

## Is There a Quadruple Bond in C<sub>2</sub>?

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### INTRODUCTION

The chemical structure of the C<sub>2</sub> molecule in its ground state (<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) has been the subject of intense debate in the literature<sup>1</sup> after the suggestion that the molecule could exhibit a fourth covalent bond, between the singlet-coupled orbitals  $\varphi_1$  and  $\varphi_2$  shown in the perfect-pairing diagram (Figure 1). However, the fact of the stretching mode frequency for the supposed quadruple bond in C<sub>2</sub> (1855 cm<sup>-1</sup>) is smaller than the respective one for the triple bond in C<sub>2</sub>H<sub>2</sub> (1974 cm<sup>-1</sup>) gave rise to more debate. In this work we investigate this problem explicitly avoiding all the points of conflict from the previous papers to show that there is no quadruple bond in the C<sub>2</sub> molecule.

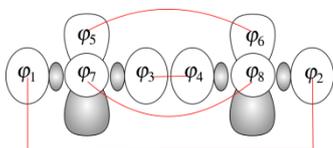


Figure 1. GVB-PP diagram of C<sub>2</sub> ground state.

### METHODS

The Generalized Product Function Energy Partitioning (GPF-EP) method<sup>2</sup> was used in order to decompose the total electronic energy in quasi-classical (electrostatic) and interference (covalent) terms. Previous works have established a general rule concerning the nature of chemical bond – its formation leads to the lowering of interference energy, particularly its kinetic component. Potential energy curves were constructed at *full*-GVB/cc-pVTZ level with the programs GAMESS/VB2000. The GPF-EP code for GPF-EP, has been implemented into the VB2000 source code by our research group.

### RESULTS AND DISCUSSION

For the standard  $\sigma$  and  $\pi$  bonds, interference acts like the expected for a regular covalent bond, while for the proposed “fourth bond”

interference is a destabilizing factor (Figure 2). In order to make sure that this misbehavior could not be attributed to a new kind of bond, we performed an equivalent analysis for the <sup>3</sup>Σ<sup>-</sup> excited state of the C<sub>3</sub> molecule in which a bond similar to the “fourth bond” of C<sub>2</sub> could be formed between the two carbon atoms at the ends of the linear chain (1-3 bond). The interference energy for this case shows exactly the same pattern of the equivalent one in C<sub>2</sub>.

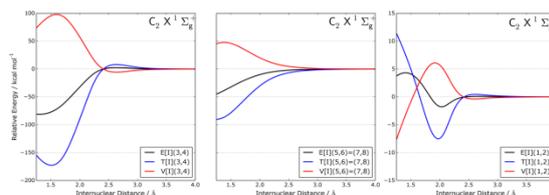


Figure 2. Interference energy and its components for the  $\sigma$  bond (a), the  $\pi$  bonds (b) and for the supposed fourth bond (c) of the C<sub>2</sub> molecule.

Analysis of the orbital overlaps along the internuclear axis shows that for C<sub>2</sub> there is an excess of charge density relative to C<sub>2</sub>H<sub>2</sub>. This explains the difference in the stretching frequencies of the C-C bonds in C<sub>2</sub> and C<sub>2</sub>H<sub>2</sub>. Although singlet coupling of the “fourth bond” in C<sub>2</sub> leads to energy stabilization, it also “weakens” the chemical bond in terms of the force constant.

### CONCLUSION

The energy partition clearly shows that in C<sub>2</sub> only three electron pairs are contributing for the chemical bond, while the fourth pair exhibits exactly the opposite behavior expected for a covalent bond. Since the results are the same for the analogous C<sub>3</sub> state, unless one is ready to accept that there is a “1-3 bond” in C<sub>3</sub> one must conclude that there is no quadruple bond in C<sub>2</sub>.

<sup>1</sup> See D. Danovich *et al*, Chem. Eur. J., 20, 6220, (2014) and references therein.

<sup>2</sup> T.M. Cardozo, M.A.C. Nascimento, J. Chem. Phys., 130, 14102, (2009).