_{\rm B}^2} \rho(\mathbf{r}) \mathrm{d}\mathbf{r}$$
(5)
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The above two equations imply that at equilibrium,

$$F^{\rm A} + F^{\rm B} = Z_{\rm A} + Z_{\rm B}$$
 (6)  $\frac{286}{287}$ 

It is possible to define binding and antibinding regions in 288 diatomic molecules from Eq. (1). Since the density can not 289 be negative it is possible to separate the integral in Eq. (1) 290 into contributions from two regions, in the first of which f >291 0 and in the second, f < 0 as in Eq. (7) 292

$$F = \frac{Z_{A}Z_{B}}{R^{2}} - \frac{1}{2} \int_{f>0} f\rho(\mathbf{r})d\mathbf{r} - \frac{1}{2} \int_{f<0} f\rho(\mathbf{r})d\mathbf{r}$$
(7) 294  
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Negative charge in the regions where f is positive is 297 binding and negative charge in the region of space where f is 298 negative is in antibinding. The binding region with f > 0; is 299 separated from the antibinding region having f < 0; by the 300 non-binding surface where f=0. Force approach has been 301 successfully used in many chemical problems [23–25]. 302

#### 4. Earlier force analysis of CO

306 Ishida and Ohno have studied [26] some of the second 307 row diatomics using force approach. They partition the 308 Hellmann-Feynman force into different contributions. This 309 paper includes a study for CO molecule. The authors 310 calculated the wavefunctions of the molecules by the closed 311 shell Hartree-Fock-Roothan SCF method, in which they 312 employed the Huzinaga-Dunning-Hay basis-set with its 313 first derivative functions [27-29]. According to their 314 analysis the force due to the two core orbitals are mainly 315 coming from the localized electronic charge on C and O 316 atom. The  $\sigma(1)$  orbital (in their terminology it is  $3\sigma$ ) orbital 317 exerts the largest binding force.  $\sigma(2)$  orbital (in their 318 terminology it is  $4\sigma$ ) exerts an inward force on C nucleus 319 and an outward force on O nucleus. However, they find the 320 force to be of non-binding nature. The  $\pi$  orbitals exert 321 inward forces on both the nuclei and hence they are binding 322 in nature. The  $\sigma(3)$  orbital (in their terminology it is  $5\sigma$ ) 323 orbital exerts an inward force on O nucleus and an outward 324 force on C nucleus and they conclude the force due to this 325 orbital to be of non-binding nature. 326

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### 5. Force calculations on CO, (QCO)<sup>+</sup> and (COQ)<sup>+</sup>

Though the Hartree-Fock approximation and the basis-331 set expansion approximations are widely employed, in case 332 of force calculations when we employ these two approxi-333 mations in combination, the Hellmann-Feynman theorem 334 does not hold anymore. Nakatsuji et al. [27-29] have shown 335 that the Hellmann-Feynman theorem holds for the Hartree-336

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Table 1

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Basis sets used	$r_{\text{C-O}}$ (Å)	Sum of the charge equivalent of force on O	Sum of the charge equivalent of force on C
5-31G**	1.1137	5.49	7.75
$6-311 + + G^{**}$	1.1045	5.78	7.77
Aug-cc-pVTZ	1.1040	5.88	7.93
D95V + + ** containing derivative functions	1.1044	5.99	7.99
Experimental value	1.1282	_	_

Experimental value of  $r_{\rm C-O}$  is included.

Fock wavefunction within the closed shell, open shell and multi-configurational schemes, if the basis-set contains the derivatives of every order of each basis function. In addition, they presented numerical evidence that Hellmann–Feynman theorem is essentially valid if the split valence quality basis sets are used with their first derivative functions [27].

We calculated the wavefunctions of the molecules by 356 closed shell Hartree-Fock method, in which we employed 357 D95V++\*\* (Huzinaga-Dunning-Hay [30,31] with polar-358 ization and diffuse functions) along with their first 359 derivative functions. The first derivative of a p-type GTO 360 is obtained as linear combinations of s- and d-type GTOs 361 and the first derivative of a d-type GTO is obtained as linear 362 combinations of p- and f-type GTOs. We however added the 363 s- and d-terms independently in the former and p- and 364 f-terms independently in the later case. This gives a lower 365 energy value. This procedure does not alter the validity of 366 the Hellmann–Feynman theorem [27]. 367

The total electron density is given by

$$\rho(\mathbf{r}) = \sum_{i}^{\mathrm{occ}} n_i \psi_i^2$$

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where  $\psi_i$  is the *i*-th molecular orbital and  $n_i$  is its occupation number. So Eq. (3) can be rewritten as

$$F^{\rm A} = \frac{Z_{\rm A} Z_{\rm B}}{R^2} - Z_{\rm A} \sum_{i}^{\rm occ} n_i \int \psi_i^2 \frac{\cos \theta_{\rm Ai}}{r_{\rm Ai}^2} \,\mathrm{d}\tau_i \tag{8}$$

This equation shows that the total force on a nucleus is the sum of orbital contributions, whereas, total energy is not the sum of orbital energies. So the force approach has an advantage over the energy method and so is elegantly suited to study this problem.

The wavefunctions, calculated using Hartree-Fock 383 methods, are used to get the three dimensional charge 384 density for each molecular orbital. The amount of force the 385 orbital charge densities exert on each nucleus is calculated 386 numerically. We have followed the convention that any kind 387 of force, which contributes to binding is positive. Thus a 388 389 force on C nucleus towards O and a force on O nucleus towards C, both are taken to be positive. For the numerical 390 integration we have used a 96 point Gaussian-Quadrature 391 method [32]. The equilibrium geometry for free carbon 392

404 monoxide molecule were calculated using 6-31G\*\*, 405 6-311G\*\*, Aug-cc-pVTZ and D95V++\*\* containing its 406 derivative functions. The  $r_{C-O}$  distance changes slightly 407 with the basis-set (Table 1). Here we have reported the 408 results for the calculations done using D95V + +\*\* along 409 with their derivative functions, as it gives the most reliable 410 results. Forces too were computed with all these basis sets 411 and the results are given in the same table. Obviously the 412 basis which contains the derivatives perform significantly 413 better than other functions. Our numerical calculation has 414 the advantage that we can calculate 415

- 1. How much electron density of an MO is located in the binding region (see for example Tables 7–14).
- 2. The forces exerted by this electron densities on each nucleus.

For  $(QCO)^+$  and  $(COQ)^+$  we have placed Q<sup>+</sup> at 4, 3 and 421 2 Å away from CO molecule. Particularly, we are interested 422 in the  $(QCO)^+$  systems, as these resemble the non-classical 423 metal carbonyls. We use the concept of the charge 424 equivalent of the force, which is defined in Eq. (4). We 425 can rewrite the same expression for a particular MO as: 426

$$F_i^{\rm A}(R) = R^2 \int \frac{\cos \theta_{\rm A}^2}{r_{\rm A}^2} \rho_i \mathrm{d}\tau$$
<sup>428</sup>
<sup>429</sup>
<sup>430</sup>

where  $\rho_i$  is the electron density due to the two electrons in *i*-431 th molecular orbital. Since  $F_i^A$  is an electric field at nucleus 432 A multiplied by  $R^2$ , it has dimensions of charge. Each  $F_i^A(R)$ 433 is equal to the number of electronic charges which when 434 placed at the position of the nucleus B, will exert the same 435 force on nucleus A as does the *i*-th molecular orbital 436 electron density. During the approach of two atoms A and B 437 which form a bound molecular state, the sum  $F_i^A(R)$  + 438  $F_i^{\rm B}(R)$  will effectively tell us the nature of the MO. If the 439 sum is two (which is the occupation number of the orbital) it 440 is non-binding. If the sum is greater than two, it is binding. If 441 it is less than two, it is antibinding [33]. 442

A negative sign of  $F_i^A(R)$  indicates that putting two electrons into that orbital is equivalent to putting a positive charge of magnitude  $|F_i^A(R)|$  at the site of the nucleus B, which will only increase the repulsion on the nucleus A. Hence this will be antibinding. At equilibrium, the nuclear repulsions have to be balanced by the attraction to the 448

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Systems	$r_{\rm C-O}({\rm A})$
CO (expt.)	1.1282
CO	1.1044
+4 ACO	1.0996
+3 ACO + 2Å CO	1.0963
2 A co	1 1089
CO3 Å+	1.1117
CO2 Å+	1.1185
Results obtained using HF/D95V+	** containing derivative functions.
	// 4.70
	$\sigma(1)$ - Electron density 1.70
8 1	in binding region
0.1	Net electronic
	force (a.u) - 1.68
8.0	
8.70	
о 7.9 Ц	
7.8	
7.7	
	0 1 2 3 4 5 22 23 24 25 26 27
	Distance in Angstroms
Fig. 2. The variation of the electron	ensities and the net electronic force (a.u.) due to the charge in the binding region for $(QCO)^+$ systems (free CO, +
4 ÅCO, $+$ 3 ÅCO and $+$ 2	ÅCO plotted for $\sigma(1)$ orbital). Entries corresponding to 25 Å are for free CO molecule.

Table 3

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The	charge	equivalent	of force	acting	on	the	nuclei	due to	different
mole	cular or	bitals cente	red on C	and O f	or f	ree (	CO mol	ecule	

Molecule	МО	Charge equivalent of force on C	Charge equivalent of force on O	Nature of the orbitals
СО	<b>σ</b> ( <i>c</i> )	2.0007	0.2622	Non-bind-
	<b>σ</b> ( <i>c</i> )	0.2301	2.0018	ing Non-bind- ing
	σ(1)	2.4990	2.3494	Strongly binding
	σ(2)	1.2683	-1.2984	Antibinding
	$\pi(1), \pi(2)$	1.5057	0.8609	Weakly
	σ(3)	-1.0100	0.9586	binding Antibinding

503 Method HF/D95V++\*\* containing derivative functions, orbitals are 504 doubly occupied.

and 
$$\sum_{i} F_{i}^{\mathrm{B}} = Z_{\mathrm{A}}$$

$$\sum_{i} F_{i}^{\mathrm{B}} = Z_{\mathrm{A}}$$

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$$545$$

In the calculations, we find: for the C nucleus is

$$\sum_{i} F_{i}^{\rm C} = 7.99$$
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and O nucleus is

$$\sum_{i} F_{i}^{O} = 5.99$$
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for D95V++\*\* basis-set containing derivative functions, 554 which should have been equal to 8.00 and 6.00, respectively 555 (Table 1). The deviation from the expected values reflect the 556 quality of the basis set and needless to say the values are far 557 better when derivatives of the basis-set is used in the 558 calculation, and this justifies the use of this wave function in 559 our calculations. For the systems  $(QCO)^+$  or  $(COQ)^+$  the 560

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Table 4 561 The charge equivalent of force acting on the nuclei due to different molecular orbitals centered on C and O for (QCO)<sup>+</sup>, with Q<sup>+</sup> at 2, 3 and 4 Å distance from 562 618 C-side of CO molecule

Molecule	МО	Charge equivalent of force on C	Charge equivalent of force on O
+4 ÅCO	$\sigma(c)$	2.0007	0.2716
	$\sigma(c)$	0.2012	2.0017
	σ(1)	2.4973	2.3672
	σ(2)	1.2298	-1.3002
	$\pi(1), \pi(2)$	1.4963	0.8863
	σ(3)	-0.9989	0.9272
+3 ÅCO	$\sigma(c)$	2.0008	0.2908
	$\sigma(c)$	0.1741	2.0016
	σ(1)	2.4963	2.3780
	σ(2)	1.1999	-1.2986
	$\pi(1), \pi(2)$	1.4911	0.9037
	σ(3)	-0.9947	0.8947
+2 ÅCO	$\sigma(c)$	2.0008	0.3115
	$\sigma(c)$	0.1031	2.0012
	σ(1)	2.4926	2.4066
	σ(2)	1.0933	-1.2757
	$\pi(1), \pi(2)$	1.4811	0.9451
	σ(3)	-0.9764	0.7859

Method HF/D95V++\*\* containing derivative functions, orbitals are doubly occupied.

582 geometry of CO is optimized such that  $r_{C-O}$  is optimized but 583 the distance of  $Q^+$  from C (or O) remains the same. We then 584 study the effect of the positive charge on the molecular 585 orbitals, in terms of electronic charge in the binding region 586 and the force exerted on the nuclei by this charge (Table 2).

587 The values of the charge equivalent of forces on C/O 588 nucleus, for CO,  $(QCO)^+$  and  $(OCQ)^+$  are given in Table 3, 589 Table 4 and Table 5, respectively. From the values of charge 590 equivalent of force on both the nuclei, we find that for the 591  $\sigma(c)$ -type core orbitals the sum  $F_i^{\rm C}(R) + F_i^{\rm O}(R)$  is close to 2. 592 So these orbitals are non-binding (Table 6).  $\sigma(1)$  orbital in 593 all the cases are very strongly binding. The degenerate  $\pi$ 594 orbitals are weakly binding in nature. We find  $\sigma(2)$  and  $\sigma(3)$ 595

638 orbitals to be of antibinding nature for free CO molecule. 639 When a unit positive charge is brought near along the bond 640 axis of CO molecule on the carbon side, the binding nature 641 of  $\sigma(1)$  increases. The antibinding nature of  $\sigma(2)$  orbital 642 increases and the antibinding nature of  $\sigma(3)$  orbital also 643 increases, but the increase is not very high. The fact that 644 these two orbitals remain antibinding in nature is contrary to 645 the results obtained by Lupinetti and his co-workers [2] in 646 1997. But, since both the strongly binding  $\sigma(1)$  and weakly 647 binding  $\pi(1)$ ,  $\pi(2)$  orbitals increase their binding nature 648 considerably, the net effect is reflected in more stronger 649 binding between C and O, which decreases the  $r_{C-O}$  distance 650 (Table 1). On the other hand, if we look into the charge 651

596 Table 5

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597 The charge equivalent of force acting on the nuclei due to different molecular orbitals centered on C and O for (COQ)<sup>+</sup>, with Q<sup>+</sup> at 2, 3 and 4 Å distance from 508 O-side of CO molecule

Molecule	МО	Charge equivalent of force on C	Charge equivalent of force on O
CO4 Å+	$\sigma(c)$	2.0006	0.2498
	$\sigma(c)$	0.2472	2.0019
	σ(1)	2.4986	2.3258
	σ(2)	1.3001	-1.2933
	$\pi(1), \pi(2)$	1.5168	0.8313
	σ(3)	-1.0367	0.9753
CO3 Å+	$\sigma(c)$	2.0006	0.2391
	$\sigma(c)$	0.2649	2.0019
	σ(1)	2.4969	2.3074
	σ(2)	1.3172	-1.2910
	$\pi(1), \pi(2)$	1.5243	0.8112
	σ(3)	-1.0560	0.9837
CO2 Å+	$\sigma(c)$	2.0005	0.1889
	$\sigma(c)$	0.3006	2.0021
	σ(1)	2.4923	2.2521
	σ(2)	1.3467	-1.2905
	$\pi(1), \pi(2)$	1.5452	0.7636
	σ(3)	-1.1042	0.9958

Method HF/D95V++\*\* containing derivative functions, orbitals are doubly occupied. 616

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699 Fig. 3. The variation of the electron densities and the net electronic force (a.u.) due to the charge in the binding region for (QCO)<sup>+</sup> systems (free CO, +... 4 Å...CO, +...3 Å...CO and +...2 Å...CO plotted for  $\sigma$ (2) orbital). Entries corresponding to 25 Å are for free CO molecule. 700

701 equivalent of forces on C/O for  $(COQ)^+$  systems, we see 702 that  $\sigma(1)$  and degenerate  $\pi$  orbitals, which are binding in 703 nature, become less binding. The antibinding nature of  $\sigma(2)$ 704 decreases and  $\sigma(3)$  increases slightly. Hence the net effect is 705

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Table 7 708 The total charge in the binding region, the force on C nucleus and O nucleus 709 due to the electron densities in the binding and antibinding regions for free CO and CO with unit positive charge placed 4, 3 and 2 Å apart on the C side 710

a decreased binding force between the two nuclei and a 758 increase in  $r_{C-O}$  bond-length (Table 1). 759

The values of the electron densities in the binding regions 760 for various orbitals (except the core orbitals) are given in 761

#### Table 8

764 The total charge in the binding region, the force on C nucleus and O nucleus due the electron densities in the binding and antibinding regions for free CO 765 and CO with unit positive charge placed 4, 3 and 2 Å apart on the C side of 766

$\sigma(1)$ orbital	co	$\begin{array}{cccc} CO & + \dots 4 \ \text{Å} \dots & + \dots 3 \ \text{Å} \dots & + \dots 2 \ \text{Å} \dots & \sigma(2) \text{ orbital} \\ CO & CO & CO \\ r_{0} = 1 & r_{0} = 1 & r_{0} = 1 \\ \end{array}$	2) orbital CO	+4 Å CO	+3Å CO	+2 Å CO			
	1044	0996	0963	0881		1044	0996	0963	0881
Charge in binding region Force on C (a.u.)	1.6539	1.6605	1.6651	1.6759	Charge in binding region Force on C (a.u.)	0.5941	0.5884	0.5840	0.5700
Binding	5.8833	5.9861	6.0616	6.2561	Binding	3.8191	3.8454	3.8685	3.9617
Antibinding	-2.4414	-2.5161	-2.5721	-2.7190	Antibinding	-2.0723	-2.1367	-2.1912	-2.4102
Total	3.4419	3.4700	3.4894	3.5371	Total	1.7468	1.7088	1.6773	1.5515
Force on O (a.u.)					Force on O (a.u.)				
Binding	23.0807	23.0931	23.0976	23.1060	Binding	11.0820	11.1920	11.2519	11.2832
Antibinding	-18.7662	-18.7074	-18.6654	-18.5526	Antibinding	-13.4663	-13.6008	-13.6722	-13.6969
Total	4.3144	4.3857	4.4322	4.5534	Total	-2.3843	-2.4088	-2.4203	-2.4137
Net force (a. u.)	7.7563	7.8557	7.9216	8.0905	Net force (a. u.)	-0.6375	-0.7000	-0.7430	-0.8622

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Table 9

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Table 11 The total charge in the binding region, the force on C nucleus and O nucleus due the electron densities in the binding and antibinding regions for free CO and CO with unit positive charge placed 4, 3 and 2 Å apart on the C side of CO for  $\sigma(3)$  orbital. Double occupancy of the orbital is accounted for

$\sigma(3)$ orbital	СО	+4 Å CO	+3 Å CO	+2 Å. CO
	r <sub>C-O</sub> =1. 1044	r <sub>C-O</sub> =1. 0996	r <sub>C-O</sub> =1. 0963	r <sub>C-O</sub> =1. 0881
Charge in binding region	0.5969	0.5744	0.5463	0.4537
Force on C				
(a.u.)				
Binding	4.9254	4.6929	4.4734	3.8097
Antibinding	-6.3165	-6.0808	-5.8639	-5.1953
Total	-1.3911	-1.3879	-1.3905	-1.3856
Force on O				
(a.u.)				
Binding	2.1580	2.1524	2.1268	2.1174
Antibinding	-0.3977	-0.4345	-0.4592	-0.6304
Total	1.7603	1.7179	1.6676	1.4869
Net force (a.	0.3692	0.3300	0.2771	0.1013
u.)				

807 Tables 7–14 and plots (Figs. 2–9). In all the plots the value 808 corresponding to free CO is plotted in the same graph 809 assuming the point charge is placed at a distance of 25 Å 810 from C or O atom. We have also made contour plots of the 811 HOMO of CO in Fig. 10. 812

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Table 10 817

The total charge in the binding region, the force on C nucleus and O nucleus 818 due the electron densities in the binding and antibinding regions for free CO 819 and  $(QCO)^+$  with unit positive charge placed 4, 3 and 2 Å apart for  $\pi(1)$ 820 orbitals

$\pi(1)$ and $\pi(2)$ orbi- tals	СО	+4 Å CO	+3 Å CO	+2 Å. CO
	r <sub>C-O</sub> =1. 1044	r <sub>C-O</sub> =1. 0996	$r_{\rm C-O} = 1.$ 0963	<i>r</i> <sub>C-O</sub> =1. 0881
Charge in	1.4306	1.4371	1.4406	1.4479
binding				
region				
Force on C				
(a.u.)				
Binding	1.9864	2.0171	2.0405	2.1027
Antibinding	0.0874	0.0619	0.0438	-0.0008
Total	2.0738	2.0791	2.0843	2.1018
Force on O				
(a.u.)				
Binding	4.8433	4.8511	4.8621	4.8987
Antibinding	-3.2623	-3.2092	-3.1776	-3.1105
Total	1.5810	1.6419	1.6844	1.7882
Net force (a. u.)	3.6548	3.7210	3.7687	3.8900

839 Values are for two electrons in the orbital. All values are to be doubled due 840 to degeneracy, for net results.

841 The total charge in the binding region, the force on C nucleus and O nucleus 842 due the electron densities in the binding and antibinding regions for free CO 843 and CO with unit positive charge placed 4, 3 and 2 Å apart on the O side of 844 CO for  $\sigma(1)$  orbital. Double occupancy of the orbital is accounted for

$\sigma(1)$ orbital	CO	CO 4 Å+	CO 3 Å+	CO 2 Å+
	$r_{\rm C-O} = 1.$			
-	1044	1089	1117	1165
Charge in binding region	1.6539	1.6451	1.6384	1.6196
Force on C				
(a.u.)				
Binding	5.8833	5.7856	5.7210	5.5576
Antibinding	-2.4414	-2.3717	-2.3265	-2.2106
Total	3.4419	3.4139	3.3945	3.3470
Force on O				
(a.u.)				
Binding	23.0807	23.0868	23.1024	23.1675
Antibinding	-18.7662	-18.8497	-18.9199	-19.1350
Total	4.3144	4.2371	4.1825	4.0325
Net force (a.	7.7563	7.6510	7.5770	7.3795
u.)				

#### 6. Discussion

Quantitative measures of change in electron densities in the binding regions and the forces due to this density on the nuclei C and O as the charge Q<sup>+</sup> approaches, are discussed below. The core orbitals are almost unaffected by Q<sup>+</sup>. The results for the other orbitals are given in the Tables 7–14.

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#### 6.1. $\sigma(1)$ orbital

For this orbital, the total charge in the binding region

#### Table 12

The total charge in the binding region, the force on C nucleus and O nucleus due the electron densities in the binding and antibinding regions for free CO and CO with unit positive charge placed 4, 3 and 2 Å apart on the O side of CO for  $\sigma(2)$  orbital. Double occupancy of the orbital is accounted for

$\sigma(2)$ orbital	СО	CO 4 Å+	CO 3 Å+	CO 2 Å+
	r <sub>C-O</sub> =1. 1044	r <sub>C-O</sub> =1. 1089	r <sub>C-O</sub> =1. 1117	r <sub>C-O</sub> =1. 1185
Charge in binding region Force on C	0.5941	0.5970	0.5973	0.5901
(a.u.) Binding	3 8 1 0 1	3 7951	3 7720	3 6782
Antibinding	-2.0723	-2.0187	-1.9813	-1.8696
Total	1.7468	1.7764	1.7907	1.8086
Force on O				
(a.u.)				
Binding	11.0820	10.8743	10.6903	10.068
Antibinding	-13.4663	-13.2303	-13.0304	-12.3787
Total	-2.3843	-2.3560	-2.3401	-2.3107
Net force (a.	-0.6375	-0.5796	-0.5494	-0.5021
u.)				

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897 Table 13 The total charge in the bind

$\sigma(3)$ orbital	CO	CO 4 Å+	CO 3 Å+	CO 2 Å+
	r <sub>C-O</sub> =1. 1044	r <sub>C-O</sub> =1. 1089	r <sub>C-O</sub> =1. 1117	r <sub>C-O</sub> =1. 1185
Charge in binding region	0.5969	0.6007	0.6014	0.6009
Force on C				
Binding	4.9254	5.0943	5.2004	5.469
Antibinding	-6.3165	-6.5108	-6.6360	-6.951
Total	-1.3911	-1.4165	-1.4356	-1.482
Force on O (a.u.)				
Binding	2.1580	2.1254	2.1008	2.0390
Antibinding	-0.3977	-0.3485	-0.3178	-0.256
Total	1.7603	1.7769	1.7830	1.783
Net force (a. u.)	0.3692	0.3604	0.3474	0.300

919 increases as  $Q^+$  approaches the C nucleus (Fig. 2). This is 920 accompanied by an increase of the binding and antibinding 921 forces on the C nucleus (Table 7). The increase of 922 antibinding force indicates concentration of electron density 923 behind the C nucleus. The net force on C towards O 924 increases, slightly. When O nucleus is considered, the 925 binding force on O nucleus increases very weakly and the 926 antibinding force decreases considerably, hence the net 927

929 Table 14

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The total charge in the binding region, the force on C nucleus and O nucleus due the electron densities in the binding and antibinding regions for free CO and  $(COQ)^+$  with unit positive charge placed 4, 3 and 2 Å apart for  $\pi(1)$ orbitals

$\pi(2)$ orbitals		4 Å+	3 Å+	2 Å+
	<i>r</i> <sub>C-O</sub> =1. 1044	<i>r</i> <sub>C-O</sub> =1. 1089	r <sub>C-O</sub> =1. 1117	r <sub>C-O</sub> =1. 1185
Charge in	1.4306	1.4202	1.4123	1.3928
binding				
region				
Force on C				
(a.u.)				
Binding	1.9864	1.9595	1.9429	1.9075
Antibinding	0.0874	0.1129	0.1293	0.1675
Total	2.0738	2.0724	2.0722	2.0750
Force on O (a.u.)				
Binding	4.8433	4.8512	4.8619	4.9112
Antibinding	-3.2623	-3.3367	-3.3914	-3.5438
Total	1.5810	1.5145	1.4705	1.3674
Net force (a. u.)	3.6548	3.5869	3.5427	3.4424

Values are for two electrons in the orbital. All values are to be doubled dueto degeneracy, for net results.

binding force on O increases. Thus the effect of bringing in a 953 unit positive charge, nearer to C-side of CO molecule is to 954 increase the binding nature of this molecular orbital. This 955 increase in binding nature must result from the fact that with 956 a positive charge near C nucleus the system resembles a 957 homonuclear diatomic molecule. Thus, the system becomes 958 less polar or more covalent, as suggested by previous 959 workers [2,3]. 960

If we now consider the charge approaching from O side 961 of CO molecule. Here, the binding and the antibinding 962 forces on both the atoms decrease gradually as the charge is 963 brought nearer (Table 11 and Fig. 6). The result is a net 964 decrease in the force on C towards O and vice-versa and the 965 orbital becomes less binding. The electron density in the 966 binding region also decreases as the charge comes in from 967 O-side. 968

6.2. $\sigma(2)$ orbita	. σ(2) orbit	a
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This orbital is of antibinding nature for free CO 972 molecule. When a unit charge is brought near the molecule 973 from the C-side the electron density in the binding region 974 decreases (Table 8 and Fig. 3). Force on C from the binding 975 region increases and that from antibinding region increases, 976 strongly. Net force on C towards O thus decreases which 977 indicates an electron density buildup behind the C nucleus. 978 Now if O nucleus is considered, as Q<sup>+</sup> approaches there is a 979 increase in the force due to the charge in the binding region 980 and there is an increase due to the charge in antibinding 981 region. The net effect is an increase in the force away from 982 C. When the net electronic force is considered (Table 8) the 983 negative value suggests a repulsive and antibinding nature 984 of force for this orbital in free CO molecule. Further, as the 985 positive charge approaches it becomes more negative and 986 thus the orbital becomes more antibinding. 987

For the  $(COQ)^+$  systems, there is a anomalous trend in 988 electron density as far as  $\sigma(2)$  orbital is concerned (Table 12 989 and Fig. 7). Here we see that the electron density increases 990 initially when the charge is brought nearer from O-side till 991 3 Å and then it suddenly decreases for 2 Å. As far as force 992 on C atom is considered we find a very small and steady 993 increase in the net force, which can be attributed mainly to 994 the fact that there is a reduction of the force due to the 995 electron density in the antibinding region. The net force on 996 O atom increases weakly (becomes less negative) as the 997 charge approaches. This force is negative, indicative of the 998 fact that its direction is away from the oxygen atom. 999 Considering the effect of force on both the nuclei we can see 1000 that there is a decrease in the antibinding character of this 1001 orbital. 1002

#### 6.3. $\sigma(3)$ orbital

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As discussed earlier, there are contradictory opinions in 1006 the literature about the nature of  $\sigma(3)$  orbital. But, we find 1007 this orbital to be of antibinding nature. In free CO molecule 1008

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Fig. 4. The variation of the electron densities and the net electronic force (a.u.) due to the charge in the binding region for (QCO)<sup>+</sup> systems (free CO, +... 4 Å...CO, +...3 Å...CO and +...2 Å...CO plotted for  $\sigma(3)$  orbital). Entries corresponding to 25 Å are for free CO molecule.

it has been claimed that in the bonding region this MO has no node. We have plotted  $\sigma(3)$  orbital (Fig. 10) and also calculated the non-binding surfaces, using Eq. (7) in Section 3. Our studies show that the nodal surface on C atom, extends into the binding region, as shown in the Fig. 10. The electronic forces given in Table 9 indicate that this orbital is antibinding. The value though not negative (thus it is of attractive nature) as it was in  $\sigma(2)$  orbital, but, the magnitude of the force is insufficient to screen one unit of nuclear charge. For this orbital (details are given in Table 9 and Fig. 4) electron density in the binding region decreases steadily when the positive charge is brought nearer to the C atom. Also as the positive charge approaches: 

1. Force on C towards O, due to the electron density in the binding region decrease strongly and that due to the electron density in the antibinding region, increase strongly. So even though the electron density in the binding region decreases, the density near C atom gets polarized towards O atom. The net effect is a repulsive antibinding force on C towards O, which almost remains same as the charge approaches. 

As far as the force on O nucleus is concerned, the force due to the electron density from binding region decreases slightly and antibinding region, increases rapidly, but the net effect is a decrease in the force towards C.



1064 1 Å...CO and +...2 Å...CO plotted for  $\pi(1)$  and  $\pi(2)$  orbitals). Entries corresponding to 25 Å are for free CO molecule. 1120

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Fig. 6. The variation of the electron densities and the net electronic force (a.u.) due to the charge in the binding region for (COQ)<sup>+</sup> systems (free CO, CO... 4 Å...+, CO...3 Å...+ and CO...2 Å...+ plotted for  $\sigma(1)$  orbital). Entries corresponding to 25 Å are for free CO molecule.

Looking at the net electronic force (considering both the nuclei) in Table 9 we conclude that this orbital is more antibinding in nature for (QCO)<sup>+</sup>, than in free CO. This again, must be due to the increase in the covalent nature of the bonding in CO, caused by the approach of the positive charge.

When we consider the changes in the nature of this orbital for charge approaching from O side, we find there is almost no change in the electron density in the binding region (Table 13 and Fig. 8). The binding force on C nucleus increases, but the antibinding force increases more strongly, resulting in a increase in antibinding force on this nucleus. The direction of the force on C is away from O and it increases when Q<sup>+</sup> is brought nearer to O atom. Force on 

oxygen atom towards carbon atom increases weakly. As a result the net force considering both the nuclei decreases for  $(COQ)^+$  systems. This orbital for free CO is antibinding and for  $(COQ)^+$  it becomes only slightly more antibinding.

6.4. 
$$\pi(1)$$
 and  $\pi(2)$  orbitals 1204

When the degenerate  $\pi(1)$ ,  $\pi(2)$  orbitals are taken into account (Table 10 and Fig. 5) we find the electron density in the binding region to increase slightly, when the positive charge is brought near the C nucleus. This results from the more equal distributions of the  $\pi$  orbitals between the two atoms. The force on C nucleus from the electron density of binding region increases and from antibinding region, 1212



Fig. 7. The variation of the electron densities and the net electronic force (a.u.) due to the charge in the binding region for (COQ)<sup>+</sup> systems (free CO, CO... 1231 4 Å...+, CO...3 Å...+ and CO...2 Å...+ plotted for  $\sigma(2)$  orbital). Entries corresponding to 25 Å are for free CO molecule.



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Fig. 8. The variation of the electron densities and the net electronic force (a.u.) due to the charge in the binding region for  $(COQ)^+$  systems (free CO, CO... 4 Å...+, CO...3 Å...+ and CO...2 Å...+ plotted for  $\sigma(3)$  orbital). Entries corresponding to 25 Å are for free CO molecule.

decreases. The total effect on this nucleus, is a increase in binding force towards O, but the change is small. The force on O nucleus from the electron density of binding region increases weakly and from the electron density of antibinding region decreases, so the total effect is a increase in force towards C nucleus. The net effect (considering both C and O nuclei) is an increase in binding force for  $(QCO)^+$ in comparison to CO. 

<sup>1263</sup> For the degenerate  $\pi$  orbitals the electron density in the <sup>1264</sup> binding region decreases when the charge approaches from <sup>1265</sup> oxygen side (Table 14 and Fig. 9). The force on C atom <sup>1266</sup> towards O remains almost unaltered. The force on O atom towards C decreases, resulting a net decrease in the binding nature of the orbital.

### 6.5. Effect of all orbitals

All our observations described above can be added up to have an overall effect for the  $\sigma$  and  $\pi$  orbitals together, for  $CO, (QCO)^+$  and  $(COQ)^+$  systems. As  $Q^+$  approaches CO from C-side, the C-O distance is reduced (Table 2) and the case is reversed when the charge is allowed to approach from O side of CO molecule. We have calculated the net force as the sum of nuclear and electronic forces for CO. We have already mentioned forces which cause binding are 



 1287
 Fig. 9. The variation of the electron densities and the net electronic force (a.u.) due to the charge in the binding region for  $(COQ)^+$  systems (free CO, CO...
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 4 Å...+, CO...3 Å...+ and CO...2 Å...+ plotted for  $\pi(1)$  and  $\pi(2)$  orbitals). Entries corresponding to 25 Å are for free CO molecule.
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taken as positive. Nuclear force always oppose binding and
is, in this notation, always negative. The net force
considering both nuclear and electronic contributions are
calculated using Eq. (1). These values for free CO are
presented in the Table 6.

 $\begin{array}{ll} 1390 & \text{We arrive at the following conclusions about the} \\ 1391 & \text{individual orbitals of CO as } Q^+ \text{ approaches from C-side:} \end{array}$ 

13921393 1.  $\sigma(1)$  becomes more binding

- 1394 2.  $\sigma(2)$  becomes more antibinding
- 1395 3.  $\sigma(3)$  becomes more antibinding

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1396 4.  $\pi(1)$ ,  $\pi(2)$  become slightly more binding

In this case the overall increase in the binding nature of the C–O bond occurs, which is reflected in the shortening of C–O bond. It is important to note that here we could consider the effect of all the orbitals and indeed there are visible changes in the nature of all the orbitals.

We also arrive at the following conclusions about the individual orbitals of CO as  $Q^+$  approaches from O-side:

1.  $\sigma(1)$  becomes much less binding14452.  $\sigma(2)$  becomes slightly less antibinding14463.  $\sigma(3)$  becomes slightly more antibinding14474.  $\pi(1), \pi(2)$  become slightly less binding1449In this case the overall decrease in the binding nature of1450145114511452145114531452

the C–O bond occurs, which is reflected in the lengthening of C–O bond. Here the decrease in the binding nature of  $\sigma(1)$  and degenerate  $\pi$  orbitals are playing a more important role in changing the bond-length.

We also conclude that  $\sigma(3)$  orbital in free CO is 1456

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antibinding. This antibinding nature of the orbital may be 1457 understood by looking at the Fig. 10, where contour plot for 1458 this orbital is given. It is seen that the orbital has two nodal 1459 surfaces, one near the Oxygen atom, which is very close to 1460 the non-binding surface passing through the Oxygen atom. 1461 This node, would make the electron density in its vicinity 1462 low, thus reducing the binding forces that the orbital would 1463 be able to exert. The other nodal surface cuts the non-1464 binding surface and only its out regions lie in the binding 1465 region. So it may seem surprising that the orbital is non-1466 binding. However, it is to be noted that the orbital has a 1467 1468 large negative lobe, lying behind the Carbon atom (i.e. away from the internuclear region) and this concentration of 1469 electron density in the antibinding region contributes to 1470 making this orbital antibinding. Thus the orbital is 1471 1472 antibinding, though to a lesser extent than the  $\sigma(2)$  orbital. 1473

#### 1475 **7. Conclusion**

1477 Our study shows that the  $\sigma(3)$  orbital of free CO has an 1478 antibinding nature and when a positive charge is brought near the molecule from the Carbon side, this antibinding 1479 nature increases, possibly due to the increase in covalency 1480 on the bonding. Our study of CO,  $(QCO)^+$  and  $(COQ)^+$ 1481 systems using the force approach, throws light on the 1482 bonding in these systems and consequently on the bonding 1483 in non-classical carbonyls, demonstrating that the force 1484 approach is very useful in answering conceptual questions 1485 in chemical bonding. 1486

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