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► To cite this version:

Gernot Frenking, Markus Hermann. Comment on “The Quadruple Bonding in C₂ Reproduces the Properties of the Molecule”. Chemistry - A European Journal, 2016, 22 (52), pp.18975–18976. 10.1002/chem.201601382 . hal-01627877

HAL Id: hal-01627877

<https://hal.science/hal-01627877>

Submitted on 10 Nov 2017

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Comment on “The Quadruple Bonding in C₂ Reproduces the Properties of the Molecule”

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Keywords: C₂, Bonding analysis, Multiple bonding, Bond strength, Electronic state, σ bonding

The title publication by Shaik et al.^[1] on the chemical bonding in C₂ is an important contribution to understand the origin of the conflicting views about the strength of the interatomic interactions in dicarbon which are presented in their paper and in the publications of other groups using a variety of methods.^[2,3] The original claim of a quadruple bond in C₂ possessing two σ bonds which are stronger than the single σ bond in acetylene^[4] is now substantiated with a calculated intrinsic (“in-situ”) bond strength of 156.6 kcal/mol for the total σ bonding in dicarbon and 138.7 kcal/mol for the σ bond in HC $\equiv$ CH. The results come from valence bond (VB) calculations, which give bond dissociation energies and bond lengths that are in good agreement with experimental data and with the results of the other methods. We want to point out that the core of the controversy is not the number of bonds but the strength of the total σ bonding in C₂, which is suggested by several groups to be much weaker than in acetylene.^[2]

We studied the paper in order to understand how the value of 156.6 kcal/mol for the σ bonding in C₂ was calculated. There are contradicting statements and missing information which make the numerical result and the conclusion questionable. The authors determine their value for the in-situ bond strength for the σ binding by comparing the spin-coupled structure $\Psi_{2\sigma}$ which has two σ bonds with a quasiclassical state Ψ_{QC} where the two σ bonds (σ_{in} and σ_{out}) are decoupled. They calculate the in-situ strength of the σ bonding $D_{2\sigma}^{in-situ}$ from the energy difference between $\Psi_{2\sigma}$ and Ψ_{QC} . This is shown in Figure 1 which is adopted from

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Scheme 4 of Shaik et al.^[1] The left part 1a shows the quasiclassical state $\Psi_{\text{QC}(1)}$ that is depicted as Ψ_{QC} in their scheme 4. The two electrons at each carbon have opposite spin which means that the carbon atoms have a ^3P state, because the $p(\pi)$ electrons that are not shown have identical spin. This contradicts the statement of the authors: “*If, however, the molecule is indeed quadruple bonded, then each carbon atom must have four singly occupied orbitals in the molecule. In such a case, the legitimate reference state is ^5S .*”^[5] It is puzzling that the authors refer to the ^5S of carbon as reference in the text, but then they sketch the ^3P state for the quasiclassical reference state Ψ_{QC} .

Figure 1

Decoupling the two σ bonds in C_2 actually leads to *two* quasiclassical states, the second of which $\Psi_{\text{QC}(2)}$ is shown on the right hand side in Figure 1a. The latter state $\Psi_{\text{QC}(2)}$ has two carbon atoms in the ^5S state. The two reference states $\Psi_{\text{QC}(1)}$ and $\Psi_{\text{QC}(2)}$ are very different in energy, because the ^5S state of carbon atom is 96.4 kcal/mol above the ^3P ground state.^[6] Thus, the energy difference between $\Psi_{\text{QC}(1)}$ and $\Psi_{\text{QC}(2)}$ is 192.8 kcal/mol. Estimating the in-situ σ bond strength in C_2 strongly depends on the choice of the quasiclassical reference state. The authors mention the existence of a second quasiclassical reference state in the caption of Scheme 4 saying that they took “*the average of the two*” with further reference to the Supporting Information. On page S23 of the Supporting Information^[1] one finds a sketch of the two determinants Det1 and Det2 that describe the coupling between two carbon atoms in the ^3P state (Det1) and the ^5S state (Det2), which agrees with our descriptions of $\Psi_{\text{QC}(1)}$ and $\Psi_{\text{QC}(2)}$ in Figure 1. It is important to recognize that both reference states $\Psi_{\text{QC}(1)}$ and $\Psi_{\text{QC}(2)}$ are associated with four bonding components in C_2 , albeit with drastically different σ bond strengths.

The crucial question concerns the two determinants Det1 and Det2 and their use to determine the numerical value of 156.6 kcal/mol for the in-situ σ bond strength $D_{2\sigma}^{\text{in-situ}}$ in C_2 . The authors are saying in the Supporting Information that “*their averaged energies were used as the reference state*”. This is in conflict with their own statement that the ^5S state should be used as reference. There is equal spin distribution between the carbon atoms in C_2 , but that does not mean that $\Psi_{\text{QC}(1)}$ (Det1) and $\Psi_{\text{QC}(2)}$ (Det2) are equally valid reference states, because they differ in energy by 192.8 kcal/mol. The calculated dissociation of C_2 in the $X^1\Sigma_g^+$ ground

state exhibits a smooth curve toward carbon atoms in the ^3P ground state^[7]. The analysis of the full-valence CASSCF calculation of C_2 shows that the contribution of the configuration which has a genuine (electron-sharing) quadruple bond between carbon atoms in the ^5S state to the total wave function is only 13.7%.^[2b] The weight of the configuration which comes from the interaction between carbon atoms in the ^3P state is 71.0%. This makes us wonder about the choice of averaged energies of $\Psi_{\text{QC}(1)}$ (Det1) and $\Psi_{\text{QC}(2)}$ (Det2) for estimating the strength of the σ bonds in the VB calculations of Shaik et al.^[1]

It would be helpful to know the individual values of $D_{2\sigma}^{\text{in-situ}}(1)$ and $D_{2\sigma}^{\text{in-situ}}(2)$ with respect to $\Psi_{\text{QC}(1)}$ (Det1) and $\Psi_{\text{QC}(2)}$ (Det2) as reference states. The authors should also inform the general community of chemists, who are less familiar with VB calculations than with MO methods, about the reason why averaged values of the two reference states, which are vastly different in energy, were used. They should also elucidate why carbon atoms with a ^3P state are shown for the quasiclassical reference state in Scheme 4, when the ^5S state was earlier proposed as reference. There is no 1:1 connection between VB and MO terms but the interpretation of the numerical data that are provided by the two methods, which give both correct values for bond dissociation energies and bond lengths, must not lead to fundamentally opposite conclusions concerning the nature of the bonding. Breaking rules is fun, but only when it comes from traceable procedures.^[8]

We also want to comment on the very small overlap population of the antibonding $2\sigma_u$ MO of C_2 that may even become positive, which is suggested by the authors as evidence that the orbital “*be only weakly antibonding, if not bonding*”.^[9] The small overlap population comes from the antisymmetry constraint of the orbitals due to the Pauli principle. The enforcement of orthogonality to the orbitals of C_2 , which removes electronic charge from the overlapping region of the $2\sigma_u$ MO, is associated with an energy change (Pauli repulsion) in the order of 250 kcal/mol.^[10] The small negative or even positive values for the overlap population are the final result but not the driving force of the electronic interactions that are subject to the Pauli principle. It is therefore misleading to use small overlap populations as indicator of weak or even absence of antibonding forces.

Acknowledgement. This work was supported by the Deutsche Forschungsgemeinschaft.

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Figure 1. Determining in-situ singlet-coupling interaction energies for the σ bonds in C_2 as described by Shaik et al. in reference 1. Part 1a shows the 3P state of carbon as reference state $\Psi_{QC(1)}$ as adapted from their Scheme 4. Part 1b shows the 5S state of carbon as reference state $\Psi_{QC(2)}$ which is depicted in their Supporting Information. The energies of $\Psi_{QC(1)}$ and $\Psi_{QC(2)}$ differ by 192.8 kcal/mol.