



Equilibrium CO bond lengths[☆]

Jean Demaison^{a,*}, Attila G. Császár^b

^aLaboratoire de Physique des Lasers, Atomes et Molécules, Université de Lille I, 59655 Villeneuve d'Ascq Cedex, France

^bLaboratory of Molecular Spectroscopy, Institute of Chemistry, Eötvös University, P.O. Box 32, H-1518 Budapest 112, Hungary

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ABSTRACT

Based on a sample of 38 molecules, 47 accurate equilibrium CO bond lengths have been collected and analyzed. These ultimate experimental (r_e^{EX}), semiexperimental (r_e^{SE}), and Born–Oppenheimer (r_e^{BO}) equilibrium structures are compared to r_e^{BO} estimates from two lower-level techniques of electronic structure theory, MP2(FC)/cc-pVQZ and B3LYP/6-311+G(3df,2pd). A linear relationship is found between the best equilibrium bond lengths and their MP2 or B3LYP estimates. These (and similar) linear relationships permit to estimate the CO bond length with an accuracy of 0.002 Å within the full range of 1.10–1.43 Å, corresponding to single, double, and triple CO bonds, for a large number of molecules. The variation of the CO bond length is qualitatively explained using the Atoms in Molecules method. In particular, a nice correlation is found between the CO bond length and the bond critical point density and it appears that the CO bond is at the same time covalent and ionic. Conditions which permit the computation of an accurate *ab initio* Born–Oppenheimer equilibrium structure are discussed. In particular, the core–core and core–valence correlation is investigated and it is shown to roughly increase with the bond length.

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1. Introduction

The most unequivocal geometrical structure of a molecule is its equilibrium structure, r_e , which corresponds to a minimum of the Born–Oppenheimer potential energy surface (PES) [1]. Estimates of equilibrium structures can be obtained experimentally via high-resolution spectroscopy and a few well-defined assumptions. Purely experimental determination of r_e structures is generally straightforward for diatomic molecules [2], but the level of difficulty increases rapidly with the number of atoms because it requires the analysis of, at least, all the fundamental vibrational states of all the isotopologues required for the structural determination. Furthermore, this analysis is often complicated by Coriolis interactions or anharmonic resonances [3]. For this reason, the number of purely experimental equilibrium structures for polyatomic molecules is quite small and is limited to molecules of moderate size.

Ab initio methods have become successful in accurately estimating equilibrium structures of even complex molecules. However, these determinations involve substantial computer resources because to achieve an accuracy similar to experimental techniques requires high-level electron–correlation treatments, such as coupled-cluster (CC) theory including single and double

excitations (CCSD) [4] augmented with a perturbational estimate of the effects of connected triple excitations, CCSD(T) [5]. Furthermore, large basis sets, at least of quadruple zeta quality, are also required. For these reasons high-level wavefunction-based *ab initio* methods are also restricted to relatively small molecules [6].

The semiexperimental (SE) method, resulting in r_e^{SE} structures, uses equilibrium rotational constants obtained from experimental ground-state rotational constants and computed rovibrational corrections [7]. It is faster, simpler and often more accurate than either the purely experimental method or the high-level *ab initio* techniques for the determination of equilibrium structures [8]. Thanks to this method employing both experimental and theoretical information, the number of equilibrium structures that are accurately known, with uncertainty estimates on the order of 0.001–0.002 Å for bond lengths and 0.1–0.2° for angles, has grown exponentially during the last twenty years. The SE technique has been successfully used for molecular systems containing several atoms, such as the amino acids glycine [9], alanine [10], and proline [11]. However, this technique is still computationally too expensive for molecules containing more than about 20 atoms.

For large systems, lower-level electronic structure methods have to be used as, for instance, second-order Møller–Plesset perturbation theory (MP2) [12] or Kohn–Sham density functional theory (DFT) [13]. One problem with using these methods is that the computed bond lengths are subject to errors which can be substantial. Nevertheless, if the basis sets employed are large enough (note the less stringent demand in case of DFT), the errors generally turn out to be mainly systematic and can thus be estimated,

[☆] In honor of Professor Jaan Laane for his many contributions to Science.

* Corresponding author.

E-mail addresses: jean.demaison@univ-lille1.fr (J. Demaison), csaszar@chem.elte.hu (A.G. Császár).

as demonstrated, for instance, for the CH [14], NH [15], OH [16] and CC [17] bond lengths.

Besides the CC and CH bonds, the CO bond is another important bond in (organic) chemistry. It is involved in alcohols, aldehydes, ketones, acids, esters, and ethers, as well as in many heterocyclic molecules. Over the last few years, accurate equilibrium structures of many molecules containing CO bonds have been determined. One of the goals of this paper is to collect and analyze the accurately known CO bond lengths. Furthermore, such a collection of validated data allows to investigate whether it is possible to estimate the CO bond length employing either the MP2 or the even more widely applicable DFT methods, for example via Becke's three-parameter hybrid exchange functional [18] and the Lee–Yang–Parr correlation functional [19], together denoted as B3LYP. Third, it is also important to know whether the variation of the CO bond lengths can be explained in simple terms, for example via the atoms-in-molecules (AIM) method.

2. *Ab initio* computation of Born–Oppenheimer (BO) equilibrium CO bond lengths

The CCSD(T) method of electronic structure theory is known to give accurate structures provided the basis sets employed are large enough [6,20,21]. For relatively small molecules, it is convenient to use the correlation-consistent polarized core–valence quadruple zeta basis set, cc-pwCVQZ, in brief, wCVQZ, [22], all electrons being correlated (AE). For larger molecules, the optimization is usually performed with the smaller correlation-consistent polarized quadruple-zeta basis set cc-pVQZ [23], abbreviated as VQZ, in the frozen core approximation (FC). The analogous cc-pVnZ functions with $n = T, Q, 5, 6$ are abbreviated as VnZ. Then, the core–valence and core–core correlation [24] is estimated at the much cheaper MP2 level using the wCVQZ basis set. It is indeed known that the MP2 method is accurate enough for first-row atoms [25]. To estimate the accuracy of the computed BO structure, three questions have to be answered: (i) As the atom of oxygen is electronegative, is it justified to neglect diffuse functions? (ii) Is convergence achieved at the quadruple zeta level or is it advisable to use still larger basis sets? (iii) How large is the core correlation and is it constant for a given bond?

2.1. Effect of diffuse functions in the basis

The results of geometry optimizations performed with the aug-cc-pVnZ (in short AVnZ) and cc-pVnZ (VnZ) basis sets, where only the former contains diffuse functions, are given in Table 1 for a selection of molecules. The effect of diffuse functions is generally quite large at the triple-zeta level, up to 0.004 Å for HF, but it decreases rapidly, it is almost negligible at the quadruple-zeta level for most molecules, less than 0.001 Å except for highly polar bonds such as HF and OO. The conclusion is that if the basis set is large enough, of quadruple-zeta quality or better, it is not necessary to take into account the diffuse functions for a structure optimization unless an extrapolation is subsequently carried out. Furthermore, it is obvious that if the effect of the diffuse functions is calculated at the triple-zeta level, their contribution will be overestimated.

2.2. Convergence of the basis set for the CO bond length

As shown in Table 2, going from VTZ to VQZ leads to a significant shortening of the bond length, typically a few thousandths of an Å. In view of this relatively large change, the question arises whether the computed bond length is already converged at the quadruple zeta level. Further basis set improvement, from VQZ to V5Z, leads to a very small change (usually the expected decrease)

Table 1
Effect of diffuse functions on bond lengths (in Å).

Molecule	Bond	N/A ^a	VTZ	VQZ	V5Z	V6Z
HF		A	0.9210	0.9177	0.9173	0.9173
		N	0.9172	0.9162	0.9168	0.9177
		A–N	0.0038	0.0015	0.0006	–0.0004
N ₂		A	1.1040	1.1005	1.0995	1.0992
		N	1.1038	1.1003	1.0994	1.0992
		A–N	0.0002	0.0002	0.0001	0.0000
F ₂		A	1.4181	1.4130	1.4109	1.4101
		N	1.4158	1.4129	1.411	1.4102
		A–N	0.0023	0.0001	–0.0001	–0.0001
CO		A	1.1360	1.1318	1.1309	1.1306
		N	1.1357	1.1314	1.1307	1.1305
		A–N	0.0003	0.0004	0.0002	0.0001
HCCH	C≡C	A	1.2102	1.2069	1.2059	1.2056
		N	1.2097	1.2065	1.2057	1.2055
		A–N	0.0005	0.0004	0.0001	0.0001
HCCH	C–H	A	1.0640	1.0636	1.0631	1.0631
		N	1.0637	1.0634	1.0630	1.0630
		A–N	0.0003	0.0002	0.0001	0.0001
NH ₃	N–H	A	1.0147	1.0128	1.0124	1.0123
		N	1.0141	1.0124	1.0121	1.0121
		A–N	0.0006	0.0004	0.0003	0.0002
H ₂ O	O–H	A	0.9616	0.9589	0.9584	0.9583
		N	0.9594	0.9579	0.9580	0.9582
		A–N	0.0022	0.0010	0.0004	0.0002
H ₂ O ₂	O–H	A	0.9665	0.9635	0.9624	
		N	0.9640	0.9627	0.9620	
		A–N	0.0025	0.0008	0.0004	
H ₂ O ₂	O–O	A	1.4610	1.4535	1.4515	
		N	1.4579	1.4525	1.4512	
		A–N	0.0031	0.0010	0.0003	

All calculations were performed at the CCSD(T) level of theory.

^a N means the standard VnZ basis set and A the corresponding aug-cc-pVnZ basis set.

of the CO bond length, the largest one being 0.001 Å for the OC_e bond in HCOOCH₃ and the median value is only 0.0003 Å.

Thus, it appears that there is no need to go beyond VQZ unless an accuracy higher than about 0.002 Å is required, which would furthermore require to take into account many other small effects as higher-order correlation effects up to quadruple excitations, CCSDTQ [26], relativistic effects, adiabatic correction, etc. [27]. Moreover, the small decrease when going from VQZ to V5Z is partially compensated by the small increase when going from V5Z to AV5Z.

2.3. Core correlation

One last point worth discussing is the effect of the core–core and core–valence correlation on the Born–Oppenheimer CO bond lengths. It was computed for a large subset of the molecules considered in this work and is detailed in Table 3. The wCVQZ basis set (and in some cases, the original CVQZ basis set) was used in the computations. For the smallest molecules, the CCSD(T) method was used while for larger ones the less expensive MP2 method was preferred. It is known that for molecules containing first-row atoms the MP2 method is accurate enough because it gives values almost identical to the CCSD(T) method and the usual difference of 0.0003 Å [25] is negligible for most applications.

At first sight, there are two values of the core correlation, one around 0.0021 Å for the CO multiple bonds and another one around 0.0028 Å for the CO single bond. In both cases, the range is rather small, about 0.0006 Å. However, a plot of the core correlation correction, Δr^{cc} , as a function of the equilibrium bond length r_e shows that Δr^{cc} increases with r_e , see Fig. 1. The correlation is far from

Table 2

Convergence of the CO bond lengths (in Å) computed with the VnZ basis sets.

Molecule	Bond	Method	VTZ	VQZ	V5Z	V6Z	Q-5 ^a	6-5
CO		CCSD(T)	1.13571	1.13139	1.13073	1.1305	0.0007	-0.0002
CO ₂		CCSD(T)	1.16629	1.16263	1.16207	1.1618	0.0006	-0.0003
H ₂ CO		CCSD(T)	1.20957	1.20658	1.20634	1.2062	0.0002	-0.0001
H ₂ C=C=O		MP2	1.16751	1.16431	1.16395		0.0004	
HCOOCH ₃	H ₃ C—O	MP2	1.43622	1.43434	1.43462		-0.0003	
	O—C _e	MP2	1.33998	1.33550	1.33657		-0.0011	
	C=O	MP2	1.20564	1.20355	1.20357		0.0000	
HCOOH <i>trans</i>	C=O	MP2	1.20322	1.20100	1.20100		0.0000	
	C—O	MP2	1.34571	1.34270	1.34220		0.0005	
HCOOH <i>cis</i>	C=O	MP2	1.19690	1.19450	1.19440		0.0001	
	C—O	MP2	1.35199	1.34930	1.34910		0.0002	
HOC ⁺		MP2	1.15930	1.15550	1.15490		0.0006	
HOCN		MP2	1.30324	1.29945	1.29860		0.0009	
CH ₃ OH		MP2	1.41848	1.4174	1.41816		-0.0008	
CH ₂ =CHOH		MP2	1.36011	1.35818	1.35821		0.0000	
HCOCH ₂ OH	C—O	MP2	1.39848	1.39602	1.39592		0.0001	
	C=O	MP2	1.21525	1.21247	1.21227		0.0002	
CH ₃ CH ₂ OH		MP2	1.42356	1.42259	1.42323		-0.0006	
HOCO ⁺	C≡O	MP2	1.13519	1.13176	1.13122		0.0005	
	C=O	MP2	1.22827	1.22453	1.22387		0.0007	
HCONH ₂		MP2	1.21497	1.21324	1.21340		-0.0002	
(CH ₃) ₂ O		MP2	1.40840	1.40660	1.40690		-0.0003	
c-C ₂ H ₄ O		MP2	1.43168	1.43030	1.43030		0.0000	

^a VQZ–V5Z value.

being perfect, with a correlation coefficient of 0.718. Part of the scatter may be explained by the fact that two different methods, CCSD(T) and MP2, were used to compute the correlation. However,

Table 3

Magnitude of the core correlation effect for a subset of the molecules of Table 2 (all values in Å).

Molecule	r(CO) ^a	Method	Core
HCO ⁺	1.1056	CCSD(T)/wCVQZ	0.0021
HOCO ⁺	1.1226	CCSD(T)/wCVQZ	0.0021
CO	1.1271	CCSD(T)/CVQZ	0.0022
HOC ⁺	1.1287	CCSD(T)/wCVQZ	0.0026
OCS	1.1562	MP2/CVQZ	0.0021
CO ₂	1.1600	CCSD(T)/CVQZ	0.0020
H ₂ C=C=O	1.1609	MP2/CVQZ	0.0022
HNCO	1.1641	MP2/CVQZ	0.0021
OCFCI	1.1730	MP2/wCVQZ	0.0022
HCOF	1.1773	MP2/wCVQZ	0.0022
OCHCl	1.1820	MP2/wCVQZ	0.0022
c-C ₂ H ₂ (CO) ₂ O	1.1894	MP2/wCVQZ	0.0022
HCOOH <i>cis</i>	1.1916	MP2/wCVQZ	0.0022
HCOOH <i>trans</i>	1.1977	MP2/wCVQZ	0.0021
HCOOCH ₃	1.1997	MP2/wCVQZ	0.0022
H ₂ CO	1.2047	CCSD(T)/CVQZ	0.0020
CH ₃ CHO	1.2063	CCSD(T)/wCVQZ	0.0021
HCOCH ₂ OH	1.2080	MP2/wCVQZ	0.0023
HCONH ₂	1.2109	MP2/wCVQZ	0.0022
HOCO ⁺	1.2233	CCSD(T)/wCVQZ	0.0026
HOCN	1.2999	MP2/wCVQZ	0.0027
HCOOCH ₃	1.3343	MP2/wCVQZ	0.0027
HCOOH <i>trans</i>	1.3406	MP2/wCVQZ	0.0027
HCOOH <i>cis</i>	1.3477	MP2/wCVQZ	0.0027
c-C ₂ H ₂ N ₂ O	1.3540	MP2/wCVQZ	0.0028
CH ₂ =CHOH	1.3593	MP2/wCVQZ	0.0028
c-C ₄ H ₄ O	1.3594	MP2/wCVQZ	0.0028
c-C ₂ H ₂ (CO) ₂ O	1.3848	MP2/wCVQZ	0.0028
HCOCH ₂ OH	1.3955	MP2/wCVQZ	0.0028
(CH ₃) ₂ O	1.4062	MP2/CVQZ	0.0028
c-C ₂ H ₄ O ₃	1.4080	MP2/wCVQZ	0.0027
c-C ₂ H ₄ O ₃	1.4135	MP2/wCVQZ	0.0027
CH ₃ OH	1.4172	MP2/wCVQZ	0.0026
CH ₃ CH ₂ OH	1.4221	MP2/wCVQZ	0.0027
c-C ₂ H ₄ O	1.4273	MP2/wCVQZ	0.0032
HCOOCH ₃	1.4338	MP2/wCVQZ	0.0031

^a See Table 5 for references.

the scatter remains within each method. Another possible explanation is that the accuracy of the equilibrium bond lengths is limited, about 0.002–0.003 Å, for some molecules. But it is not yet enough to fully explain the scatter. One even more likely explanation is that the scatter is genuine and that there is no exact linear correlation between the core correlation contribution and the equilibrium bond length of the CO bond. This is confirmed by the value found for HOC⁺, 0.0026 Å, which is much larger than the expected value, about 0.0021 Å.

2.4. Computational details

During the structure optimizations with the MP2 method performed in this work, the VQZ basis set was employed. B3LYP computations were also performed with the split-valence 6-311+G(3df,2pd) basis set, as implemented in Gaussian 03 (g03) [28], because it is known [29,30] to give relatively accurate results with the B3LYP DFT technique. Furthermore, as this basis is rather small compared to the aug-cc-pVTZ or VQZ basis sets, it promotes the computation of equilibrium structures of large molecules. All DFT computations utilized the g03 program suite.

The equilibrium CO bond lengths are either taken from the literature or are computed as part of this study. In some rare cases (CO, CO₂, OCS, OCSe, etc.), the CO bond lengths correspond to experimental structures. In most cases, however, they are either semiexperimental structures, r_e^{SE} , or Born–Oppenheimer *ab initio* structures, r_e^{BO} , the latter computed at the CCSD(T) level with a basis set of at least quadruple-zeta quality. In all cases, the accuracy of the structure was checked by redoing the original geometry optimizations. In some cases, the structure was also computed at the CCSD(T) level with the cc-pwCVQZ basis set [22], all electrons being correlated, as the core correlation correction is significant, see Ref. [24] and Section 2.3. These geometry optimizations were performed with the CFOUR package [31] and employed analytic first derivatives [32].

3. Semiexperimental structures of F₂CO and Cl₂CO

The semiexperimental equilibrium rotational constants are obtained by correcting the experimental ground-state rotational

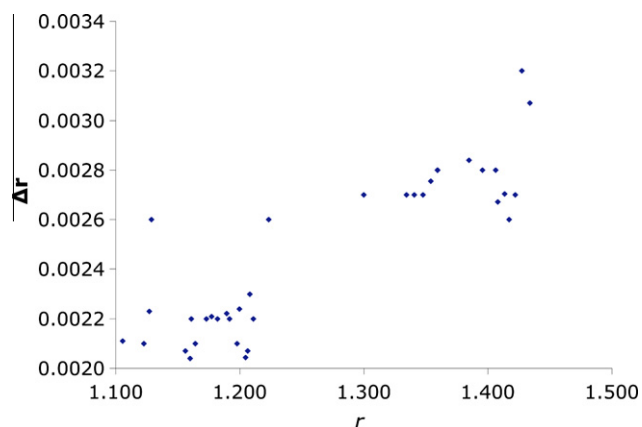


Fig. 1. Plot of the core-valence and core-core correlation against $r(\text{CO})$ bond lengths for a subset of the molecules of Table 2 (all values in Å).

constants with lowest-order vibration-rotation interaction constants (α) [33] determined quantum chemically. The vibration-rotation interaction constants can be estimated if the cubic force field of the molecule, expanded about a reference (usually the equilibrium) structure, is known. We chose the MP2 level of electronic structure theory to determine the anharmonic force fields. The quadratic force fields were evaluated analytically [34] in Cartesian coordinates at the optimized molecular structure, in order to avoid the nonzero force dilemma [35]. The cubic (ϕ_{ijk}) and semi-diagonal quartic (ϕ_{ijkl}) normal coordinate force constants were then determined at the same reference structure with the use of finite difference procedures involving displacements along reduced normal coordinates (with step size $\Delta q = 0.03$) and the calculation of analytic Cartesian second derivatives at these displaced geometries [32,36]. The evaluation of anharmonic spectroscopic constants was based on second-order rovibrational perturbation theory [33,37,38]. The anharmonic force fields in normal coordinates were determined for all the isotopologues whose ground-state rotational constants are known. The r_e^{SE} structures were obtained via a weighted least-squares fit to the semiexperimental moments of inertia.

The ground-state rotational constants of the four isotopologues of F_2CO were taken from Refs. [39,40] and those of the nine isotopologues of Cl_2CO were taken from Refs. [41,42]. The anharmonic force field of all species was calculated at the MP2 level with the VTZ basis set [23] for F_2CO and the V(T+d)Z basis set [43] for Cl_2CO . The theoretical lowest-order vibration-rotation interaction constants deduced from the *ab initio* cubic force field were combined with the known experimental ground-state rotational constants to yield the semiexperimental rotational constants.

The semiexperimental equilibrium structures of F_2CO and Cl_2CO are given in Table 4. The new semiexperimental structures are in perfect agreement with the previous experimental structures. The precision of the r_e^{SE} structures seems to be much higher but it has to be noted that the standard deviations from the fits are

Table 4
Semiexperimental structures of F_2CO and Cl_2CO (bond lengths in Å, angles in degrees).

Molecule	Parameter	Previous work	Present work
F_2CO	$r(\text{C}=\text{O})$	1.170(2) ^a	1.1699(4)
	$r(\text{C}-\text{F})$	1.311(2)	1.3100(2)
	$\angle(\text{FCF})$	107.6(8)	107.80(3)
Cl_2CO	$r(\text{C}=\text{O})$	1.1756(23) ^b	1.1759(4)
	$r(\text{C}-\text{Cl})$	1.7381(19)	1.7375(2)
	$\angle(\text{ClCCl})$	111.79(24)	111.85(2)

^a Ref. [71].

^b Ref. [72].

given for the semiexperimental structures whereas the uncertainty of the experimental structures takes into account all possible (random and systematic) sources of error.

4. CO bond lengths

The length of the CO bond ranges from 1.11 Å, in HCO^+ (note that this is shorter than in $\text{C}\equiv\text{O}$), to 1.43 Å, in HCOOCH_3 . See Table 5 for the complete list of 38 molecules studied here.

Using the values of the covalent radii for the C and O atoms, it is possible to roughly estimate the CO bond length: it is 1.12 Å for the triple bond [44], 1.24 Å for the double bond [45] and 1.38–1.42 Å for the single bond [46,47].

The shortest bond is found for HCO^+ , $r(\text{CO}) = 1.1056$ Å, which is shorter than in CO, $r = 1.1287$ Å. It may be explained by the presence of a positive point charge, H^+ , located on the carbon side of the bond axis. This simple Coulombic field increases the C–O stretching force constant and decreases the bond length by stabilizing the resonance form $\text{C}^-\equiv\text{O}^+$ [48]. The next shortest bond is found in HOCO^+ . Then comes CO with a partial triple bond character, as indicated by the resonance form $\text{C}^-\equiv\text{O}^+$.

It is possible to use the Atoms in Molecules (AIMs) theory of Bader [49,50] to rationalize the changes in the CO bond length. The bond length is mainly determined by three factors, the amount of electron density shared between the two bonded atoms which is given by the bond critical point density, ρ_b , the atomic charges on the bonded atoms, and steric interactions. These first two quantities can be calculated with the AIM theory. The calculations were performed at the B3LYP/6-311+G(3df,2pd) level with the implementation of the AIM method in g03 by Cioslowski et al. [51] and the results are given in Table 6. The value of ρ_b for HCO^+ , 0.542, is significantly larger than the corresponding value for CO, 0.517. At the same time, the CO bond is more polar in HCO^+ than in CO. In other words, the CO bond in HCO^+ is both more “covalent” and “ionic” than in CO, i.e., it is stronger. For HOCO^+ , the situation is slightly more complicated because ρ_b at 0.512 is slightly smaller than in CO but the polarity is much larger than in CO, the charge on the carbon being +2.320 e in HOCO^+ but only +1.186 e in CO. In this case, the CO bond in HOCO^+ is much more “ionic” than in CO.

Next comes a cluster of double bonds starting with OCSe , $r(\text{CO}) = 1.1533$ Å, and ending with the other CO in HOCO^+ with $r(\text{CO}) = 1.223$ Å. Variation of the bond length can again be explained with the help of the AIM theory, see Table 6. In particular, $\rho_b(\text{CO})$ decreases from 0.479 for OCSe to only 0.411 for HOCO^+ . Inspection of Table 6 and Fig. 2 shows that there is a nice correlation between ρ_b and $r(\text{CO})$. However, this correlation is not perfect, in particular ρ_b for HOC^+ at 0.441 seems to be too small for the bond length $r(\text{CO}) = 1.155$ Å but the bond is more polar than for the neighboring molecules OCSe ($\rho_b = 0.479$) and OCS ($\rho_b = 0.476$) which have almost the same bond length. Likewise, the CO bond length OCF_2 at 1.170 Å seems to be too long when taking into account the value of $\rho_b = 0.475$ and the strong polarity of the CO bond. This apparently abnormal behavior may be qualitatively explained by the ligand close-packing model (LCP) [50]. In this model, the geometry of the molecule is determined by the repulsive interactions between ligands. The ligands adopt a close-packed arrangement and each ligand can be considered to be touching each neighbors and can be assigned a non-bonded radius which is 1.08 Å for F and 1.14 Å for O. The interligand distance should be nearly constant and equal to the sum of the radii, 2.22 Å. It is indeed what is observed, the $\text{F}\cdots\text{O}$ distance being 2.21 Å for OCHF [52], OCFCI [53] and OCF_2 , see Table 4.

Then, there is the cluster of single bonds, starting with HOCN and ending with the CH_3-O bond in HCOOCH_3 , $r(\text{H}_3\text{C}-\text{O}) = 1.4338$ Å. The relatively short value in HOCN has to be mentioned. It is again straightforward to explain the difference of these two bond lengths

Table 5
Equilibrium CO bond lengths (in Å).

Molecule	r_e	Method ^a	Refs.	MP2 ^b	B3LYP ^c	r_1^d	r_2^e
HCO ⁺	1.1056	EX, BO	[61,62]	1.1153	1.1009	-0.0035	0.0006
HOCO ⁺	1.1226	BO	[16]	1.1318	1.1212	-0.0033	-0.0022
C=O	1.1287	EX, BO	[63,64]	1.1346	1.1245	-0.0001	0.0007
OCSe	1.1533	EX, BO	[56,58]	1.1640	1.1518	-0.0055	-0.0015
HOC ⁺	1.1546	BO	[16]	1.1555	1.1532	0.0045	-0.0015
OCS	1.1562	EX, BO	[65,66]	1.1651	1.1549	-0.0037	-0.0015
CO ₂	1.1600	EX, SE	[67,68]	1.1662	1.1591	-0.0010	-0.0019
H ₂ C=C=O	1.1609	SE, BO	[69]	1.1643	1.1589	0.0018	-0.0008
HNCO	1.1641	BO, SE	[15,70]	1.1696	1.1631	-0.0004	-0.0017
OCF ₂	1.1699	EX, SE	[71] ^f	1.1742	1.1700	0.0007	-0.0026
OCFCl	1.1730	SE, BO	[53]	1.1775	1.1715	0.0004	-0.0010
OCCL ₂	1.1759	EX, SE	[72] ^f	1.1813	1.1730	-0.0005	0.0004
OCHF	1.1773	BO	[52]	1.1812	1.1752	0.0010	-0.0003
OCHCl	1.182	SE, BO	[73]	1.1862	1.1772	0.0005	0.0024
c-C ₂ H ₂ (CO) ₂ O	1.1894	SE, BO	[74]	1.1938	1.1887	0.0002	-0.0014
HCOOH <i>cis</i>	1.1916	SE, BO	[75]	1.1945	1.1896	0.0017	-0.0001
HCOOH <i>trans</i>	1.1977	SE, BO	[75]	1.2010	1.1962	0.0011	-0.0004
HCOCOOH	1.1977	BO	[76]	1.2025	1.1970	-0.0004	-0.0012
HCOOCH ₃	1.1997	SE, BO	[77]	1.2055	1.1987	-0.0015	-0.0009
c-C ₃ H ₅ NO	1.201	BO	[78]	1.2044	1.2008	0.0010	-0.0016
H ₂ CO	1.2047	BO	[79]	1.2082	1.1986	0.0008	0.0043
C ₂ H ₂ O ₂	1.2049	BO	[80]	1.2102	1.2002	-0.0010	0.0028
CH ₃ CHO	1.2063	BO	^g	1.2108	1.2029	0.0003	0.0016
HCOCH ₂ OH	1.2080	BO	[16]	1.2125	1.2049	-0.0003	0.0014
HCOCOOH	1.2087	BO	[76]	1.2114	1.2014	0.0015	0.0055
HC(O)NH ₂	1.2109	BO	[81]	1.2132	1.2091	0.0019	0.0001
OC(NH ₂) ₂	1.2116	BO	[81]	1.2148	1.2143	0.0009	-0.0042
(CH ₃) ₂ CO	1.2117	SE	[82]	1.2152	1.2086	0.0006	0.0014
HOCO ⁺	1.2233	BO	[16]	1.2245	1.2185	0.0027	0.0033
HOCN	1.2999	BO	[16]	1.2995	1.2952	0.0027	0.0050
HCOCOOH	1.3317	BO	[76]	1.3322	1.3329	0.0011	-0.0001
HCOOCH ₃	1.3343	SE, BO	[77]	1.3366	1.3364	-0.0008	-0.0009
HCOOH <i>trans</i>	1.3406	SE, BO	[75]	1.3427	1.3430	-0.0008	-0.0012
HCOOH <i>cis</i>	1.3477	SE, BO	[75]	1.3493	1.3498	-0.0004	-0.0007
c-C ₂ H ₂ N ₂ O	1.3540	BO	[83]	1.3514	1.3559	0.0038	-0.0003
CH ₂ =CHOH	1.3593	BO	[16]	1.3582	1.3594	0.0022	0.0016
c-C ₄ H ₄ O	1.3594	SE, BO	[83]	1.3575	1.3599	0.0030	0.0012
c-H ₂ COO	1.3846	SE, BO	[32]	1.3874	1.3853	-0.0024	0.0015
c-C ₄ H ₂ O ₃	1.3846	SE, BO	[83]	1.3877	1.3893	-0.0025	-0.0022
HCOCH ₂ OH	1.3955	BO	[16]	1.3960	1.3975	-0.0003	0.0005
(CH ₃) ₂ O	1.4062	BO	[81]	1.4066	1.4095	v0.0004	-0.0006
c-C ₂ H ₄ O ₃	1.4080	SE, BO	[83]	1.4069	1.4110	0.0011	-0.0002
c-C ₂ H ₄ O ₃	1.4135	SE, BO	[83]	1.4136	1.4174	-0.0002	-0.0010
CH ₃ OH	1.4172	BO	[16]	1.4174	1.4210	-0.0005	-0.0009
CH ₃ CH ₂ OH <i>trans</i>	1.4221	BO	[16]	1.4226	1.4275	-0.0008	-0.0023
c-C ₂ H ₄ O	1.4273	SE, BO	[83]	1.4303	1.4271	-0.0035	0.0033
HCOOCH ₃	1.4338	SE, BO	[77]	1.4343	1.4399	-0.0011	-0.0027

^a Method: EX = experimental; SE = semiexperimental; BO = *ab initio*.^b MP2/VQZ.^c B3LYP/6-311+G(3df,2pd).^d Residuals from Eq. (1), see text.^e Residuals from Eq. (2), see text.^f This work, see Section 3.^g This work, CCSD(T)(AE)/wCVQZ value.

with AIM theory: both the bond critical point density, ρ_b , and the polarity of the CO bond are much larger in HOCN, explaining the shorter bond length, see Table 6. Here, the correlation between ρ_b and $r(\text{CO})$ is extremely pleasing, see Fig. 2. For the whole set of molecules of Table 6, the correlation coefficient is 0.9888.

In conclusion, the AIM theory permits to rationalize the apparent changes in the CO bond although, in some cases, the effect of the bond critical point density is obscured by the effect of the polarity of the bond as well as by steric effects. Inspection of Table 6 also shows that the charge on the oxygen is almost always larger than $-1.0 e$ (the exceptions are the ions and the peroxy oxygens in ethylene ozonide and dioxirane) indicating that the bond is very polar. Finally, note that the charge on the oxygen does not vary much whereas the charge on the carbon varies a lot, from $0.44 e$ for $c\text{-C}_2\text{H}_4\text{O}$ to $+2.39 e$ for F_2CO .

5. Approximate MP2 and DFT bond lengths

It is useful to check whether CO bond lengths could be estimated with reasonable accuracy at lower levels of electronic structure theory. We computed the structure of the molecules of Table 5 at two modest levels of electronic structure theory, MP2(FC)/VQZ and B3LYP/6-311+G(3df,2pd). The MP2 values are almost systematically too large, with a median deviation of -0.0044 \AA for multiple bonds and -0.0005 \AA for single bonds, whereas the B3LYP values are generally too small for multiple bonds and too large for single bonds with median values of $+0.0018 \text{ \AA}$ and -0.0021 \AA , respectively. Furthermore, the differences are not constant. However, a plot of the equilibrium values of the CO bond lengths as a function of the computed bond lengths displays a linear relationship in both cases, see Fig. 3 for the case of

Table 6

Bond lengths (Å), bond critical point densities ρ_b (au) and atomic charges $q(\text{C})$ and $q(\text{O})$ for the CO bond in some molecules (B3LYP/6-311+G(3df,2pd).

Molecule	r_e^a	ρ_b	$q(\text{C})$	$q(\text{O})$
HCO ⁺	1.1056	0.542	1.463	-0.910
HOOCO ⁺	1.1226	0.512	2.320	-0.941
C=O	1.1287	0.517	1.186	-1.186
OCSe	1.1533	0.479	0.824	-1.106
HOC ⁺	1.1546	0.441	1.434	-1.259
OCS	1.1562	0.476	0.605	-1.111
CO ₂	1.1600	0.471	2.271	-1.137
H ₂ C=C=O	1.1609	0.472	0.863	-1.131
HNCO	1.1641	0.468	1.946	-1.145
OCF ₂	1.1699	0.475	2.390	-1.139
OCFCl	1.1730	0.470	1.849	-1.120
COCl ₂	1.1759	0.464	1.348	-1.101
OCHF	1.1773	0.466	1.720	-1.177
OCHCl	1.1820	0.459	1.230	-1.104
c-C ₂ H ₂ (CO) ₂ O	1.1894	0.452	1.557	-1.124
HCOOH <i>cis</i>	1.1916	0.451	1.646	-1.152
HCOOH <i>trans</i>	1.1977	0.444	1.644	-1.174
HCOCO ⁺	1.1977	0.444	^b	^b
HC ⁺ OCH ₃	1.1997	0.441	1.636	-1.176
c-C ₃ H ₅ NO	1.201	0.438	1.483	-1.206
H ₂ CO	1.2047	0.435	1.081	-1.099
C ₂ H ₂ O ₂	1.2049	0.434	1.038	-1.081
CH ₃ CHO	1.2063	0.432	1.059	-1.129
HCOCH ₂ OH	1.2080	0.429	^b	^b
HCOCO ⁺	1.2087	0.432	^b	^b
HC(O)NH ₂	1.2109	0.432	1.511	-1.178
OC(NH ₂) ₂	1.2116	0.432	1.827	-1.211
(CH ₃) ₂ CO	1.2117	0.428	1.031	-1.149
HOOCO ⁺	1.2233	0.411	2.320	-1.142
HOCN	1.2999	0.341	1.637	-1.161
HC(O)COOH	1.3317	0.322	^b	^b
HC ⁺ OCH ₃	1.3343	0.317	1.636	-1.104
HCOOH <i>trans</i>	1.3406	0.313	1.644	-1.140
HCOOH <i>cis</i>	1.3477	0.307	1.646	-1.125
c-C ₂ H ₂ N ₂ O	1.3540	0.297	1.117	-1.097
CH ₂ =CHOH	1.3593	0.295	0.526	-1.138
c-C ₄ H ₄ O	1.3594	0.290	0.468	-1.109
c-H ₂ CO	1.3846	0.281	0.969	-0.527
c-C ₄ H ₂ O ₃	1.3848	0.287	1.557	-1.050
HC ⁺ OCH ₂ OH	1.3955	0.279	^b	^b
(CH ₃) ₂ O	1.4062	0.268	0.594	-1.084
c-C ₂ H ₄ O ₃	1.4080	0.277	1.016	-0.557
c-C ₂ H ₄ O ₃	1.4135	0.271	1.016	-1.050
CH ₃ OH	1.4172	0.260	0.587	-1.107
CH ₃ CH ₂ OH <i>trans</i>	1.4221	0.257	0.570	-1.110
c-C ₂ H ₄ O	1.4273	0.256	0.441	-0.938
HC ⁺ OCH ₃	1.4338	0.242	0.526	-1.104

^a See Table 5 for references.

^b AIM code fails.

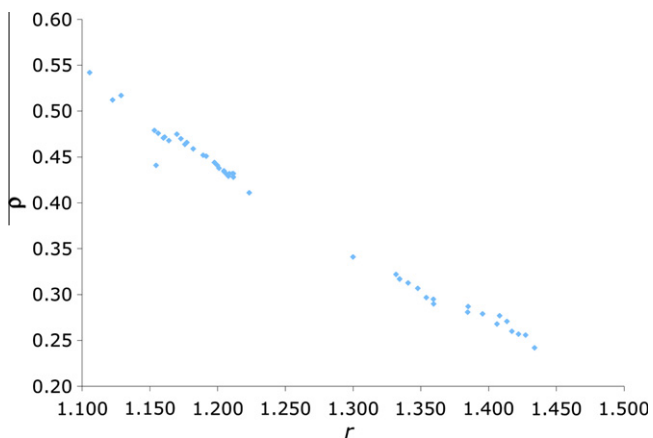


Fig. 2. Plot of bond critical point density, $\rho_b(\text{CO})$ in au, against $r(\text{CO})$ bond length (Å) for the molecules of Table 6.

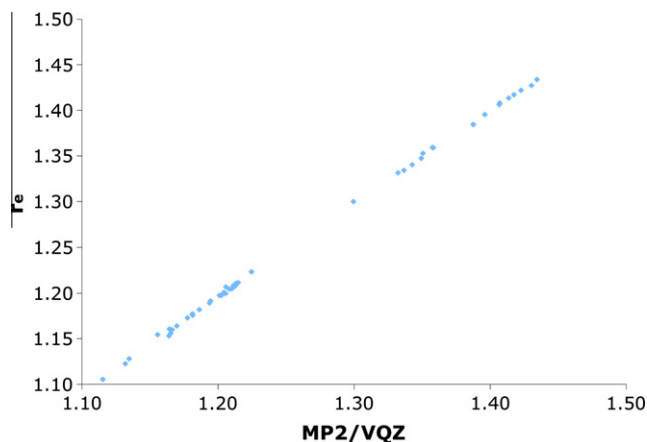


Fig. 3. Plot of r_e as a function of $r[\text{MP2}/\text{VQZ}]$ for the CO bond lengths (in Å).

MP2(FC)/VQZ. A linear least-squares fit of the 47 data of Table 5 yields the following relation at the MP2(FC)/VQZ level (in Å):

$$r_e(\text{CO}) = 1.0215(30) \times r_e^{\text{BO}}[\text{MP2}(\text{FC})/\text{VQZ}] - 0.0303(37), \quad (1)$$

with a correlation coefficient of $\rho = 0.9996$ and a standard deviation of $\sigma = 0.0020$ Å. For the B3LYP/6-311+G(3df,2pd) prediction the result of the fit is (in Å):

$$r_e(\text{CO}) = 0.9780(29) \times r_e^{\text{BO}}[\text{B3LYP}/6-311+\text{G}(3\text{df},2\text{pd})] + 0.0283(37), \quad (2)$$

with a correlation coefficient of $\rho = 0.9996$ and a standard deviation of $\sigma = 0.0021$ Å. In these two cases a careful analysis of the residuals does not indicate any significant deviation from linearity. Only one large residual, -0.0054 Å, was found, for OCSe at the MP2(FC) level. The molecules of this study fit perfectly well the two linear relationships established. If the OCSe value is removed from the fit, it slightly improves the results. The correlation improves to

$$r_e(\text{CO}) = 1.0197(27) \times r_e^{\text{BO}}[\text{MP2}/\text{VQZ}] - 0.0279(34), \quad (3)$$

with a standard deviation of $\sigma = 0.0018$ Å.

To check further the predictive power of Eqs. (1) and (2), they were used to calculate the CO bond lengths of the amino acid conformers glycine-**Ip**, alanine-**I**, and proline-**I**, for which reliable semiexperimental structures are available [9–11] (see Table 7). The nucleobase uracil, whose r_e^{BO} and r_e^{SE} structures were recently determined [54], is also used for this comparison. Finally, the ion FCO⁺ is also added to this list. The interest of this last molecule is that its T_1 diagnostics at 0.019 is rather large [55] and, therefore, the MP2 method may behave poorly. It is indeed what is observed. On the other hand, the B3LYP method delivers an accurate prediction. For the other molecules, the agreement is satisfactory and shows that it is possible to estimate the CO bond length with an accuracy of about 0.002 Å, in agreement with the standard deviation of the fits.

6. The case of OCSe

Taking into account the large residual found for OCSe, one may wonder whether the experimental r_e structure is accurate [56]. Actually, the two bond lengths $r(\text{CO})$ and $r(\text{CSe})$ were determined using the equilibrium rotational constants of seven isotopologues which significantly strengthens the reliability of the results. Furthermore, the accuracy was checked using two different empirical mass-dependent methods which are known to be reliable for such a small molecule without hydrogen [57]. Finally, the potential energy surface was computed using multireference

Table 7

CO bond lengths in selected conformers of the amino acids glycine, alanine and proline (in Å).

	MP2 ^a	B3LYP ^b	r from Eq. (1)	r from Eq. (2)	r_e^{SE}	Refs.
Glycine-Ip C=O	1.206	1.202	1.201	1.204	1.207(2)	[9]
Glycine-Ip C—O	1.351	1.352	1.349	1.351	1.353(1)	[9]
Alanine-I C=O	1.207	1.203	1.203	1.205	1.208(5)	[10]
Alanine-I C—O	1.352	1.353	1.350	1.352	1.348(4)	[10]
Proline-I C=O	1.206	1.201	1.201	1.203	1.198	[11]
Proline-I C—O	1.334	1.336	1.332	1.335	1.327	[11]
Uracil C ₂ =O ₇	1.213	1.210	1.209	1.212	1.210	[54]
Uracil C ₄ =O ₈	1.217	1.213	1.212	1.214	1.213	[54]
FCO ^c	1.127	1.114	1.121	1.118	1.117	^c

^a MP2(FC)/VQZ.^b B3LYP6-311+G(3df,2pd).^c This work, CCSD(T)/wCVQZ(AE) value.

configuration interaction theory [58]. The derived bond length, r_e (C=O) = 1.1536 Å is in perfect agreement with the experimental value, 1.15327(25) Å. The discrepancy for the MP2/VQZ CO bond length might be explained by relativistic effects, not negligible for this molecule, one of the few molecules of the test set containing a third-row atom. However, the relativistic effects should mainly affect the CSe bond. A more likely explanation is that non-dynamical electron correlation is not negligible for this molecule. This is confirmed by the large value of the T_1 diagnostic [55], which at 0.021 [computed at the CCSD(T)/6-311+G(3df,2pd) level] is above the cut-off value of 0.02, indicating that lower-level single-reference methods are not adequate for describing electron correlation effects.

7. Summary and conclusions

The range of the CO bond is large but its variation can be qualitatively explained using the AIM theory. In particular, an almost linear relation is found between the bond length and the bond critical point density. Although this result is interesting, it does not permit to easily predict the variation of the bond length. It would be useful to have a simple intuitive way to roughly predict the variation. However, as several factors are involved, it is safer to only compare closely related molecules. For instance, for the formyl derivatives, HCOX, or the acetyl derivatives, CH₃COX, an electronegative substituent X will attract charge density from the carbon and the increased positive charge should strengthen the CO bond. In other words, the CO bond length will decrease when the electronegativity of the substituent X increases. The difficulty is to determine reliable electronegativities for groups of atoms. Several scales are available [59]. If we sort the substituents X by order of increasing electronegativity (with the CO bond length of formyl derivatives given in parentheses and in Å), we find:

H (1.205) < NH₂ (1.211) < CHO (1.205) < OH (1.198) < COOH (1.198) < Cl (1.182) < F (1.177). With the exception of acetamide, HCONH₂, there is a rather satisfactory agreement. Nevertheless, the case of acetamide may be explained with the help of the resonance structure O⁻—CH=N⁺H₂. Alternatively, the LCP model may be invoked to explain the long CO bond length as in F₂CO. It is also difficult to estimate a reliable value for the electronegativity of the methyl group which is supposed to be close to that of H. However, the effect of the methyl group is easy to understand. For instance, the structure of CH₃CHO is intermediate between the resonance structures H₃C⁺=CH—O⁻ and H₃C—CH=O which explains why the CO bond is slightly longer than in H₂CO, and implies a shorter C—C bond. Indeed, the C—C bond length in CH₃CHO is 1.499 Å, significantly shorter than in CH₃—CH₃, 1.522 Å [60]. In conclusion, it is rather easy to explain the trends in the CO bond lengths although it is not easy to make reliable predictions.

However, if the problem is to predict the length of the CO bond, both the MP2(FC)/cc-pVQZ and B3LYP/6-311+G(3df,2pd) methods

give satisfactory results, after a small correction. The MP2(FC)/cc-pVQZ method is slightly more accurate except when single-reference methods are no more suitable. Furthermore, it is much more expensive in computation time and memory. For these reasons, the simplest and most reliable method for predicting CO bond lengths is the B3LYP/6-311+G(3df,2pd) one combined with Eq. (2).

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