



C₂: More complicated than it sounds

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Abstract The present work is another contribution to a better understanding of the chemical bond in C₂. A density functional approach is employed, and the obtained results (bond distance and bond dissociation energy) agrees very well with the previously [2-4] valence bond results. The obtained results also points to a bond order of four, reinforcing previously obtained data [3]. Furthermore, based on the calculated IR and Raman spectra, is proposed that C₂ exhibits, at an electronic level, an asymmetry, and that such molecule has not, in fact, a centre of inversion.

Keywords C₂, chemical bonding, bond energy

Introduction

Although not stable (isolable) species C₂ is of great practical importance, being present, for example, in the blue flame resulting from the combustion of hydrocarbons. From a theoretical point of view, C₂ is a real challenge given the intriguing and even enigmatic nature of the chemical bond in this molecule. The present work is another contribution to a better understanding of the chemical bond in C₂.

Methodology

C₂ molecule was modelled by density functional (DFT) approach (ω B97X-D/6-31+G* and ω B97X-D/6-311+G** basis sets).

Results and Discussion

As can be verified form Table 1 data, the DF- ω B97X-D/6-31+G* theoretical approach is the one that provide a bond dissociation energy (kJ mol⁻¹) calculated value of 593.40, only 3.2% below the available experimental value [1] of 613.08±0.25. The Mulliken and Löwdin bond orders are respectively, 3.42 and 3.66.

Table 1: C₂ modelled with zero unpaired electrons

	Bond distance/pm	Mulliken Bond order	Löwdin bond order	Bond dissociation energy/kJmol ⁻¹
DF- ω B97X-D/6-31+G*	125.4	3.42	3.66	593.40 (613.08±0.25)*
DF- ω B97X-D/6-311+G**	125.1	3.55	3.97	584.71

*Experimental value, Ref. 1.



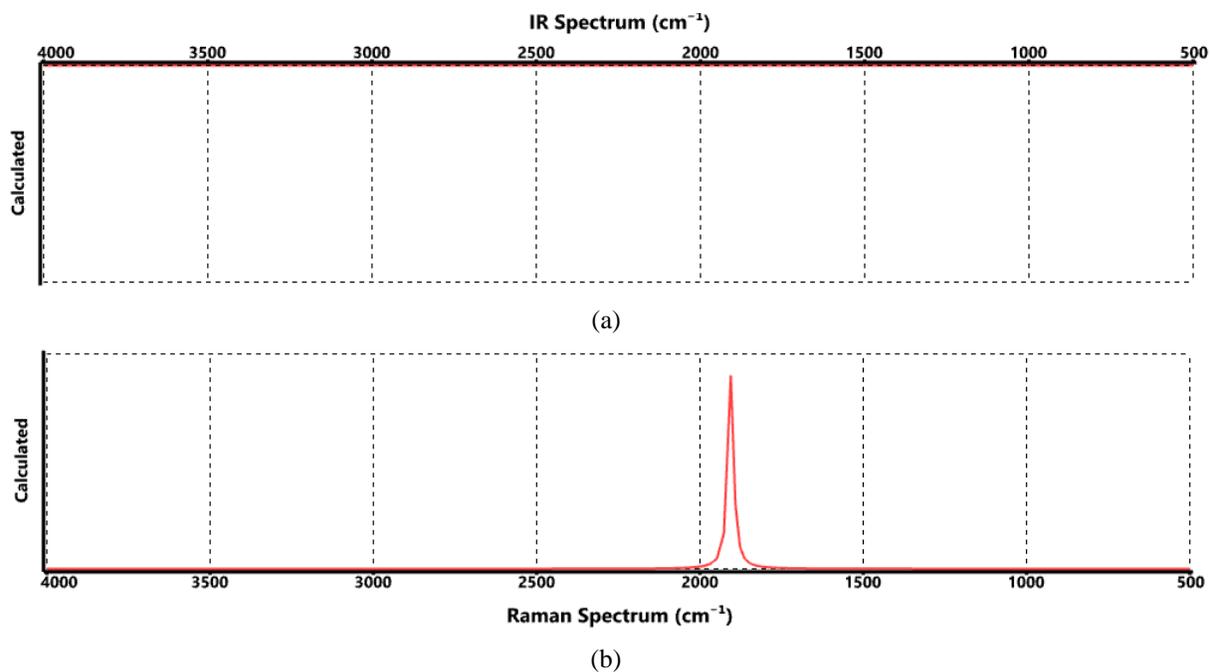


Figure 1: Calculated infrared (a) and Raman (b) spectra to C_2 (DF- $\omega\text{B97X-D/6-31+G}^*$)

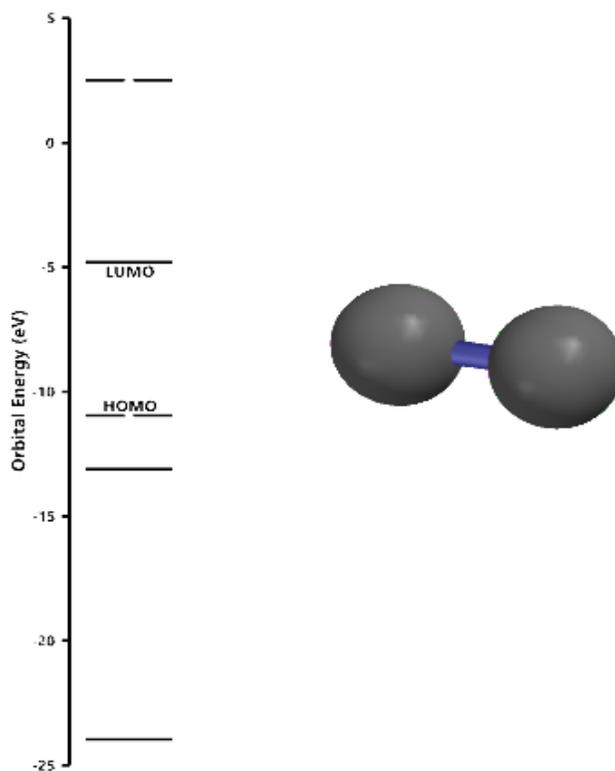


Figure 2: Calculated energies of the molecular orbitals to C_2 (DF- $\omega\text{B97X-D/6-31+G}^*$)

The obtained bond distance and bond energy are in very good agreement with the values previously obtained by Su et al [2] by the ab initio VB study for the electronic structure of the C_2 molecule in the ground state (the calculations involved 78 chemically relevant VB structures).

The obtained results are also in very good agreement with those obtained by Xu et al [3] by full generalized valence bond (GVB) calculations.

Despite the minor bond dissociation energy value ($584.71 \text{ kJmol}^{-1}$) the DF- ω B97X-D/6-311+G** approach provides Mulliken and Löwdin bond orders of 3.55 and 3.97, respectively. Such results are in very good agreement with the ones obtained by Shaik [4] showing that the properties of C_2 are reproduced when such specie is modelled as a quadruple bonding one.

By following a molecular orbital approach, the calculated MO energies (DF- ω B97X-D/6-31+G*) to C_2 are shown in Figure 2. If the first four orbitals are ligand orbitals, then, a bond order of 4 can be calculate (considering only the 2s and 2p eletrons).

Shaik [4] has concluded that “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 $17\text{--}21 \text{ kcalmol}^{-1}$ ”.

Hence, as can be verified, the DFT approach employed in the present work agrees very well with the VB approach [2,4] previously employed. However, some surprisingly results were obtained, as follows:

The calculated (DF- ω B97X-D/6-31+G*) IR and Raman spectra for C_2 are shown in Figure 1. In the Raman spectrum a very intense band at 1906 cm^{-1} is observed. In the IR spectrum no band is observed. However, checking the calculated IR bands table, a band at 1906 cm^{-1} is present. Hence, can be concluded that such band is really very little intense, and is because this that is cannot be seen in the “drawn” spectrum.

At a first looking, C_2 belongs to the $D_{\infty h}$ point group. Such point group has an inversion centre as symmetry element. However, as is well known, a molecule that has a vibrational mode active simultaneously in IR and Raman can not have an inversion centre.

Hence, in fact, C_2 has not an inversion centre, and such asymmetry between the two carbon atoms can only be explained at an electronic level, that is, from a geometrical point of view, C_2 has an inversion centre ($D_{\infty h}$ point group) but, at an electronic level, there is a asymmetric distribution of electrons. In order words, one of the carbon atoms must be “richer” in electrons than the other one.

Since in C_2 we have two carbon atoms, it is not possible to explain such asymmetric electron distribution based on the electronegativity values.

As is well known, despite the strong bond in C_2 , this molecule is very highly reactive and is not isolable. Hence, is valid to suppose that the two carbon atoms in C_2 “prefers” to make bonds with another elements (hydrogen, for example) and that the C_2 specie is formed only while a “better thermodynamic option” is not available. In a simple image, the two carbon atoms in C_2 “try hard” to remain bonded, until they cannot take part in reactions with other elements and, in such “effort” an asymmetric electronic distribution between the two atoms can provide an “extra” thermodynamic stability (by “adding some ionic character to the C-C bond). Such qualitative proposal is also in agreement with the VB modelling previously performed [2,4] in which a set of covalent and lowest energy mono-ionic and di-ionic structures were involved.

Furthermore, Xu et al have concluded that “ C_2 does not possess a set of traditional covalent σ and π bonds. Instead, the full GVB calculations show that the molecule is best, although still incompletely, described as having a traditional covalent σ bond with the electrons in the remaining orbitals on the two centers antiferromagnetically coupled”. Such conclusion reinforces, in some sense, the previous proposal of an “electronic asymmetry” in C_2 (even a slight one, not enough to be detected, by conventional means, since the asymmetry is not enough to change, in a measurable amount, the dipole moment).

Reference

- [1]. B. Ruscic, Active Thermochemical Tables: Sequential Bond Dissociation Enthalpies of Methane, Ethane, and Methanol and the Related Thermochemistry, *J. Phys. Chem. A*, (119) (28) (2015) 7810 –7837; ZPE correction from NIST data base, <http://cccbdb.nist.gov>.
- [2]. P. Su, J. Wu, J. Gu, W. Wu, S. Shaik, P.C. Hiberty, Bonding conundrums in the C_2 molecule: a valence bond study, *J. Chem. Theory Comput.*, 7(2011) 121-130.



- [3]. L.T. Xu, T.H. Dunning Jr., Insights into the perplexing nature of the bonding in C_2 from generalized valence bond calculations, *Chem. Theory Comput.*, 10 (2014) 195–201.
- [4]. S. Shaik, D. Danovich, B. Braïda, P.C. Hiberty. The quadruple bonding in C_2 reproduces the properties of the molecule, *Chemistry - A European Journal*, 22 (12) (2016) 4116–4128.