C_2: An asymmetric specie ?

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Abstract

The present work is another contribution to a better understanding of the chemical bond in C_2. Several density functional approach/basis set provided calculated IR and Raman spectra with simultaneous active bands. Hence, the hypothesis of electronic asymmetry in C_2 [1] was reinforced.

Keywords: C_2, chemical bonding, IR spectra, Raman spectra.

Introduction

Although not a stable (isolable) specie, C_2 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, C_2 is a real challenge given the intriguing and even enigmatic nature of the chemical bond in this molecule, and according to Hoffmann, it epitomizes many of the fundamental questions of chemistry [1].

After all, C_2 exhibits a double, triple or quadruple bond ? The last possibility seems, at a first looking, the less probable one, since carbon has not (as Cr, for example) suitable *d* orbitals to form a *δ* bond.

In a previous work [2], C_2 was modelled by using a density functional approach, and it was verified that the calculated bond distance and bond dissociation energies were in very good agreement with the previously [3-6] valence bond results. Furthermore, the obtained results also points to a bond order of four, reinforcing previously obtained data [5,6]. Hence, based on the calculated IR and Raman spectra, was proposed that C_2 exhibits, at an electronic level, an asymmetry, and that such molecule has not, in fact, a centre of inversion. This last hypothesis needs, of course, to be well explored.

The present work is another contribution to a better understanding of the chemical bond in C_2 and expands the previous one [2]. Its main goal is to verify if the hypothesis of an electronic asymmetry in C_2 could be proved. .

Methodology

C_2 molecule was modelled by density functional (DFT) approach. The specifically employed bases set are summarized in Table 1. For all calculations, C_2 was modelled with zero charge and zero unpaired electrons.

Results and discussion

As can be verified form Table 1 data, the DF- ωB97X-D/6-31+G* theoretical approach provides a bond dissociation energy (kJ mol^{-1}) calculated value of 593.40, only 3.2% below the available experimental value of 613.08 ± 0.25 [2]. Such fact, as well a bond order close to four, in agreement with previous calculated data, reinforced the hypothesis of a quadruple bond in C_2 [2,5,6].

As can also be verified from Table 1 data, the calculated bond distance and bond order can be very different, depending on the employed theoretical approach. Of course, this is not a surprise, as is well known that different theoretical approach can exhibits different strong and weak points: some are well succeeded to calculate bond energies but not calculate another properties, some works well for light species but not to heavy ones, etc. Of course, in such cases, experimental data are always the “touchstone”, since nature always has the last word. Furthermore, the agreement between the calculated data and another ones, obtained by other researchers employing different theoretical approach is also a possible way to validation.

However, taking into account the elusive nature of the chemical bond in C_2, how can one be sure about how is the right/reliable/trustable theoretical approach to be employed, and hence, how high is the reliability of the calculated data ?

As previously reported [2] DF- ωB97X-D/6-31+G* and DF- ωB97X-D/6-311+G** approach have provided support to a bond order of four and trustable bond energy values, with good bases on experimental and theoretical data [2-6]. However, as also previously noted [2] C_2 belongs to the $D_{\infty h}$ point group. Such point group has an inversion centre as symmetry element and, as is well known, a molecule that has a vibrational mode active simultaneously in IR and Raman cannot have an inversion centre. Nevertheless, simultaneously active IR and Raman bands were calculated for C_2 [2]. Hence, was proposed that C_2 has not an inversion centre, with the and asymmetry between the two carbon atoms been 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 an asymmetric distribution of electrons. It was supposed that such asymmetric electronic distribution could even be a slight one, not enough to change, in a measurable amount, the dipole moment. .

As can be verified by Table 1 data and Figure 1, DF- SOGGA11-X/6-31G*, DF- M06-2X/6-311-G** and DF-B97-3/6-311-G**approach provides very intense calculated IR and Raman bans, simultaneously active. Hence, the hypothesis of electronic asymmetry is reinforced (proved ?).

The calculated Mulliken and Löwdin bond orders are 2.43 and 2.84, respectively, in excellent agreement with the photoelectron spectroscopy experimental data obtained in 2019 by Laws et al [7], which concludes that "this result suggests that the dominant contribution to the dicarbon bonding involves a double-bonded configuration, with 2π bonds and no accompanying σ bond." Our present calculations, supported by such experimental data [7] of course contradicts the hypothesis of a fourth order bond.

The DF-B3PW91/6-311+G** approach provides higher bond orders, but an inconsistent bond energy of only 136 $kJmol^{-1}$.

As a preliminary finding, I can say that my previous study [2] supports a quadruple bond to C_2 and that the present one supports a double (or triple) bond ?

In order to "keep the eye in the ball", lets return to the safe territory of bond dissociation energy ($kJmol^{-1}$) values [9]: H_3C-CH_3, 377.4 ± 0.8; $H_2C=CH_2$, 728.4 ± 6.3 and CH≡CH 960.2 ± 4.2. hence, taking into account these values and the value reported in Table 1 to the chemical bond in C_2, it is necessary to conclude that the bond in C_2 is closer to a double, not triple or quadruple bond.

Another "safe territory" is the bond lengths: C-C, 153 pm; C=C 134 pm and C≡C 120 pm [10]. Once again, can be concluded that the carbon-carbon bond in C_2 is about "two and half".

Such conclusions, besides the experimental validation mentioned [7] is also support by the theoretical investigation (magnetic shielding studies) of Karadakov and Kirsopp [8] which conclude that “dicarbon has less total electron density than ethyne along and around the carbon-carbon bond”.

Hence, the only “constant” present for all calculated data is the simultaneously active IR and Raman bands (sometimes both as very strong bands, sometimes the IR band is very weak and appears only in the table of calculated bands, not in the “drawn” spectra). Hence, so far I can see, the present study reinforces the hypothesis of an asymmetry (at an electronic level) for C_2.

Based on the results obtained here, as well as literature data [1-9], some conclusion can be pointed out:

a) For C_2 both, bond distance and bond dissociation energy are compatible with a double or “2 ½” bond. Such facts are also reinforced by other experimental and theoretical data;
b) The facts pointed in (a) are not in contradiction with the bond order 3 or 4, calculated in many works: the third and fourth bonds are extremely weak if compared with the “conventional” double bond and hence, have a little effect on the bond distance and energy; Some theoretical approach (due to their physical-mathematical idiosyncrasies) can “detect” such third and fourth bond, some cannot. That’s all;
c) As shown on the present work, many theoretical approach allows to calculate for C_2 IR and Raman bands simultaneously active (in many cases, both IR and Raman band are very intense), suggesting that an electronic level C_2 is not a symmetrical specie;
d) Nevertheless, at the present point t is not possible (?) to be sure if such asymmetry is a real physical fact or if the simultaneity of the IR and Raman band are not only an error due to the physical-mathematical idiosyncrasies of the employed theoretical approach.

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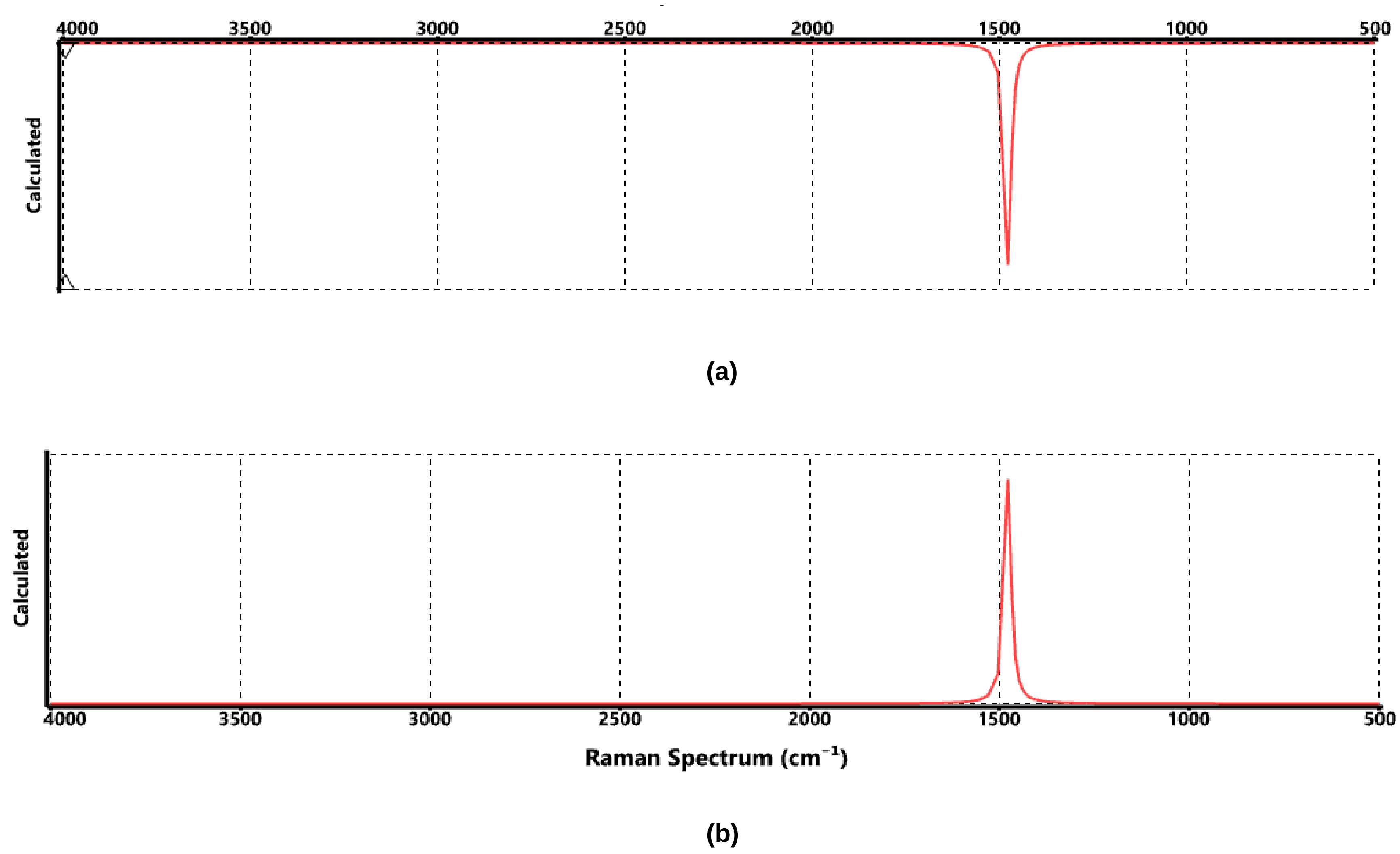
Captions of figures

Figure 1. Calculated infrared (a) and Raman (b) spectra to C_2 (DF- SOGGA11-X/6-31G*).

Table 1. Summary of the calculated parameters to C_2 (modelled with charge and zero unpaired electrons).

Theoretical approach	Bond distance /pm	Mulliken bond order	Löwdin bond order	Bond dissociation energy/kJmol^{-1}	IR bands /cm^{-1}	Raman bands /cm^{-1}
DF- ωB97X-D/6-31+G* [Ref. 2]	125.4	3.42	3.66	593.4 (613.08±0.25)$^{\#}$	1906^{vw}	1906^{vs}
DF- ωB97X-D/6-311+G** [Ref. 2]	125.1	3.55	3.97	584.7	1886^{vw}	1886 ^{vs}
DF- SOGGA11-X/6-31G*	137.9	2.43	2.84	326.2	1478^{vs}	1478^{vs}
DF-B3PW91/6-311+G**	139.0	3.09	3.57	136.0	1435^{vw}	1435^{vs}
DF- M06-2X/6-311-G**	124.9	3.53	3.96	444.8	1894^{vs}	1894^{vs}
DF-B97-3/6-311-G**	138.7	2.83	3.37	201.6	1451^{vs}	1451^{vs}

$^{\#}$Experimental value, Ref. 3; vw = very week; s = very strong.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3500
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Calculated
(a)
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4000
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Raman Spectrum (cm^{-1})
(b)

Figure 1