

Bonding Analysis

The Quadruple Bonding in C₂ Reproduces the Properties of the MoleculeSason Shaik,^{*[a]} David Danovich,^[a] Benoit Braida,^[b] and Philippe C. Hiberty^{*[c]}*The paper is dedicated to Andreas Savin, a great scientist and a Mensch, on occasion of his 65th birthday*

Abstract: Ever since Lewis depicted the triple bond for acetylene, triple bonding has been considered as the highest limit of multiple bonding for main elements. Here we show that C₂ is bonded by a quadruple bond that can be distinctly characterized by valence-bond (VB) calculations. We demonstrate that the quadruply-bonded structure determines the key observables of the molecule, and accounts by itself for about 90% of the molecule's bond dissociation energy, and for its bond lengths and its force constant. The quadruply-bonded structure is made of two strong π bonds, one strong σ bond and a weaker fourth σ -type bond, the bond

strength of which is estimated as 17–21 kcal mol⁻¹. Alternative VB structures with double bonds; either two π bonds or one π bond and one σ bond lie at 129.5 and 106.1 kcal mol⁻¹, respectively, above the quadruply-bonded structure, and they collapse to the latter structure given freedom to improve their double bonding by dative σ bonding. The usefulness of the quadruply-bonded model is underscored by "predicting" the properties of the $^3\Sigma_u^+$ state. C₂'s very high reactivity is rooted in its fourth weak bond. Thus, carbon and first-row main elements are open to quadruple bonding!

Introduction

Ever since Cotton described the Re \equiv Re quadruple bonding in Re₂Cl₈²⁻,^[1] there has been a surge of interest in multiple bonding,^[2] reaching quintuple and even sextuple bonding in, for example, Cr₂, W₂ and U₂ complexes and dimers.^[3] In contrast to these high bond multiplicities among transition metals and rare earths elements, we and our students with us have been taught that the maximum bond multiplicity between two main elements is a triple bond,^[4] for example, as in acetylene, which was asserted by Lewis^[4a] to possess the highest possible union between two atoms. Nevertheless, there are diatomic molecules, for example, C₂, which possess eight valence electrons and a singlet ground state. Could it be that carbon breaks the glass ceiling and has a quadruple bonding in this molecule?^[5-7]

This fundamental question guided us ever since we started the research on C₂ and its isoelectronic species.^[6,7] Meanwhile, C₂ is interesting also because of its chemistry and spectroscopic properties.^[8-10] Thus, C₂ is no exotic curiosity, but an important chemical species.^[11] It is responsible for the blue glow ("Swan bands") emanating from hydrocarbon flames^[12] and for cometic light.^[8c,11] It is a constituent of solid-state carbides,^[9] and it is implicated in diamond growth^[13] and in the formation of fullerenes.^[14] C₂ is also one of the most strongly bound diatomic molecules in nature.^[15] However, quite paradoxically, despite the strong bond in C₂, this molecule is very highly reactive^[8d,15] and is not isolable. Its reactivity may reflect the presence of the diradicaloid $^3\Pi_u$ state^[8d] very close to the ground state, or to simply originate from the multiply-bonded nature of the ground state (or its inverted weak σ bond; see later). Indeed, based on experience, the reactivity of multiply-bonded CC-based molecules increases with the bond multiplicity, so that triple bonds are frequently more reactive than double bonds,^[8e] and both multiple bonds, in turn, are more reactive than single bonds. And for all these fundamental and practical reasons, it is very important to reach a consensus about the nature of its bonding. Bonding is after all at the heart of chemistry.

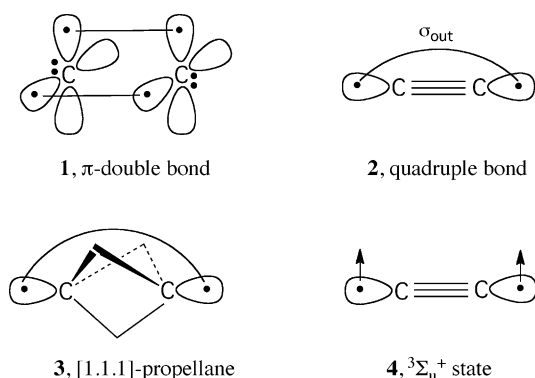
A simplified molecular orbital (MO) consideration of bond orders (BOs) suggests that C₂ possesses a π double bond, as in **1** in Scheme 1. There is no underlying σ bonding in **1**, because presumably the occupied bonding and anti-bonding orbitals, $2\sigma_g$ and $2\sigma_u$, cancel one another and contribute zero to the total BO. A related doubly-bonded picture was supported from energy decomposition analysis of a DFT calculation.^[16a] Howev-

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Scheme 1. Bonding cartoons: the π doubly-bonded model for C_2 (1) suggested by bond order consideration of the MO diagram, and the quadruply-bonded model for C_2 (2) suggested by qualitative VB consideration. The inverted bond in [1.1.1] propellane (3), and the bonding cartoon of the triplet $^3\Sigma_u^+$ state (4) of C_2 .

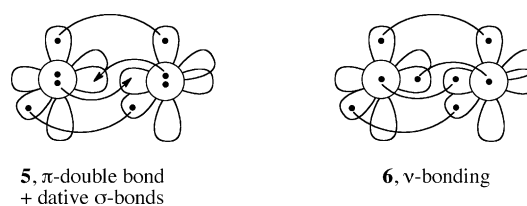
er, usage of standard DFT may be questioned, since C_2 has a multireference character.^[16b] Similarly, usage of a full-valence CASSCF and wave function or other correlated methods leads to effective BO (EBO) values of 2.2–3.0.^[6] Other BO (e.g., or Wiberg's WBI, NBO-based BO) or EBO determination methods reveal values of 3.30, 3.40, 3.51, 3.71, and 3.9,^[6,17] raising the doubt whether the naïve BO/EBO calculations are reliable methods for determining the bond multiplicity of a molecule like C_2 , because of the fuzzy status of $2\sigma_u$. Indeed, as argued several times,^[6,15,18] the $2\sigma_u$ orbital is weakly antibonding if not simply non-bonding, and hence counting this orbital in BO/EBO considerations may distort the bonding picture (see later).

An alternative starting point to the qualitative MO picture in 1 is 2 (Scheme 1), which can be deduced from qualitative valence bond (VB) considerations. Thus, sp -hybridization at each carbon atom leads to the straightforward model of C_2 shown in 2. Here, C_2 possesses a quadruple bond made of an inner triple bond (one σ and two π bonds) and an outer fourth σ bond made from the inverted hybrids in 2.

At first sight, the inverted hybrids in 2 might look rather poorly matched for bonding. However, similarly inverted hybrids as in [1.1.1]propellane, 3 (Scheme 1), were shown to bring about significant bonding.^[19] So why dismiss the inverted fourth σ bond in C_2 ? Indeed, as we showed in recent VB and full configuration interaction (FCI) studies,^[6,7] C_2 and all its iso-electronic molecules have major quadruply-bonded characters; a strong internal triple bond and a weak inverted fourth bond. For C_2 we determined the bond interaction energy of the fourth bond as 17–21 kcal mol⁻¹ using several methods, including an experimentally based one.^[7]

Our early work^[6] has been criticized by several groups,^[20a–c] and despite our efforts to respond,^[7,20d,e] the main criticism has just recently resurfaced in several studies raising more issues.^[21,22] In a nutshell, the criticism is based on observables as well as on theoretical indices of bonding. The main observables, which were emphasized, are the stretching force constant of C_2 compared with that in $HC\equiv CH$, the corresponding CC bond lengths, and the bond dissociation energies (BDEs) of

the CC bonds. These observable properties indicate that the bond in C_2 is somewhere between those in ethylene and acetylene.^[20a,b,21] In addition, theoretical indices such as EBOs,^[21] bond-strength orders (BSOs),^[21b] and BOs based on localized natural orbitals^[22] indicate bond orders of slightly more than two, reaching 2.5–2.6 (note however the $BO(C_2)$ in references [22b,c] is as large as that of $HC\equiv CH$ and larger than in $N\equiv N$.^[22d]). Furthermore, the domain-averaged Fermi holes (DAFH) analysis^[22b,c] suggests that C_2 has only a residual sigma bonding akin to Be_2 (so-called “a non-classical sigma component”^[22c]). Thus, these studies dismiss a “genuine quadruple bond”^[23] in C_2 and suggest a species like 1, with a π double bond and “a residual σ interaction”, which Hermann and Frenking^[21a] suggest to be two weak dative σ bonds, as described in 5 in Scheme 2. Alternatively, Weinhold and Landis^[24] proposed a similar type of σ interaction, called “ v bonding” (6), which they did not define as weak or residual bonding (recall that BOs with NBO^[17b] are close to 4). Thus, all the recent criticisms of the quadruple bonding idea in C_2 ^[20a,b,21,22] agree on a “double-bond-plus” model, and their major criticism^[21a,b] is that the proposed quadruple bonding model is, allegedly, disconnected from any observable of the C_2 molecule.



Scheme 2. The dative bonding model (5), and the v -bonding model (6).

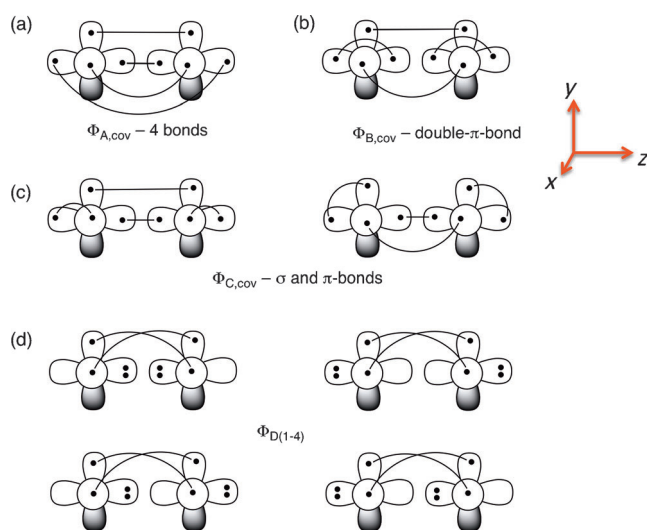
Therefore, in order to respond to this challenge, we focus herein on the quadruply-bonded structure of C_2 with an aim of establishing that this structure by itself determines the key observable properties of the molecule, while other VB structures have a marginal effect on these properties. Moreover, VB theory does not interpret the wave function, as done by usage of EBO or other indices, but rather it directly gives a snapshot description of the bonds in terms of chemical Lewis structures. At the same time, the method provides the means to determine the contribution of the various VB structures to the total bonding interaction of the molecule,^[6,7,25] and to rank the VB structures by energy relative to the most stable one. As will be shown, the four electron pairs that contribute to bonding in the quadruply-bonded VB structure of C_2 account for more than 90% of the total bond dissociation energy (BDE) of the molecule in the $^1\Sigma_g^+$ ground state, its bond length, and its force constant, as well as for the properties of its associated triplet state, $^3\Sigma_u^+$ state, wherein the fourth bond is decoupled to a triplet as shown in 4 in Scheme 1. By contrast, we shall demonstrate that all doubly-bonded models of C_2 are much higher in energy (> 100 kcal mol⁻¹), for a good physical reason (see later), and given the variational freedom they collapse to the quadruply-bonded structure.

Results and Discussion

The technical details are described in the Computational Methods section and the Supporting Information document, while here we display key structures and discuss the key results.

Valence bond structures and their bonding characteristics

Since C_2 has eight atomic- and hybrid-atomic orbitals (AOs and HAOs) and eight valence electrons, according to the Rumer rules,^[26a] the configuration in which all HAOs/AOs are singly occupied form a set of 14 covalent structures, of which only part are important (see Supporting Information, Scheme S1) and are depicted in Scheme 3. The lines connecting the corresponding singly occupied orbitals indicate either the covalent bonds or other singlet-pairs. Thus, $\Phi_{A,cov}$ in Scheme 3a is the covalent quadruply-bonded structure.^[26b] Similarly, $\Phi_{B,cov}$ and $\Phi_{C,cov}$ in Scheme 3b and 3c, respectively, are the covalent structures with doubly-bonded C_2 ; $\Phi_{B,cov}$ describes the doubly- π -bonded structures and $\Phi_{C,cov}$ the two ethylenic ($\sigma + \pi$)-bonded structures. Finally, $\Phi_{D(1-4)}$ in Scheme 3d are four symmetry-related VB structures, which have no covalent bonds and are unimportant at the equilibrium distance, being essential only at the dissociation limit of the energy curve.



Scheme 3. Covalent structures of C_2 arranged according to bonding groups. The lines connecting the corresponding singly occupied orbitals indicate covalent bonds. The orbitals in the x and y axes are 2p atomic orbitals (AOs), while those on the z axis are hybrid AOs (HAOs). a) $\Phi_{A,cov}$ is the quadruply-bonded covalent structure.^[26b] b) $\Phi_{B,cov}$ is the doubly- π -bonded covalent structure. c) The $\Phi_{C,cov}$ set involves two structures, each with ethylenic ($\sigma + \pi$)-bonded covalent structures. d) $\Phi_{D(1-4)}$ are four symmetry related ionic VB structures (generated from the covalents of group D, in Scheme S1b in the Supporting Information), which are essential at the dissociation limit for the full A+B+C set of 84 structures.

Each of the above covalent structures generates a corresponding set of ionic structures. By limiting ourselves to no more than di-ionic structures, we generate a group of 21 VB structures, comprising of one covalent, eight mono-ionic and

twelve "di-ionic" structures. Our selection avoids generation of C^{+2} and C^{-2} centers, ensures that the di-ionic structures are overall neutral or at most have C^{+1} and C^{-1} species, and excludes structures with two doubly occupied orbitals on the same atom (see Computational Methods and Supporting Information). Thus, the four covalent structures in Scheme 3a–c generate a set of 84 VB structures, which fall into three groups A, B, and C, and which together with the four structures in Scheme 3d, which are necessary for correct dissociation, lead to a set of 88 VB structures. This VB(88)-set leads to a total energy, which is as close as $8.9 \text{ kcal mol}^{-1}$ at the equilibrium R_{CC} distance to the energy of the complete set of VB structures that involves 1764 structures,^[27] and at 10.0 \AA the energies of the two sets are identical (see Supporting Information, Scheme S1 and Table S6). At the equilibrium R_{CC} distance, adding structures $\Phi_{D(1-4)}$ to Groups A–C lowers the total energy by merely $0.27 \text{ kcal mol}^{-1}$. As we already noted, the importance of the D structures is significant only close to the dissociation limit. We can therefore consider only groups A–C in the following discussion of bonding in C_2 .

Bonding crossover and the quadruply-bonded nature of the ground state

As has been noted,^[6,7,21a,b] a meaningful estimation of the "bond strength" in a molecule may differ from the bond dissociation energy (BDE). Indeed, the BDE of a molecule AB is the difference between the energy of this molecule and that of the fragments A and B in their respective ground states, while the bond strength is estimated by reference to fragments A and B in states reflecting their actual electronic configurations in the molecule.^[6,7,15,21b] Thus, if the molecular electronic state of C_2 resembles the doubly-bonded structures of groups B or C, it is legitimate to take the 3P ground states of the C atoms as reference states. If, however, the molecule is indeed quadruply bonded, then each carbon must have four singly occupied orbitals in the molecule. In such a case, the legitimate reference state is 5S .^[28a] Let us now see which of these two options passes the test of ab-initio VB calculations. Since a doubly-bonded C_2 was proposed^[20b,21a,b] to be a potential model for representing the bonding in the molecule (see above), the usage of groups A, B, and C, which constitute the quadruply (A)- and doubly-bonded (B and C) representations, is suitable for testing the bonding preference of the molecule. Which one will it be, quadruply bonded like A, or doubly bonded like B and C?

Figure 1a and 1b show the variation of the weights of these bonding groups as a function of the C–C distance between 1.2 and 2.5 \AA . Figure 1a depicts the variations in the weights for the covalent-only structures (displayed in Scheme 3a–c), while Figure 1b plots the full group-structural weights (for 21 structures in A and 63 in B+C). It is seen that at R_{CC} distances are equal to or longer than $1.85\text{--}1.95 \text{ \AA}$, and the dominant structures are those with a double bond between the two carbon atoms. However, at distances shorter than 1.85 \AA and at the equilibrium distance (1.244 \AA), the wave function is dominated by the quadruply-bonded structure, the weight of which is

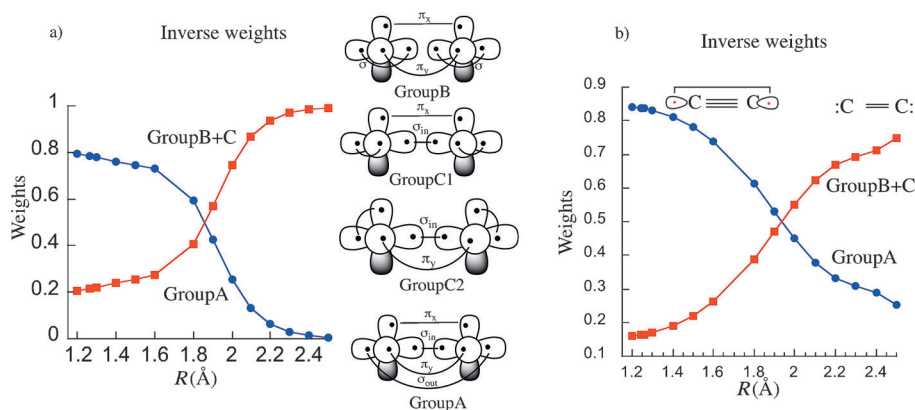


Figure 1. Bonding-crossover pattern as reflected in the change of the total weights of the quadruply-bonded-group A (blue curve), and the combined weights of the doubly-bonded-groups B+C (red curve), as a function of the C–C distance, R_{CC} (Å). a) Covalent-only structures and their weights; group A with one structure, and groups B and C with three structures. b) Weights of the full structural groups, A (21 structures), and B+C (63 structures). The cartoons adjacent to the curves highlight the bonding-crossover pattern that occurs at ca. 1.85 Å. Note that at long distances (> 1.85 Å) all the structures become polyradicaloids with singlet-coupled pairs that bring about weak bonding interactions.

massively dominant (ca. 0.85). The same pattern is found whether we use only the four covalent VB structures of A–C without the ionic structures or the full set of 84 structures. Thus, no matter how we plot the weights, they reveal a bonding crossover pattern from a quadruple bond, at equilibrium, to a double bond from 1.85 Å and up to 2.5 Å. At $R_{CC} > 2.5$ Å (not shown in Figure 1) and up to the dissociation limit, the four structures of group D dominate the wave function and describe eventually the two carbon atoms at their 3P group states.

As shown by the bonding cartoons depicted adjacent to the curves, this bonding-crossover pattern reflects an avoided crossing between a quadruply-bonded state, in which each carbon atom has four odd electrons in a promoted s^1p^3 configuration (5S), and a doubly-bonded state, in which the carbon atoms are in their ground states (3P). These results provide a clear justification for taking the 5S states of carbon as reference states of the $^1\Sigma_g^+$ ground state of C_2 , despite opposite claims.^[20b,21a] In fact, we verified in the present study that the covalent structure A at 10.0 Å is identical to the 5S - 5S state. The bonding crossover pattern in Figure 1 is observed in all multi-reference treatments of C_2 .^[28] It is the root cause for the failure of single-reference methods to reproduce the potential energy curve at long distances (e.g. CCSD(T) fails and a renormalized coupled cluster is needed to restore a smooth curve^[29]).

Clearly, Figure 1 shows that the quadruply-bonded structure is the dominant descriptor of the ground-state wave function. For further verification of this feature we turn to Figure 2, which displays the relative energies of the A–C structure groups at the equilibrium distance. Thus, the doubly-bonded groups, B and C, reside above the quadruply-bonded covalent structure A or the entire group A by 130.3/137.9 (covalent only) and 129.5/106.1 kcal mol⁻¹ (full group energies). As such, the energy gap of groups B and C relative to group A shows that the additional two bonds in A are of considerable strength! This will be confirmed later by calculating independently the bond interaction energies of C_2 .^[6,7]

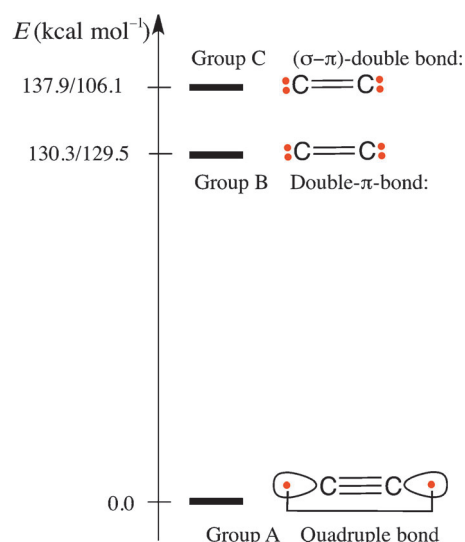


Figure 2. Relative energies (in kcal mol⁻¹) of the doubly-bonded VB structure groups (groups B and C) to the quadruply-bonded one (group A). The relative energies are shown in the order of covalent-structures/full-sets. B and C are higher than A, since they suffer from Pauli repulsion of the dangling lone pair electrons, while in A these electrons are used for bonding.

There is a fundamental reason^[29] why the doubly-bonded structures (B or C) are much higher in energy than the quadruply-bonded structure at equilibrium. At this short distance (1.244 Å), the dangling electron pairs on each carbon atom (in B and C) are engaged in severe Pauli repulsion with the electron pair on the other atom. As we shall see later, this repulsion is retained when we allow for dative interactions as in **5** (Scheme 2), which is expected by the “two-bond plus” model.^[20b,21a,b,22] On the other hand, engaging these idle electron pairs in bonding stabilizes the quadruply-bonded structure well below the doubly-bonded ones.

Figure 3 is a VB-mixing diagram, showing that the quadruply-bonded set A benefits by 16.0 kcal mol⁻¹ from the mixing

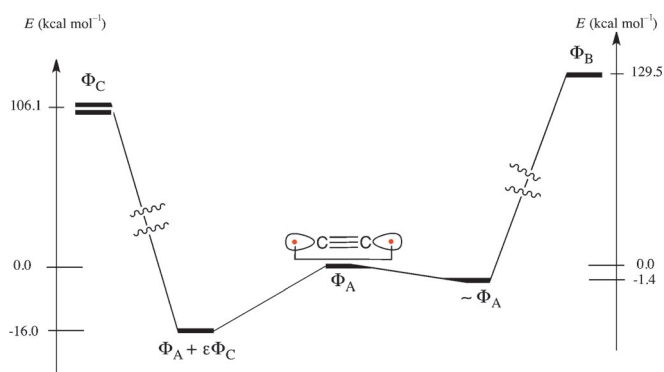


Figure 3. VB mixing diagrams: stabilization of the quadruply-bonded structure (A) by VB mixing with C and B, where A, B and C are the corresponding full groups. All relative energies are calculated at $R_{CC} = 1.244 \text{ \AA}$, the equilibrium distance of A. ϵ signifies a small mixing coefficient of C into A.

in of set C. However, the mixing of set B has almost no effect on A, just $1.4 \text{ kcal mol}^{-1}$. As such, set B with the doubly- π -bonded structures is virtually an excited state that does not mix with the quadruply-bonded structures of set A. On the other hand, set C with its two ($\sigma + \pi$)-ethylenic doubly-bonded structures stabilizes set A by mixing with it, and further augments the σ bonding in A. Nevertheless, considering the energy gap between sets A and C, this resonance energy stabilization is a perturbation on the energy of the quadruply-bonded structure. What remains to be established is how well does the quadruply-bonded structure set A alone reproduce key molecular properties?

How well does the quadruply-bonded structure reproduce the BDE of C_2 ?

To gauge the energetic contribution of the quadruply-bonded structure vis-à-vis the full VB wave function, we calculated the corresponding bond dissociation energy (BDE) values, which are collected in Table 1, along with the experimental datum.^[30] It is seen that at the best level, the VBSCF(1764) calculation reproduces closely the FCI^[7,31] value with the same basis set. The BDE value with VBSCF(1764) and FCI are also close to the experimental datum of $146.67 \text{ kcal mol}^{-1}$.^[30] The VBSCF(88) in entry 3 corresponds to the set of 88 VB structures (84 A–C, and 4 D), and its BDE value is 93.6% of VBSCF(1764).

Thus, the VBSCF(88) wave function, which is dominated by the quadruple bond with a small resonance-energy contribution from the ethylenic double bond (see Figure 3), practically accounts for most of the BDE value at VBSCF(1764)/6-31G*. Furthermore, as seen in entry 4, the BDE of the quadruply-bonded structure, VBSCF(4-bonds), by itself is 88% of BDE for VBSCF(88) and 82% of the BDE of VBSCF(1764). With some dynamic correlation, the BDE at the VBCISD(4-bonds) level reaches 94% of the VBSCF(1764) value. Finally, from the quantum Monte Carlo augmented VBSCF-QMC calculations (entries 7 and 8), which add the missing dynamic correlation using a flexible quadruple-zeta basis set,^[32] the BDE(88) level in entry 7 accounts for 98% the experimental DBE datum. At the same VB-

Table 1. Bond dissociation energies (BDE) of the quadruply-bonded structure (group A) and the full VB wave function, and the corresponding experimental value.

VB Method	BDE [kcal mol^{-1}] ^[d]	%BDE ^[e]
1 VBSCF (1764) ^[a]	137.9	100
2 full configuration interaction (FCI)	138.1	100
3 VBSCF (88)	129.1	93.6
4 VBSCF (4-bonds) ^[b]	112.9	81.9/87.5 ^[f]
5 VBCISD (4-bonds) ^[b]	129.3	93.6 ^[g]
6 Experimental datum ^[c]	146.67 ± 0.06	100
7 VBSCF-QMC (88)	143.7 ± 0.4	98.0
8 VBSCF-QMC (4-bonds)	134.9 ± 0.4	92.0/93.9 ^[h]

[a] The full VBSCF wave function involves 1764 VB structures. [b] Group A has 21 structures to which a few structures are added to reproduce correctly the dissociation limit (${}^3P-{}^3P$). The effect of these structures at the equilibrium distance is less than 1 kcal mol^{-1} (see Table S6 in the Supporting Information) [c] From Ref. [30]. [d] Relative to VB at 10.0 \AA . [e] $[\text{BDE}(\text{truncated VB})/\text{BDE}(\text{full})] \times 100$. [f] %BDE of A relative to VBSCF(1764)/VBSCF(88), respectively. [g] %BDE of A relative to full CI in the same basis set. [h] %BDE of VBSCF-QMC(4-bonds) to experimental datum/VBSCF-QMC(88), respectively.

QMC level, the BDE(4-bonds), entry 8, reaches 92% of the experimental BDE. Therefore, for all intents and purposes, the quadruply-bonded structure describes the ground state of C_2 quite well.

How well does the quadruply-bonded structure reproduce the bond length and force constant of C_2 ?

One of the main sources of criticism^[21] of the quadruple-bonding model in C_2 is that the molecule has a somewhat longer bond than acetylene (1.243 \AA vs. 1.204 \AA),^[15,33] which is only triply bonded and at the same time the force constant of C_2 is smaller than that of acetylene. This is an apparent paradox if one is an orthodox adherent of the idea that force constants measure relative bond multiplicities. We shall now show that the quadruply-bonded structure accounts also for the bond length and force constant of the molecule. Such a demonstration may unravel the roots of this apparent paradox.

Table 2 shows the VB-computed equilibrium distances (R_{CC}) and force constants (k_{CC}) at different VB levels, along with corresponding experimental data. It is seen that the somewhat long R_{CC} and the small k_{CC} values, compared with the corresponding values for acetylene (entry 8), manifest already for the quadruply-bonded structure (entries 1 and 2). Firstly, the 4-bonded covalent structure $\Phi_{A, \text{cov}}$ has by itself already a longish bond and a smallish k_{CC} . Adding all the corresponding ionic structures for group A (see Supporting Information) generates $\Phi_A(4\text{-bonds})$ in entry 2, wherein all the four bonds have their covalent and ionic structures. This appears to have small effects on the R_{CC} and k_{CC} values compared with the covalent structure in entry 1. Using the balanced set of 88 structures, $\Phi(88)$ in entry 3, lengthens the bond by merely 0.01 \AA and slightly lowers k_{CC} compared with the quadruply-bonded VB structure in entry 2. Going all the way to VB(1764) further shows also small changes. The so determined VB values of R_{CC} and k_{CC} at all the VB levels, are in rather close agreement with

Table 2. Equilibrium distances (R_{CC}), and force constants (k_{CC}) for the quadruply-bonded VB structures of C_2 and the full VB wave function, compared with experimental data and data for acetylene.

VB Structures	R_{CC} [Å]	k_{CC} [Ncm ⁻¹]	Method
1 $\Phi_{A,COV}$ ^[a]	1.238	11.84	VBSCF/6-31G*
2 $\Phi_A(4-bonds)$ ^[b]	1.244	13.59	VBSCF
3 $\Phi(88)$ ^[c]	1.253	13.24	VBSCF
4 $\Phi(1764)$	1.260	12.56	VBSCF
5 configuration interaction	1.260	12.27	MRCI/6-31G* ^[d]
6 coupled cluster	1.258	12.43	CCSD(T)/6-31G* ^[d]
7 experimental (C_2)	1.243 ^[e]	12.16 ^[e]	
8 experimental (C_2H_2)	1.204 ^[f]	15.84 ^[f]	

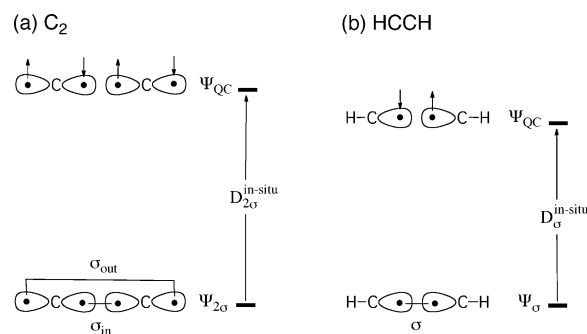
[a] The covalent quadruply-bonded structure (Scheme 3a). [b] The 21-structure set that describe the quadruple bond (see Scheme S1 in the Supporting Information). [c] 88 VB structures. [d] From reference [7]. [e] Experimental values from reference [33]. [f] Reference [34].

experimental data in entry 7. It is apparent that the quadruple-bonded structure by itself reproduces values in agreement with the experimental data, much as was found above for the BDE values. Thus, once again we conclude that the quadruple-bonded structure of C_2 reproduces its key observables, and for all intents and purposes, it is a good representation of the molecule.

Why is the quadruple bond in C_2 longer than the triple bond in $HC\equiv CH$?

It is instructive to note, from Table 2, that the force constant of the pure quadruply-bonded structure (entries 1 and 2) in C_2 is smaller than the force constant of the triple bond in $HC\equiv CH$. This in turn means that the force constant by itself does not gauge the bond multiplicity, at least not for these two molecules. Moreover, the optimum bond length of the quadruple bond in C_2 (1.244 Å in entry 2) is longer than the triple bond in $HC\equiv CH$ (entry 8), which at least for these two molecules means that the multiplicity of the bonds does not determine the corresponding bond lengths.

In the sense that the equilibrium bond length in a molecule is affected by the bond interaction energies between the bonded atoms, the primary question we should try to answer is: why is the equilibrium distance for the quadruply-bonded C_2 molecule longer than the triple bond in acetylene? VB theory enables one to calculate the singlet-coupling interaction energies (called in-situ bond energies, $D^{in-situ}$) by decoupling the electron pairs to a quasiclassical state (QCS), in which the bonding electrons are not spin paired, and quantifying the energy it takes to decouple the electron pair.^[6,7,27,35] This enables us to determine the $D^{in-situ}$ values for individual bonds or for a group of bonds and compare thereby the respective bonding-interaction energies for different molecules. Scheme 4 shows the comparison of the $D^{in-situ}$ determination for the σ bonds in C_2 and acetylene. Thus, in C_2 we decouple the inner and outer bonds, σ_{in} and σ_{out} , to the respective QCS with four unpaired electrons (and two π bonds), and determine the corresponding $D_{2\sigma}^{in-situ}$ value, and similarly, we decouple the electrons of the single σ bond in acetylene (leaving it with two π



Scheme 4. Determining in-situ singlet-coupling interaction energies for the σ bonds in a) C_2 ($D_{2\sigma}^{in-situ}$) and b) acetylene ($D_{\sigma}^{in-situ}$), relative to the reference quasi-classical state (QCS). The electron dots that are not connected by lines are not singlet coupled. In a), only one of the two possible QC determinants is represented. The QCS is the average of the two (see Supporting Information).

bonds), and determine the respective $D_{\sigma}^{in-situ}$ value. We can do the same for the π bonds of the two molecules, and have in this manner also the corresponding $D_{2\pi}^{in-situ}$ values for the two molecules.

Furthermore, we can determine these in-situ singlet-coupling interaction energies at different R_{CC} values and find the optimal intrinsic energy of the σ and π bonds. Table 3 compares acetylene and C_2 represented by the quadruply-bonded structure, Φ_A . The table lists the corresponding R_{CC} values for the σ and π components, along with the molecular R_{CC} and force constants (k_{CC}) values.

Table 3. Molecular bond lengths (R_{CC}), and force constants (k_{CC}) for acetylene and C_2 , shown along the optimum bond lengths ($R_{CC,\pi}$ and $R_{CC,\sigma}$) for the π and σ components and the $D^{in-situ}$ values for the σ components.

	$HC\equiv CH$ ^[a]	C_2 [$\Phi_A(4-bonds)$]
R_{CC} [Å]	1.217	1.244
k_{CC} [Ncm ⁻¹]	15.67 (16.39 ^[b])	13.59
$R_{CC,\pi}$ [Å] ^[b]	< 1.1	< 1.1
$R_{CC,\sigma}$ [Å] ^[b]	1.30	1.40 ^[c]
$D_{\sigma}^{in-situ}$ [kcal mol ⁻¹] ^[d]	138.7	156.6

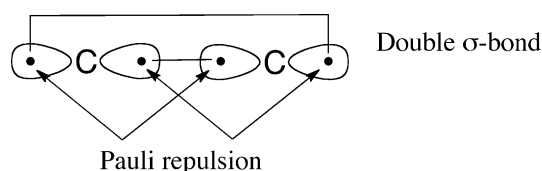
[a] The geometry of $HC\equiv CH$ was optimized using CCSD(T)/6-31G*, and k_{CC} was determined from harmonic approximation as a second derivative of energy ($k_{CC} = d^2E/d^2R_{CC}$). The value in parentheses is the relaxed force constant determined in reference [6]. [b] These R_{CC} values were calculated at 0.1 Å steps (Supporting Information Figure S5 and Tables S8 and S9). [c] $R_{CC,\sigma}$ [Å] for inner σ bond is 1.26 Å. [d] These $D_{\sigma}^{in-situ}$ values correspond to the respective σ bond minima (1.30 vs. 1.40 Å). The difference remains ca. 16 kcal mol⁻¹ in favor of C_2 , at the global respective minima of the two molecules.

The table reveals a few trends: Firstly, the π components simply prefer the shortest possible bond, while the σ components prefer longer bond lengths. As shown by Jemmis et al., this is a normal tendency for the two bond types.^[36] At the same time, the σ component of C_2 prefers a longer distance than the single σ bond in acetylene (1.40 vs. 1.30 Å, respectively). This σ bond preference to be longer in C_2 increases the σ interaction energy and is the root cause why the molecular R_{CC} of C_2 is slightly longer than in acetylene. It is thus very clear

that the molecular bond length and the force constant are determined by opposing tendencies of the bond components, namely, the relationship for multiple bonds reflects opposing tendencies of the two bond types. Thus, one cannot use simple arguments to predict the bond multiplicity from either R_{CC} or k_{CC} .

The preference of the double σ bond in C_2

A double σ bond is quite unique in chemistry, because unlike a double π bond (Scheme 1, structure 1), in which the two bond components occupy different planes, in the double σ bond the components have to cohabit in the same space. This brings about Pauli repulsion between the bonds, as shown schematically in Scheme 5. Reduction of the Pauli repulsion requires some bond lengthening for C_2 by comparison to acetylene. As such, the double σ bond is intrinsically longer than a single σ bond. But is it necessarily weaker? As shown in the last entry of Table 3, this is not the case.



Scheme 5. Pauli repulsion in the double σ bond in C_2 .

This opposition of the π bonding and the double σ bonding in C_2 leads ultimately to a bond length slightly longer and a force constant smaller as compared to acetylene (Table 3). Still, the existence of the double σ bond and its singlet-coupling interaction energy in C_2 are apparent from all the foregoing results (Table 3). Looking back at the last entry of Table 3 one sees that $D_{2\sigma}^{\text{in-situ}} > D_{\sigma}^{\text{in-situ}}$, namely, the double σ bond in C_2 displays a stronger interaction due to singlet coupling than the single σ bond in acetylene, when each σ system is in its own intrinsic optimal geometry. The difference of 17.9 kcal mol⁻¹ is right at the ballpark value of the inverted fourth σ bond, as determined by at least three different methods.^[7] Thus, we are led with a picture of one strong inner σ bond that cohabits with a weak outer one. As we already said, the strength of the fourth bond was determined in different ways, in which we took care and pain to show^[7,20d] that the factors mentioned in past and present criticisms (e.g., different bond lengths of the CC moieties, rehybridization, hyperconjugation, etc.),^[20b,37] do not contribute to this interaction energy. It is surprising to see these factors being reiterated in the present criticism,^[21a,b] which ignores our past response.^[37]

Comments about the force constants in C_2

Our findings, that the force constant $k_{CC}(A)$ of the quadruply-bonded structure of C_2 is lower than that for acetylene, question some of the tenets associated with the Badger rule. Thus, in 1934, Badger found a relationship linking the internuclear

equilibrium distance of a bond (R_e) to its force constant (k).^[38] Badger derived this relationship empirically and introduced it as a useful tool for estimating bond lengths from spectroscopy. Following Badger's work, the accuracy of the rule was shown to be somewhat limited, and improvements were sought by introducing different functional dependencies of R_e and k , and addition of other properties like electronegativity.^[39] In the course of time, chemists have also extended the original relationship to include additional properties of the chemical bond,^[34b,39a] and used the force constant as an index of "bond strength",^[20a,b,21a,b] and of bond multiplicity.^[34b] As such, on the basis of this extension of the original Badger rule, the rather low force constant of the CC bond in C_2 was used as reason to dismiss the quadruple-bond character.^[20b] Indeed, to an adherent of the generalized Badger rule, it may appear as paradoxical that C_2 , which is strongly bonded by reference to the carbon atoms taken in their ⁵S states, displays a force constant in-between those of ethylene and acetylene. However, it is a fact that the force constant of structure A alone, which by any means cannot be denied to have a quadruply-bonded wave function, is close to that of the full ground state of C_2 and is lower than that of the triple bond in acetylene, however paradoxical this may seem. Thus, the case of C_2 suggests that the force constant is not necessarily and certainly not always, an indicator of bond multiplicity.

It is important to recognize that the generalized Badger Rule has quite a few exceptions,^[20e,40] in which longer bonds are stronger, whereas shorter, and hence presumably stronger, bonds have smaller force constants. Some of these "problematic" bonds are for example, Li_2^+ ,^[20e] N–F, O–F,^[40c,d] C–C,^[40a,b,e] Si–Si,^[40a,b] Ge–Ge,^[40a,b] and Sn–Sn^[40a,g] bonds. Many of these cases have perfectly good explanations.^[40a,b,f,g] Other cases (e.g., N–F, O–F, S–F) involve charge shift bonds, which exhibit unusual features of electron density in the bond region.^[41] Given that the π bonds (and the inverted σ bond) of C_2 have significant charge-shift character, higher than in acetylene,^[7,27] simply points out that the deduction of bond multiplicity for C_2 with its unique double σ bond and π bonds, from a Badger plot for well-behaved molecules like ethane, ethylene, acetylene, and so forth rests on a belief that all these bonds are similar in nature. They are not.

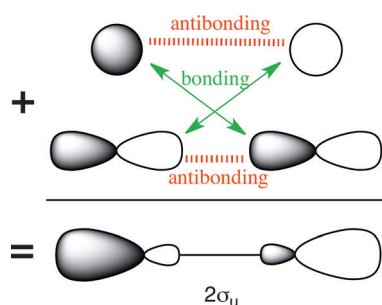
In summary, the Badger relationship does not count the number of electron-pair bonds in the molecule. Firstly, such a claim is unsupported by any fundamental argument. Secondly, as demonstrated in Table 3 the quadruply-bonded VB structure of C_2 , by itself, has a longer R_{CC} and smaller k_{CC} compared with acetylene, while at the same time providing a BDE close to the FCI value (entries 5 vs. 2, Table 1). It follows therefore that the low force constant does not prove that C_2 is not quadruply-bonded. On the contrary, the low force constant of the quadruply-bonded structure A proves that the force constant is not necessarily and indicator of bond multiplicity.

Do effective bond orders (EBOs) measure bond multiplicity?

As we argued at the outset of the paper, the EBO for C_2 falls within the range of 2.2–2.6 when one uses a correlated wave

function like full-valence CASSCF.^[21] If one adheres to the notion that EBO measures bond multiplicity, then C_2 seems to possess slightly more than a double bond between the two carbon atoms. Indeed, the EBO and similar indices^[21,42] seem to predict well the trends in the force constants and to place C_2 in between ethylene and acetylene—but do EBOs actually measure bond multiplicity? This is the question.

The EBO of a molecule is calculated from the expression $EBO = (\sum n_{\text{bonding}} - \sum n_{\text{antibonding}})/2$, which subtracts the occupation numbers (n) of the antibonding orbitals from those of the bonding orbitals, and summing the differences over all the orbitals in a CASSCF wave function. The major problem with the EBO expression is that it ceases to be meaningful when the bonding/antibonding nature of the considered orbitals is not clear.^[18] Thus, the least one can say on the problem at hand is that the $2\sigma_u$ MO of C_2 ^[15] is very far from being clearly antibonding. A schematic drawing of the components of the orbital in Scheme 6 highlights this fuzziness. Thus, $2\sigma_u$ involves $2s-2s$ and $2p_z-2p_z$ antibonding interactions, and two $2s-2p_z$ bonding interactions.



Scheme 6. A schematic drawing of the overlapping components of the $2\sigma_u$ MO of C_2 . Note that there are two antibonding interactions and two bonding interactions.

Actually, the bonding/antibonding characters of the canonical MOs arising from CASSCF(8,8) calculations are best appreciated by calculating the overlap populations (OPs) for the $2\sigma_u$ MO vis-à-vis $2\sigma_g$, as shown in Table 4 for several polarized basis sets ranging from double-zeta to sextuple-zeta. It is apparent that the $2\sigma_g$ MO displays a significant positive OP converging to about 0.42, thus clearly qualifying as a bonding orbital. On the other hand, the OP of the $2\sigma_u$ MO, while being somewhat basis-set-dependent, is found to be only weakly antibonding, if not non-bonding, with an overlap population oscillating between a small negative value of about -0.14 and values close to zero! This clearly non-bonding-like nature^[15] is not taken into account in the EBO calculation, which treats

these two MOs on equal footing; one being totally bonding and the other totally antibonding. As such, since the $2\sigma_u$ MO has a large occupation number and at the same time it is formally considered as antibonding, this orbital will contribute to a greatly diminished EBO estimate for C_2 . In such an event, the calculated EBO has not much to do with the bond multiplicity. In the case at hand, since we already know that the force constant of the quadruply-bonded structure of C_2 is in-between those of ethylene and acetylene, EBO teaches us nothing new and certainly not about the bonding nature of C_2 . Using the EBO values^[21] to dismiss quadrupling bonding in C_2 is not a sound argument.

The disparity of EBO and bond multiplicity in C_2 is highlighted by the recent treatment by Zhang et al.^[43] To begin with, this study showed that it is possible to bridge the complex full-valence CASSCF wave function and the quadruply-bonded structure, using an orbital transformation, which conserves the energy of a full-valence CASSCF wave function. We reproduced this transformed wave function in Figure 4 side by side with

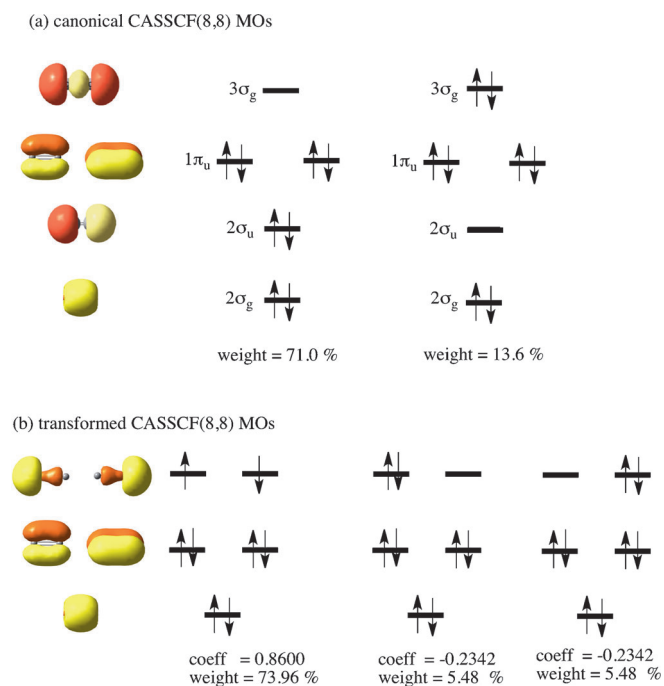


Figure 4. Orbitals, leading configurations of C_2 , and their respective weights, in: a) a standard full-valence CASSCF/6-31G* wave function, and b) the equivalent full-valence CASSCF wave function after unitary transformations of the upper two orbitals. Note the resemblance of this transformed CASSCF wave function to **2** in Scheme 1. The figure was produced based on reference [43]. The authors are thankful to M. Zhang for permission to produce this figure.

Table 4. Overlap populations of the $2\sigma_g$ and $2\sigma_u$ MOs arising from a CASSCF(8,8) calculations in various basis sets. A positive, negative or very small value qualifies the MO as bonding, antibonding or non-bonding, respectively.

	6-31G*	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	cc-pV6Z
$2\sigma_u$	-0.009244	-0.107460	-0.076436	-0.144459	-0.024913	0.0138537
$2\sigma_g$	0.4096890	0.4153799	0.4145983	0.421948	0.428672	0.4260038

the canonical symmetry-adapted canonical CASSCF MOs. As noted above, the interpretation of the canonical wave function in Figure 4a is unclear, owing to the ambiguous nature of the $2\sigma_u$ MO whose antibonding character is weak if at all existing. On the other hand, the transformed wave function in Figure 4b displays a much clearer bonding picture; in this picture there exists an internal triple bond, $C\equiv C$, with two π bonds and one σ bond, and two outer hybrids ($\Phi_{L,R}$), which are singlet coupled. Furthermore, the singlet coupling is not negligible, since the wave function has non-negligible weights of two ionic structures, C^+C^- and C^-C^+ , which augment the coupling, whereas a mere singlet diradical (like, e.g., singlet twisted ethylene) would have no ionic component at all.^[44] This quadruply-bonded CASSCF-structure comprises 85% of the total wave function, which strongly supports the qualitative VB cartoon 2, in Scheme 1. Interestingly, the canonical CASSCF wave function used by Zhang et al. leads to an EBO value of 2.15,^[43] while its transformed form in Figure 4b would suggest a bond order of 3 or higher. This disparity between the description in Figure 4b and the EBO of the same wave function in Figure 4a hints that while the EBO may be able to gauge some aspect of C_2 bonding; it certainly does not count its number of bonds.

While Zhang et al. use the term singlet diradical^[43,45] to describe the inverted bond, they were careful to note that the transformed CASSCF wave function provides no quantitative indication on the strength of this bond. This aside, the study of Zhang et al. rules out the doubly-bonded picture that has been suggested by others,^[20b,21,22] and at the same time the study shows that there is basically no opposition between the VB result of the prevalence of the fourfold bonded structure 2,

and the CASSCF wave function, provided the latter wave function is transformed so as to give maximum insight.

Does C_2 possess a double π bond with residual dative σ bonding or a quadruple bond?

The statement of quadruple bonding in C_2 was criticized by comparing C_2 to the Be_2 species, which has the same number of σ electron in the valence 2s and 2p orbitals,^[21a] on the basis of a “density averaged Fermi holes” analysis.^[22] It is known that Be_2 is very weakly bonded, at most by a few kcal mol^{-1} (and VB calculations reproduce that!). This weak bonding is attributed to the mutual cancellation of the bonding and antibonding $2\sigma_g$ and $2\sigma_u$ MOs.^[21a] However, the analogy to C_2 is not necessarily a good one, as the fuzzy $2\sigma_u$ MO of C_2 is far from cancelling the bonding $2\sigma_g$ MO. This was noted recently^[15] and demonstrated in the previous section (Scheme 6 and Table 4). In spite of this, the alleged C_2/Be_2 analogy has served as an inspiration for modeling C_2 as a molecule being bound by two strong π bonds, while the four σ electrons occupy “quasi lone pairs”.^[22] Another proposal, very close to the latter one, described C_2 as two interacting 3P carbon atoms, with doubly occupied 2s AOs mutually engaging in two $2s \rightarrow 2p(\sigma)$ very weak dative interactions (5 in Scheme 2).^[20b,21a] Rather than dwelling on an indirect qualitative discussion about the resemblance/difference of Be_2 versus C_2 , we found it more relevant to directly examine model 5 for C_2 using ab initio VB calculations. The results are displayed in Figure 5 using cartoons for the various flavors of σ bonding, including “dative” bonds.

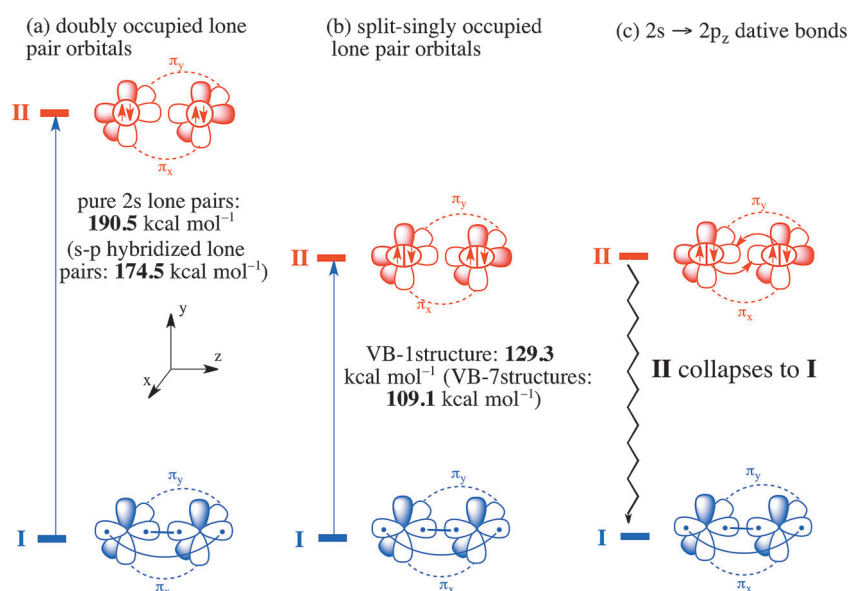


Figure 5. Testing the relative VBSCF energy of the dative doubly-bonded model, labeled as state II, proposed for C_2 vis-à-vis the quadruply-bonded structure, labeled as state I, at different variationally optimized levels: a) Level 1: State II, with a double π bond (shown in the dashed lines connecting the respective p_{xy} orbitals) and two filled 2s AOs and vacant $2p_z$ AOs resides $190.5 \text{ kcal mol}^{-1}$ higher than state I, the quadruply-bonded structure. In parentheses we show that the relative energy is $174.5 \text{ kcal mol}^{-1}$ when the 2s AOs are allowed to hybridize with the $2p_z$ AOs on the same carbon atom. b) When the doubly occupied lone pair hybrids in state II are split into two hybrid orbitals, state II resides $129.3 \text{ kcal mol}^{-1}$ above state I. In parentheses we show the relative energy of $109.1 \text{ kcal mol}^{-1}$ when both states are allowed to mix with their corresponding ionic structures. c) Using state II from (b) and allowing for the existence of two dative σ bonds by letting the orbitals on the σ lone pair of one carbon atom to delocalize into the vacant and filled σ orbitals of the other. The wiggly arrow, from state II to state I, signifies that the wave function II collapses freely to the quadruply-bonded structure I.

Figure 5 shows the energies of state II in which C₂ is doubly bonded by two π bonds, while the σ electrons are at various hybridization and bonding situations specified in a)–c), relative to state I in which C₂ is quadruply bonded. For simplicity, the two π bonds are described using doubly occupied π MOs, while the σ bonds/lone-pairs are described by VB.

The two states in Figure 5a are each described by a single VB structure. Thus, the σ bonds of the quadruply-bonded structure (state I) are purely covalent; one σ bond describes the covalent spin pairing of the two electrons in the inward σ hybrids, whereas the other couples the outward σ hybrids. Similarly, the lone pairs in π doubly-bonded structure (state II) are described by doubly occupied 2s AOs, as originally proposed.^[20b] It is seen that in these initial states, the π doubly-bonded structure resides 190.5 kcal mol⁻¹ above the quadruply-bonded one! Allowing now each lone pair of the π doubly-bonded structure to hybridize locally with the 2p_z AO of the same atom reduces slightly the gap, which remains very large, 174.5 kcal mol⁻¹. The root-causes of this very high-energy of state II are the Pauli repulsion in this state between the filled lone pairs (2s AOs or 2s–2p_z HAOs), which are replaced by two σ bonds in state I.

Next, in order to relax the lone-pair/lone-pair repulsion in the doubly-bonded structure as much as possible, we allow, in Figure 5b, the two atomic-centered lone pairs to split into singly-occupied hybrid orbitals, while keeping states I and II as covalent structures. It is seen that the π doubly-bonded structure still resides well above the quadruply-bonded structure, now by 129.3 kcal mol⁻¹. Using the same states in Figure 5b, but now allowing the variational mixing of the covalent structure with their respective ionic structures, does not change the conclusion. Even at this level, the π doubly-bonded structure (state II) remains 109.3 kcal mol⁻¹ over the quadruply-bonded state (state I). Clearly, in order for state II to become energetically, at least as low as state I, the two dative σ bond will have to be at least as strong as the σ bonds in state I.

The two dative σ bonds can be computed, in principle, by letting the σ lone pairs of the doubly-bonded structure (state II) delocalize to the other center, by having Coulson–Fisher orbitals^[25,44] as in GVB calculations. The result is shown in Figure 5c. Thus, starting from state II, and allowing its σ lone-pairs the complete freedom to delocalize to the other center, the wave function simply collapses to the quadruply-bonded structure as shown by the wiggly arrow (further details on the patterns of collapse of the doubly-bonded model to the quadruply-bonded one, see Section XI in the Supporting Information).^[46] Apparently, when the freedom is given to the σ doubly-bonded model, its dative σ bonds simply become two full σ bonds.

It follows therefore, that the π doubly-bonded structure with the σ dative bonds is in no way a good model for C₂. Clearly, the accidental match of the experimental BDE of the C₂ molecule (146.7 kcal mol⁻¹) to a model that has “two π bonds plus”^[21,22] is deceptive. On the other hand, no matter what we did in this study, we came back to the quadruply-bonded structure that confirms itself as a faithful descriptor of C₂. The reason is that in any formulation of the “two π bonds plus”

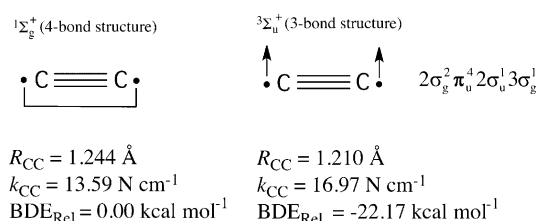
model, the severe Pauli repulsion from the largely σ lone pair orbitals on the two carbon atoms is prohibitive, due to the very short C–C distance, and the molecule prefers to replace this repulsion by two σ bonds, one strong and one weak. The outcome is fundamental and simple.

Using the quadruple bonding model to predict the properties of the ³Σ_u⁺ of C₂

Let us use the quadruply-bonded model to “predict” properties of the ³Σ_u⁺ state. These predictions are largely much easier with MO theory, but deriving them from a quadruply-bonded ground state model is instructive, in view of the debates surrounding this model. Thus, comparison of the bonding cartoons in Scheme 1 shows that relative to the quadruply-bonded structure **2**, which possesses a double–σ bond, in the ³Σ_u⁺ state **4**, we break the inverted σ bond and create a pure acetylenic bond embedded in a triplet diradical. As such, we might expect the following trends:

- 1) Since we broke a bond in the quadruply-bonded structure, we expect the resulting ³Σ_u⁺ state to lie higher in energy than the singlet state and possess as such a lower BDE.
- 2) Since the two σ bonds that cohabit in the ground state are replaced in ³Σ_u⁺ by a triplet pair and a σ bond that are mutually orthogonal (of different symmetry) and hence independent of one another, the single σ bond in ³Σ_u⁺ is free to optimize its R_{CC} value, which should come out shorter than in the ground state.
- 3) Since the R_{CC} for the ³Σ_u⁺ state is shorter than in the ground state, we expect the force constant k_{CC} to be significantly higher.

The results of the VB calculations are shown in Scheme 7. It is seen that all the above predictions are reproduced by the VB calculations (and are in accord with experiment^[8,28d]). It is further interesting to note that the calculated force constant for the triplet state is virtually identical to the relaxed force constant calculated^[6] for acetylene, while the non-relaxed value of the latter is smaller, 15.67 N cm⁻¹ (Table 3). The smaller non-relaxed value for HC≡CH arises from the fact that, unlike independence of the σ_{CC} bond of the triplet state of C₂, the σ_{CC} bond in acetylene has to cohabit with the two σ_{CH} bonds, and



Scheme 7. Equilibrium bond lengths (R_{CC} , Å), force constants (k_{CC} , N cm⁻¹), and relative bond dissociation energies (BDE_{Rel} , kcal mol⁻¹) for the quadruply-bonded structure of the ground singlet ¹Σ_g⁺ and the triply-bonded structure of the triplet ³Σ_u⁺ states (both dissociate to the ³P–³P dissociation limit with the appropriate spin). All VB data are calculated at VBSCF/6-31G* level using the corresponding VB structures from set A.

hence the C–C bond reflects this Pauli repulsion and has a lower force constant compared with the triplet state. In contrast, the relaxed force constant for HC≡CH, which is a local force constant of the C≡C bond without the effect of the C–H bonds, is virtually identical to force constant of the $^3\Sigma_u^+$ state. It is further important to emphasize that the σ bond interaction energies $D_\sigma^{\text{in-situ}}$ for $^3\Sigma_u^+$ (C_2) and HC≡CH are almost identical, 138.2 and 138.7 kcal mol $^{-1}$, respectively (See Table S12a in the Supporting Information, and Table 3 above). Both values are smaller than the corresponding value $D_{2\sigma}^{\text{in-situ}}$ (156.8 kcal mol $^{-1}$) for the σ double-bond in the ground state of C_2 . Scheme 7 and the $D^{\text{in-situ}}$ data again underscore the above conclusions that force constant does not count the number of bonds.

Conclusions

Ab initio valence-bond (VB) calculations show that the $^1\Sigma_g^+$ ground state of C_2 is accurately described by a small set of four Lewis structures, which account for more than ca. 94% of the bond dissociation energy calculated by the full VB set or the full configuration interaction in the same basis set. This set of Lewis structures involves the major quadruply-bonded structure, and three minor Σ structures; one doubly- π -bonded structure and two ethylenic ($\sigma+\pi$)-bonded ones. In fact, VB theory shows (Figure 3) that set B with the doubly- π -bonded structures makes a tiny contribution (1.4 kcal mol $^{-1}$) to the BDE of the molecules, while set C with the two ethylenic ($\sigma+\pi$)-bonded structures is more significant. Thus, the mixing of the ethylenic ($\sigma+\pi$)-bonded structures add small, but non-negligible, resonance energy that stabilizes further the σ bonding of the quadruply-bonded structure. All the more, at the equilibrium distance, the quadruply-bonded structure is the major C_2 descriptor, and it accounts by itself for more than 90% of the bond dissociation energy at the best VB computational level (Table 1). This VB description of C_2 in terms of Lewis structures is in agreement with the picture derived by Zhang et al. from the full-valence CASSCF wave function.^[43]

Alternative proposals of a two- π -bond model, with or without additional weak dative σ bonds,^[20b, 21a,b; 22] based on indirect interpretations like EBO estimations, resemblance of C_2 to Be $_2$ and so on, are not supported by computations, as the proposed structures are shown to be either high-lying in energy or unstable and collapsing to the quadruply-bonded one. At the equilibrium R_{CC} distance and up to 1.85 Å, the doubly-bonded structures are destabilized by the severe Pauli repulsion of the largely σ lone pair electrons, which in the quadruple bond structure are replaced by σ bonds. As such, the doubly-bonded structures are too high in energy to matter much for the molecule.

Plotting the energy of the ground state against the interatomic C–C distance reveals a bonding-crossover pattern from a quadruple bond at equilibrium, to a double bond, from R_{CC} = 1.85 Å on (where the Pauli repulsion as well as bonds become weak). Beyond 2.5 Å, the ground state wave function converges to a collection of unbound structures, which describe the two carbon atoms at their 3P group states at the dissociation limit (see D structures in Scheme 3 and further details in the

Supporting Information). On the other hand, by itself, the quadruply-bonded covalent structure (Scheme 3a) dissociates to a state in which each carbon atom has four singly occupied AOs (at 10 Å, the quadruply-bonded structure involves two carbons in their s^1p^3 promoted states), thus more akin to the 5S state rather than to the 3P state.^[28a] This is in accord with the result that the $D^{\text{in-situ}}$ bond-interaction energy in C_2 is stronger than that of acetylene.

In summary, in whichever way we looked at C_2 , we found that it has a quadruple bond, which possesses the following features:

- 1) The quadruply-bonded structure is composed of two strong π bonds and a double σ bond. In order to cohabit, the σ bonds prefer a longer C–C distance that lowers the Pauli repulsion. As such, the equilibrium R_{CC} value of C_2 lengthens a bit and the force constant is lowered (vis-à-vis acetylene).
- 2) The double σ bond comprises of a strong inner σ bond,^[7,43] and a weak outer σ bond. The latter has a sizeable bond interaction energy of 17–21 kcal mol $^{-1}$.^[7] An immediate outcome of having a weak fourth bond is the highly reactive nature of the molecule, for example, towards radical attack, which can be predicted from VB principles.^[47]
- 3) Our findings account also for the features of the $^3\Sigma_u^+$ triplet state of C_2 . This state is a perfect acetylenic diradical with a triple CC bond, $\uparrow\cdot C\equiv C\cdot\uparrow$. If we now flip the spin of the diradical to a singlet, the energy goes down by over 20 kcal mol $^{-1}$. This is a proof that the ground state of C_2 is more strongly bonded than a triple bond. This is reflected also by the $D^{\text{in-situ}}$ values of the corresponding σ bonds, which show that the single σ bond in the triplet state is 18.4 kcal mol $^{-1}$ weaker than the double σ bond in the ground state; a value well within the range of the fourth bond's strength of 17–21 kcal mol $^{-1}$, determined in a variety of ways.^[7]
- 4) The fact that the quadruple-bond-structure of C_2 has, by itself, a lower force constant and a longer bond length than acetylene, indicates that at least for these two molecules, these two observables do not count the relative bond multiplicities.
- 5) The double σ bond and the charge shift bonding character of the π bonds of C_2 (and of the inverted σ bond^[7]) are challenging, and holding the key to understanding the apparent paradox, that a quadruple bond shows signs of “weakness” like a “double-bond plus”.

We may therefore conclude that carbon and other first-row elements can break the glass ceiling of triple bonding and form quadruple bonds with double π and σ bonds. The number of possibilities to explore the presence of this unusual bonding is not too small.

Computational Methods

Valence bond calculations: The VB calculations were generally done for C_2 at the VBSCF/6-31G* level^[6,7] using the XMVB package.^[48] In some cases, we used also VBCISD.^[49] This method per-

forms singles and doubles CI for the local AOs and HAOs, and endows the VB wave function by dynamic correlation. In the calculations described in Figure 5c, we used semi-localized Coulson Fischer orbitals to allow variation for the dative bonds.^[50] The VBSCF-QMC calculations (QMC=Quantum Monte Carlo) were done as described recently,^[32] using a quadruple-zeta basis set, with core pseudo potential, and especially designed for QMC calculations.^[51]

Valence bond structures: The full valence shell of C₂ involves 1764 (according to the Weyl formula^[52]) structures, which are produced automatically by XMVB. As in the past,^[27] here too we devised systematically a truncated set of VB structures that reproduces closely the BDE in agreement with FCI and VBSCF(1764). This new truncated set involves 88 structures, which are given in the Supporting Information (see Scheme S1), and represent the set of covalent and lowest energy mono-ionic and di-ionics (84 structures) for groups A, B, and C, to which we add four structures generated from $\Phi_{D13, cov}$ (see Scheme 1, Supporting Information) and all with the electronic configurations necessary to describe two carbon atoms in their ³P ground states at the dissociation limit. Adding these structures generates a VB(88) structure, which at the dissociation limit differs by 0.004 kcal mol⁻¹ relative to VB(1764).

Force constants: Force constants (k_{CC} in Ncm⁻¹) based on MRCI and CCSD(T) for both C₂ and as well for HC≡CH, were calculated using frequencies (in cm⁻¹) in MOLPRO.^[53] The force constants based on VB calculations, were obtained from the fit of the VB energies to the harmonic approximation as a second derivative of energy $k_{CC} = d^2E/d^2x$ (see Supporting Information).

Keywords: bond dissociation energy · bond order · bonding · C₂ · force constants · quadruple bonds · valence bonds

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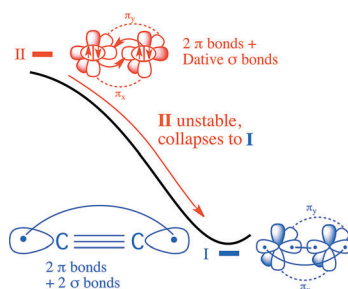
FULL PAPER

Bonding Analysis

S. Shaik,* D. Danovich, B. Braidā,
P. C. Hiberty*

■ ■ - ■ ■

 The Quadruple Bonding in C_2
Reproduces the Properties of the
Molecule



The case for four! There is only a quadruply-bonded C_2 , while all σ doubly-bonded models, without or with dative σ bonds, collapse to the quadruple bond!