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Bonding Conundrums in the C_2 Molecule: A Valence Bond Study

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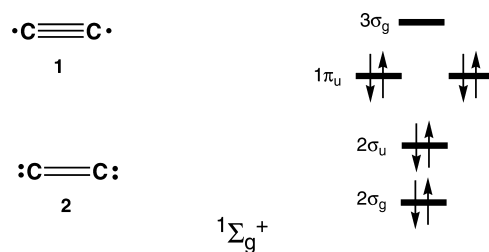Paris-Sud, 91405 Orsay Cédex, France*

Abstract: The ab initio VB study for the electronic structure of the C_2 molecule in the ground state is presented in this work. VB calculations involving 78 chemically relevant VB structures can predict the bonding energy of C_2 quite well. Sequentially, a VBCIS calculation provides spectroscopic parameters that are very close to full CI calculated values in the same basis set. Furthermore, the analysis of the bonding scheme shows that a triply bonded structure is the major one in terms of weights, and the lowest in energy at the equilibrium distance. The second structure in terms of weights is an ethylene-like structure, displaying a $\sigma + \pi$ double bond. The structure with two suspended π bonds but no σ bond contributes only marginally to the ground state. This ordering of weights for the VB structures describing the C_2 molecule is shown to be consistent with the shape of the molecular orbitals and with the multireference character of the ground state. With the triply bonded bonding scheme, the natures of the π and σ bonds are investigated, and then the corresponding "in situ" bond strengths are estimated. The contribution of the covalent-ionic resonance energy to π and σ bonding is revealed and discussed.

Introduction

The precise bonding in the C_2 molecule is quite enigmatic if not intriguing. Applying the principle of maximum coupling between overlapping atomic orbitals would lead to structure **1**, where the triple bond is made from one σ and two π bonds as in acetylene, and the two odd electrons on the carbon atoms are singlet coupled (Scheme 1). On the other hand, when a molecular orbital (MO) diagram is used,

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Scheme 1. Schematic Bonding Schemes and MO Diagram for the $X^1\Sigma_g^+$ Ground State of C_2

in Scheme 1, and the simple formula for calculating bond order is applied, one would predict that the ground state, $X^1\Sigma_g^+$, is a doubly bonded molecule, as depicted in the simple valence bond (VB) cartoon in **2**. From the MO diagram, the double bond in **2** corresponds to two suspended π bonds, whereas the two "lone pairs" on the carbon atoms

Table 1. The Lowest Seven Electronic States of C_2 Molecule[a]

term	main electronic configuration	ΔE (cm^{-1})
$X^1\Sigma_g^+$	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^4$	
$a^3\Pi_u$	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^3(\sigma_g 2p)$	716
$b^3\Sigma_g^-$	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^2(\sigma_g 2p)^2$	6434
$A^1\Pi_u$	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^3(\sigma_g 2p)$	8391
$c^3\Sigma_u^+$	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)(\sigma_g 2p)^2(\pi_g 2p)$	9227
$B^1\Delta_g$	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^2(\sigma_g 2p)^2$	~11858[b]
$B'^1\Sigma_g^+$	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^2(\sigma_g 2p)^2$	~15196[b]

[a] Experimental values taken from the literature.[17,19] [b] Estimated from Figure 1 in ref 17.

are σ lone pairs, which result from the full occupancy of the bonding and antibonding MO pair $2\sigma_g$ and $2\sigma_u$.

However, as pointed out recently,[1] the C−C bond length of 1.243 Å in $X^1\Sigma_g^{+}$ [2] is shorter than any known C≡C double bond, e.g., in ethylene.[3−5] Thus, Jemmis et al.[1] and others[6] argued that suspended π bonds are in fact shorter than σ bonds, and as a result, the π doubly bonded molecule has a shorter C−C distance than, e.g., ethylene with a $\sigma + \pi$ double bond. Nevertheless, this assessment of the bonding in C_2 rests on the supposed antibonding nature of the doubly occupied $2\sigma_u$ MO, which is assumed to compensate for the bonding nature of $2\sigma_g$ and to result in the absence of any σ bonding. However, an alternative characterization of the $2\sigma_g-2\sigma_u$ MO pair, in which the $2\sigma_u$ MO would be only weakly antibonding and would not compensate for the strongly bonding character of $2\sigma_g$, would make the C−C bonding approach a triple bond,[7,8] in support of structure **1** rather than **2**. The respective shapes of the $2\sigma_g$ and $2\sigma_u$ MOs are thus of fundamental importance for the C−C bonding assessment and will be examined below.

Another intriguing aspect of the C_2 molecule is the presence of a low-lying triplet state (Table 1), $a^3\Pi_u$, with a main configuration $|(core)2\sigma_g^2 2\sigma_u^2 1\pi_u^3 3\sigma_g^1\rangle$, lying only 2 kcal/mol above the ground state $|(core)2\sigma_g^2 2\sigma_u^2 1\pi_u^4\rangle$. Especially interesting is the fact that the bond length of this excited state, 1.313 Å, is significantly increased relative to the ground state, despite the quasi-identical bonding energy of the two states. Qualitatively, this breaking of the bond-length/bonding-energy relationship might be interpreted in two ways: (i) Assuming structure **2** for the ground state, as done by Sherrill et al.,[9−11] the $X^1\Sigma_g^+ \rightarrow a^3\Pi_u$ weakens one π bond and benefits the σ bond; in such a case, the corresponding elongation is expected according to the author's view that suspended π bonds should be shorter than $\sigma + \pi$ bonds.[9−11] (ii) If, on the other hand, the triply bonded structure **1** is assumed, the excitation cannot significantly reinforce the σ bond, which is already present in the ground state but may transform a two-electron π bond into a one-electron π bond. One-electron bonds are not necessarily weaker than two-electron bonds when the interatomic orbital overlap is weak (see, e.g., Li_2^+ vs Li_2),[12] but they are always longer, thus explaining the long C−C bond in the $a^3\Pi_u$ state.

Still, since the ground state has a longer C−C bond than acetylene, it is clear that structure **1** alone cannot account for the bonding in C_2, unless the σ bond is particularly weak, and the question is whether one should regard the molecule more as a hybrid of **1** and **2** or simply as **1** with a weak σ

bond, or perhaps having different bonding features altogether? This, as well as other questions about C_2, can be answered by modern VB calculations,[13] which are presented in this work to address a host of bonding conundrums exhibited by this diatomic molecule.

Interestingly, despite the small size of the molecule, it has proven to be a "hard nut to crack" by theoretical means, and therefore before addressing the bonding issues, it is appropriate to summarize some experimental facts and discuss some selected previous theoretical studies on C_2. The molecule is present in astrophysical environments and many chemical processes in the gas phase.[14−19] It has been observed during the photodissociation of acetylene and can be formed by the direct reaction of the $C(^3P)$ atom with CH.[16,20] Since the 1950s, many experimental and theoretical studies have been dedicated to the study of the features of C_2.[14−23] Recently, 17 electronic states of C_2 have been characterized by experimental methods. Using the orbital diagram in Scheme 1, Table 1 shows the electronic configurations and experimentally measured relative energies of the lowest seven electronic states.[17,19] As already pointed out, the ground state of the molecule is $X^1\Sigma_g^+$, and above it there are a few triplet and singlet states within 2−44 kcal/mol. The spectroscopic parameters and potential energy curves of the ground state and some of the low lying excited states have been studied since 1992 using high-level theoretical methods. Bartlett and Watts[21] studied the $X^1\Sigma_g^+$, $a^3\Pi_u$, and $b^3\Sigma_g^-$ states and found that the single reference CCSD method cannot describe the C_2 molecule qualitatively due to the multireference character of its ground state. Pradhan et al.[22] used the multireference IC-MRCI method and obtained satisfactory quantitative results for the spectroscopic parameters in the ground state. Subsequently, Halvick[20] used the EHFACE2 (extended Hartree−Fock approximate correlation energy) model[24,25] parameters fitted from ab initio MRCI calculations in the large correlation-consistent cc-pV5Z basis set and calculated the adiabatic potential energy curves of the 12 lowest electronic states of the molecule. Sherrill and Abrams[9] studied the potential energy curves of the $X^1\Sigma_g^+$, $B^1\Delta_g$, and $B'^1\Sigma_g^+$ states at the full CI/6-31G* level and used this level as a benchmark for the methods that are based on a single reference molecular orbital wave function. These authors concluded that electron correlation methods based on an UHF (Unrestricted Hartree−Fock) single reference can describe the C_2 molecule correctly, whereas the methods that are based on the RHF (Restricted Hartree−Fock) reference are wrong. Recently, Sherrill et al.[10] evaluated the performance of multireference methods such as CASSCF, CASPT2, and MRCI and renormalized single reference methods such as EOMCCSD and CR-EOMCCSD(T).[11] The authors concluded that the multireference methods give results on par with full CI. Moreover, the renormalized EOMCCSD and CR-EOMCCSD(T) methods have much better performance compared with the straightforward single reference methods CCSD and CCSD(T). Very recently, Varandas extrapolated MRCI results to complete basis set limits,[26] and Mahapatra et al. tested the state-specific multireference perturbation theory approach.[27] A very accurate binding energy for the C_2 ground state was also obtained by Bytautas and Ruedenberg,[28] who approximated full CI results with the "correlation energy extrapolation by intrinsic scaling"

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(CEEIS) method in double-, triple-, and quadruple-ζ basis sets with extrapolation to the complete basis set limit.

What emerges from all of these high level studies is the extreme difficulty in calculating the ground state and the low-lying excited states of C_2 in a meaningful way, owing to the multireference character of the wave functions and the near degeneracies which change very rapidly as a function of the C−C distance. As noted by Sherrill and Piecuch,[11] the low-lying states of C_2 are so challenging and the failures of various high-level electronic structure methods are so dramatic that it is desirable to assess the reliability of the methods against full CI results.

The multireference character of the ground state of C_2 is apparent already at the equilibrium geometry, wherein the coefficient of the primary configuration, $|(\text{core})2\sigma_g^2 2\sigma_u^2 1\pi_u^4\rangle$, is only 0.83 in a full CI calculation,[11] and the doubly excited configuration $|(\text{core})2\sigma_g^2 1\pi_u^4 3\sigma_g^2\rangle$ has a surprisingly large coefficient of 0.33. The situation complicates further near 1.7 Å, where two diexcited determinants of the type $|(\text{core})2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2\rangle$, which have six electrons in σ orbitals and only two in a π orbital, come into play and become dominant in the $X^1\Sigma_g^+$ state due to avoided crossing with the $B'^1\Sigma_g^+$ state.[11]

In summary, the studies using sophisticated theoretical methods show that the ground state has distinct multireference characteristics.[9−11] However, the simple questions posed at the outset (Scheme 1) regarding the type and number of bonds that account for the bond energy and bond length in the molecule are not discussed deeply in their work. Does C_2 have a suspended double π-bonding as in **2** or a triple bond as in **1**, or even another combination of σ and π bonds, and if so, what is the precise role of the σ bonding? These questions concerning chemical bonding will be addressed by use of the VB method, which has both multireference character and conceptual clarity suitable to answer such questions.

The article is organized as follows: It begins with the introduction of the ab initio VB methods. Second, the VB structures that are involved in the calculation are selected. Third, the computational details and the results are shown and discussed. The article is ended with a brief conclusion.

Theory and Methodology

A many-electron system wave function Ψ in VB theory is expressed as a linear combination of Heitler−London−Slater−Pauling (HLSP) functions, Φ_K, in eq 1:[29]

$$\Psi = \sum_K C_K \Phi_K \qquad (1)$$

where Φ_K corresponds to "classical" VB structures and C_K represents structural coefficients.

There are several computational approaches for VB theory at the ab initio level. In the VBSCF procedure,[30,31] both the VB orbitals and structural coefficients are optimized simultaneously to minimize the total energy. As such, the VBSCF method takes care of the static electron correlation, but it lacks dynamic correlation.

The VBCI method,[32,33] which uses a configuration inter-action technique, following VBSCF calculation, considers

Scheme 2. The VB-Orbital Representation in a Coordinate Axis[a]
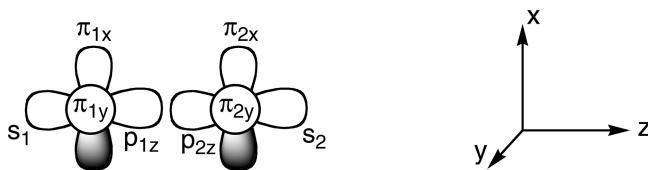
[a] The p_y orbitals are drawn with one lobe pointing at the observer.

the dynamic correlation by involving excited VB structures which are generated by replacing occupied orbitals with virtual orbitals. The virtual orbitals are strictly localized on precisely the same fragment as the corresponding occupied orbitals. In this manner, by merging all of the excited VB structures into the corresponding fundamental structures of the same electron occupancy, the VBCI wave function is condensed to a linear combination of the same minimal number of VB structures as in the VBSCF method. The VBCI computations are performed at the VBCIS level, which involves single excitations only.

The weights of the VB structures can be defined in several ways. One commonly used definition is the Coulson−Chirgwin formula,[34] eq 2, which is the equivalent of a Mulliken population analysis in VB theory.

$$W_K^{\text{Coulson}} = C_K^2 + \sum_{L \neq K} C_K C_L \langle \Phi_K | \Phi_L \rangle \qquad (2)$$

One drawback of this formula is that the second term may become more important than the first one if the overlap between VB structures is too large, possibly leading to some negative weights. Such weights, which are nonphysical, are generally interpreted as an indication that the VB structure in question is unimportant; however, eq 2 becomes inappropriate when negative weights get large absolute values. For this reason, other definitions have been proposed, among which are the Löwdin weights[35] in eq 3:
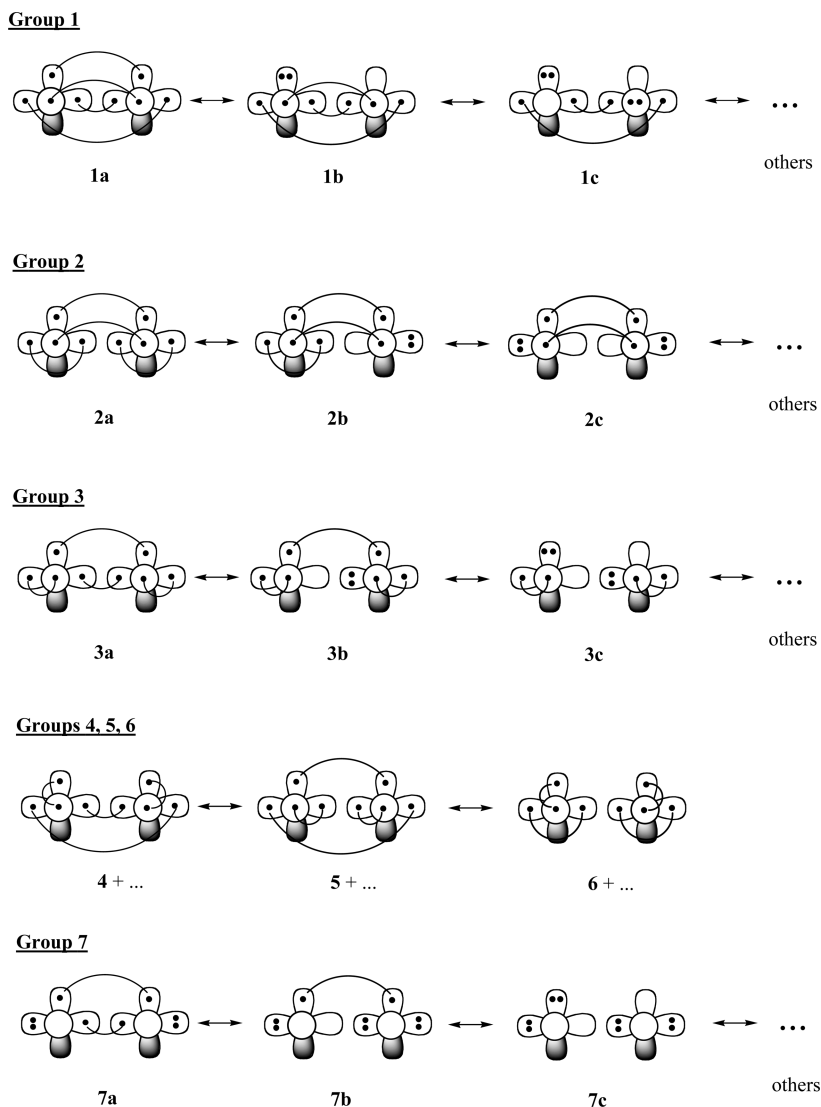
$$W_K^{\text{Lowdin}} = \sum_{I,J} S_{KI}^{1/2} C_I S_{KJ}^{1/2} C_J \qquad (3)$$

or the renormalized sum of the coefficients squares in eq 4 where N is the normalizing factor.

$$W_K^{\text{renorm}} = N C_K^2; \quad N = \sum_K \frac{1}{C_K^2} \qquad (4)$$

Throughout the work, we use eqs 2−4, except for large distances (2.0 Å), where the Chirgwin−Coulson definition was abandoned since it gave large negative weights.

Computational Details. All eight valence electrons of the C_2 molecule are involved in VB calculations. As shown in Scheme 2, the two atoms lie on the z axis, and the $2p_z$ and 2s atomic orbitals (AOs) of the C atoms are hybridized to form two hybrid orbitals pointing toward each other, labeled p_{1z} and p_{2z}, and other hybrid orbitals pointing outward, labeled s_1 and s_2. The remaining AOs are two pure p orbitals lying in the xz plane, π_{1x} and π_{2x}, and two other pure p AOs

Scheme 3. Some Representative VB Structures Gathered by Groups of Bonding Modes

Group 1

1a   **1b**   **1c**   others

Group 2

2a   **2b**   **2c**   others

Group 3

3a   **3b**   **3c**   others

Groups 4, 5, 6

4 + ...   **5 + ...**   **6 + ...**

Group 7

7a   **7b**   **7c**   others

in the yz plane, π_{1y} and π_{2y}, drawn as circles with one lobe pointing at the observer.

The VBSCF and VBCIS methods are used for the calculations of spectroscopic parameters, with the 6-31G* and cc-pVTZ basis sets. The diabatic and adiabatic potential energy curves are calculated at the VBSCF and CASSCF(8,8) levels in the 6-31G* basis set. All orbitals are strictly localized; i.e., they are expressed as combinations of basis functions that belong to single carbon atoms, without tails on the other atom. The VB calculations are carried out with the Xiamen Valence Bond (XMVB) package of programs.[36,37] Basis set integral and nuclear repulsion energy are taken from the output of Gaussian 98[38] calculations.

The VB Structure Set. For a system of spin S with N electrons and m orbitals, the number of independent VB structures is given by the Weyl formula:[39]

$$D(m, N, S) = \frac{2S + 1}{m + 1}\left(\begin{array}{c} m + 1 \\ \frac{1}{2}N + S + 1 \end{array} \right)\left(\begin{array}{c} m + 1 \\ \frac{1}{2}N - S \end{array} \right) \quad (5)$$

For the singlet ground state of C_2, taking all eight valence orbitals and electrons into account, the total number of VB

canonical structures amounts to 1764. Of course, not all of these VB structures are essential for the description of the bonding in C_2, and the first step of the VB application is to select the VB structures that are necessary and sufficient for a reliable description of the electronic state in question. Clearly, an effective way is to select the VB structures by analyzing the characteristics of chemical bonding. Scheme 3 displays some generic VB structures which are gathered by groups, each group representing a specific bonding mode. The complete set of VB structures is displayed in the Supporting Information.

Group 1 involves the VB structures needed to represent the bonding mode with two π bonds, one σ bond, and two unpaired electrons in the s_1 and s_2 orbitals, i.e., structure **1** in Scheme 1. Since each bond is a combination of a major covalent component and two relatively minor ionic components, we must take all combinations of covalent and ionic VB structures. Thus, in Scheme 3, **1a** represents the fully covalent triply bonded VB structure, while **1b** is one of the monoionic structures. The dionic structures are also included, but only if they keep the two carbon atoms neutral, as in **1c**. Triply ionic structures are neglected. As a result, a total of 21 VB structures are kept for the description of the triply bonded structure **1**.

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The same principles are applied to select the VB structures needed for the description of structure **2** of Scheme 1, which possesses two suspended π bonds. A total of 29 structures are selected (see the Supporting Information) and gathered in group 2, among which, three representative structures are **2a−c** in Scheme 3.

Another doubly bonded structure is possible with $\sigma + \pi$ bonds, while the electrons of the remaining π system are relegated to orbitals s_1 and s_2, as shown in **3a−c** in Scheme 3. Group **3** involves a total of 14 VB structures.

To complete the set of VB structures having four electrons in σ and four electrons in π orbitals, and to ensure correct dissociation of the C₂ molecule, one must make sure that all 14 ways of spin-coupling the eight electrons wherein all orbitals are singly occupied (e.g., **1a**, **2a**, **3a**, and so on) are included in the VB structure set. Such structures are gathered in groups 4, 5, and 6 in Scheme 3a. Two VB structures (group 4) display a single σ bond, four structures display a single π bond (group 5), and eight structures display no bond at all (group 6). Accordingly, the total number of VB structures of the 4-σ−4-π type amounts to 78 and constitutes what we will call hereafter the 78-set.

To ensure a correct dissociation, the description of C₂ requires also the VB structures displaying six electrons in σ orbitals and only two in π orbitals. According to full CI benchmarks, such structures are expected to play little or no role at the equilibrium distance but should become important near 1.7 Å.[9−11] Three of these 6-σ−2-π structures, out of a total of 14 selected ones, are represented in group 7 in Scheme 3. These 14 VB structures, added to the 78-set, form the 92-set that will be used to generate the ground state potential energy curve (PEC) from the equilibrium to a separation of 3.0 Å.

Hereafter, we shall use the term "group" to designate either a set of VB structures or the bonding scheme that these structures represent. For example, "group 1" or "structure **1**" will designate the triply bonding structure displayed in Scheme 1 as well as the combination of the 21 VB structures that are needed to represent it, and so on.

Calculating the Energies of the Individual Group Structures. The energy of an individual group of structures can be calculated by block-diagonalizing a Hamiltonian matrix involving only the VB structures that belong to this group, i.e., VB structures 1−21 for group 1, 22−50 for group 2, and so on. This can be done by keeping the same orbitals as those optimized for the ground state, without further orbital reoptimization. This technique is appropriate if the aim is to better analyze the properties of the ground state in terms of VB mixing. On the other hand, one may also perform a full VB calculation of the group structure alone, this time by reoptimizing the orbitals. With this latter method, called the "variational diabatic configuration (VDC) method", the energy of the group structure is variationally minimized. Both methods have been used in this work.

Computational Results and Discussion

Dissociation Energy Curve and Spectroscopic Constants for the $X^1\Sigma_g^+$ Ground State. Before discussing the bonding mode of C₂, it is important to check that our 92-set
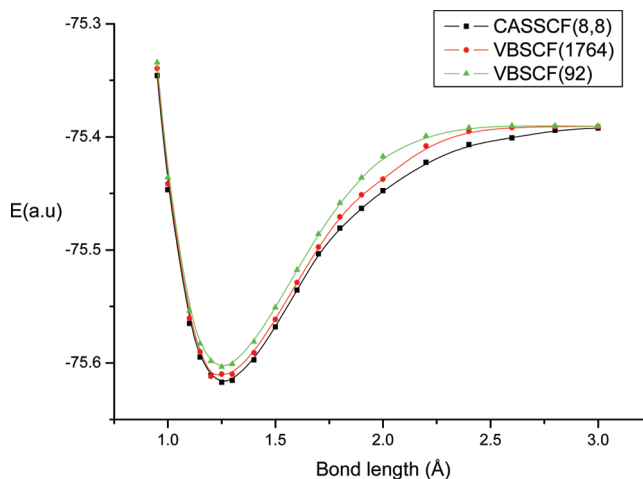

Figure 1. The PECs of the ground state of the C₂ molecule computed at the VBSCF level in the 6-31G* basis set.

of VB structures is sufficient to faithfully describe the electronic structure of this molecule at any distance. This can be done by plotting the adiabatic PEC for the $X^1\Sigma_g^+$ state as a function of the interatomic distance and comparing it with larger VB or CASSCF results. Figure 1 shows the dissociation energy curve for the $X^1\Sigma_g^+$ state as calculated at the VBSCF level with the 92-set, at the full valence VBSCF level involving 1764 spin-couplings, and at the full valence CASSCF(8,8) level in the MO framework. It can be seen that the VBSCF-92 curve is very close to the VBSCF-1764 one at all distances, especially at the equilibrium distance. The VBSCF-1764 curve is also quite close to the CASSCF(8,8) curve at the equilibrium and at large distances but somewhat departs from it in the region near 2 Å. This slight difference between the full valence VBSCF and CASSCF calculations might appear surprising, given that the two calculations span the same space of 1764 configurations. This is due to the fact that (i) the VBSCF-1764 calculation uses the orbitals of the VBSCF-92 calculation, without further reoptimization, and (ii) orbital optimization in CASSCF has a few more degrees of freedom than in VBSCF, as has been noted,[13] because the atomic orbitals (AOs) that compose the various MOs in CASSCF may be different in size and shape from one MO to another, while the set of AOs is unique in VBSCF. Of course, this VBSCF limitation disappears when further CI is performed, as in the VBCIS level. We note that the VBSCF/CASSCF difference is small, and both calculations yield the same bonding energies to within 6% using the 6-31G* basis set.

Table 2 shows the spectroscopic constants as computed by VBSCF and VBCIS methods for the ground state of C₂ molecule. These constants have been calculated using the restricted set of 78 VB structures, as the 6-σ−2-π structures proved completely negligible at the equilibrium C−C distance. A comparison is made with experimental results and with some previous theoretical calculations. The VB optimized equilibrium bond lengths range between 1.252 and 1.262 Å, very close to the full CI value[9−11] (1.260 Å) and to other computational results by high level MO methods.[21,22] The VBSCF values of dissociation energy, 5.77 eV (6-31G*) and 5.80 eV (cc-pVTZ), amount to 93% of the experimental

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Table 2. The Spectroscopic Parameters of the Ground State of C_2

method	basis set	R_{eq} (Å)	D_e (eV)	ω_e (cm^{-1})
VBSCF	6-31G*	1.256	5.77	1994
	cc-pVTZ	1.252	5.80	1996
VBCIS	6-31G*	1.262	6.29	1922
	cc-pVTZ	1.258	6.38	1895
CASSCF(8,8)	6-31G*	1.262	6.15	1858
	cc-pVTZ	1.256	6.18	1840
ICMRCI[a]	cc-pVTZ	1.252	6.09	1841
ICMRCI+Q[a]	cc-pVTZ	1.253	6.01	1840
CCSD(T)[b]	cc-pVTZ	1.245	6.21	1869
full CI[c]	6-31G*	1.260	6.00	1859
exptl.[d]		1.243	6.42	1855

[a] Reference 22. [b] Reference 21. [c] Reference 11. [d] Recent experimental data taken from reference 28 yield $D_0 = 6.305$ eV, to which one must add a ZPE of 0.115 eV, taken from http://www.cccbdb.nist.gov.

Table 3. The Weights of VB Structures Gathered by Groups from VBSCF/6-31G* Calculations at the Equilibrium C−C Distance and at 2.0 Å

structures	eq 2 (R_{eq})	eq 3 (R_{eq})	eq 4 (R_{eq})	eq 3 (2.0 Å)	eq 4 (2.0 Å)
group 1	0.628	0.472	0.679	0.203	0.182
group 2	−0.052	0.126	0.017	0.199	0.206
group 3	0.264	0.248	0.200	0.173	0.095
group 4	0.061	0.048	0.051	0.111	0.314
group 5	0.080	0.074	0.043	0.073	0.037
group 6	0.018	0.033	0.011	0.070	0.040
6-σ-2π	0.000	0.001	0.000	0.172	0.127

value. The VBCIS-computed results bring significant improvements relative to the VBSCF method. The VBCIS/6-31G* computed dissociation energy is the value of 6.29 eV, slightly overestimating the bonding energy with respect to full CI in the same basis set. This is a systematic tendency of VBCIS and related methods that are generally found to yield bonding energies intermediate between full CI and experimental values, owing to a slight excess of relative correlation energy that "fortunately" compensates for the paucity of the basis set.[13] The most accurate VB computed vibrational frequency in Table 1, 1895 cm^{-1} in the cc-pVTZ basis set, is within 2% of the experimental data. All of these successful VB results show that the VB description of the C_2 ground state is accurate, despite the small number of VB structures, and that the subsequent analysis of the bonding mode can be trusted.

Nature of the $X^1\Sigma_g^+$ Ground State. Table 3 shows the VBSCF/6-31G* weights of the various VB structures, summed up for each group, as calculated by eqs 2−4. As written already, the various formulas (eqs 2−4) lead to different values but very similar trends and have therefore a qualitative significance.

In all of the weight definitions (eqs 2−4), group 1, which represents the triply bonded structure, is the major bonding mode at the equilibrium distance with weights of 0.472−0.679 (Table 3, columns 2−4). At the same geometry, the second group, by order of importance, is group 3, which describes a $\sigma + \pi$ double bond (weights 0.200−0.264). The weights for group 2, with the "suspended double π-bonding", are small and more variable, −0.05, 0.13, and 0.02. As has been mentioned in the Theory and Methodology section, negative

weights are unphysical but may be found with the Chirgwin−Coulson definition of the weights (eq 2), in which they signify the low importance of the VB structure in question in the total wave function. This is confirmed by the low weights also found for the VB structures of group 2, as calculated by the alternative definitions (eqs 3 and 4). Last, group 7, the 6-σ−2-π bonding mode, is found to be totally negligible at the equilibrium distance by all weight definitions, in harmony with its negligible stabilizing effect (vide supra) and with the fact that the VB structures belonging to this group are strictly orthogonal to all of the others. As for groups 4−6, which are necessary to ensure correct dissociation but do not correspond to chemically significant bonding schemes, their weights are found to be small, albeit not negligible, at the equilibrium geometry. Thus, if we restrict the discussion to groups 1−3 and 7, all weight definitions (*W*) end up with a clear qualitative ordering of importance in the C_2 ground state at the equilibrium distance, eq 6:

$$W(\text{group 1}) > W(\text{group 3}) > W(\text{group 2}) \gg$$
$$W(\text{group 7}) \sim 0.0 \quad (6)$$

The description of the C_2 ground state in terms of a major triply bonded structure **1** and a less important, but significant, $\sigma + \pi$ doubly bonded structure **3** nicely accounts for the bond length of 1.240 Å, intermediate between that of ethylene (1.339 Å) and that of acetylene (1.203 Å), and closer to the latter.[2]

The ordering displayed in eq 6 is completely reshuffled at 2.0 Å, a distance at which the 6-σ−2-π bonding mode (group **7**) is found to be important with all definitions (Table 3, columns 5 and 6), in agreement with high level MO studies which stress the importance of the configuration $|(\text{core})2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2\rangle$ in this region of the PEC.

Another way to estimate the importance of the different groups for the description of the ground state is to calculate their individual energies at the equilibrium geometry. Even if there is no strict relationship between the energy of a VB structure and its weight in the ground state, it is generally assumed that the lower the energy of a VB structure or group-structure, the stronger will be its contribution to the ground state. The calculation of the energies of each group was performed by separate VB-CI involving only the VB structures of this group, while keeping unchanged the orbitals of the ground state. The results, as calculated at the equilibrium geometry, are displayed in Table 4, columns 2 and 3. It can be seen that group 1 is by far the lowest, followed by group 3 at 81.36 kcal/mol higher. Group 2 lies even higher, 36.82 kcal/mol over group 3. Finally, groups 4−6 are much higher, confirming their low contribution to the ground state in this geometry. Thus, it can be seen that the energy ordering of groups 1−3, in eq 7 below, is intuitively in agreement with the weight ordering in eq 6.

$$E(\text{group 1}) < E(\text{group 3}) < E(\text{group 2}) \quad (7)$$

Still another way to assess the relative contributions of each group to the description of the ground state is to calculate the stabilization energy that is brought about when this group is mixed with the major group 1. The results, obtained by separate VB-CI at the equilibrium geometry as

Table 4. Energies of the Individual Groups and Their Combinations with Group 1[a]

group	E (Hartrees)	E (kcal/mol)	groups	E (Hartrees)	E (kcal/mol)
group 1	−75.568055	0	group 1	−75.568055	0
group 2	−75.379708	118.18	groups 1 + 2	−75.571034	−1.88
group 3	−75.438395	81.36	groups 1 + 3	−75.591799	−14.91
group 4	−75.201470	230.0	groups 1 + 4	−75.578180	−6.36
group 7	−75.165757	252.44	groups 1 + 5	−75.572812	−3.00
group 6	−74.941845	392.94	groups 1 + 6	−75.574775	−4.23

[a] The orbitals of the ground state are used in all VB structures.

$2\sigma_g$ $\quad$ $2\sigma_u$ $\quad$ $3\sigma_g$
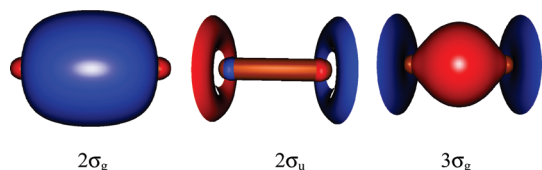
Figure 2. Shapes of the $2\sigma_g$, $2\sigma_u$, and $3\sigma_g$ molecular orbitals at the equilibrium geometry from a TCSCF calculation involving the $2\sigma_g{}^2 2\sigma_u{}^2 1\pi_x{}^2 1\pi_y{}^2$ and $2\sigma_g{}^2 1\pi_x{}^2 1\pi_y{}^2 3\sigma_g{}^2$ configurations.

above, are displayed in Table 4, columns 5 and 6. It is clear that it is group 3 that contributes the most to stabilizing the ground state by mixing with group 1, with a stabilization energy of ca. 15 kcal/mol, vs only 2−6 kcal/mol for each of the other groups. On the other hand, group 2 contributes very weakly to the stabilization energy of the ground state relative to group 1, by barely 2 kcal/mol. It is therefore clear that the three types of test calculations that have been done are consistent with each other and that the emerging bonding picture of C₂ involves the major triply bonded structure **1**, with an important contribution of the $\sigma + \pi$ doubly bonded structure **3**, and a minor contribution of the $\pi + \pi$ structure **2**.

How can the unimportance of group 2 at the equilibrium geometry be reconciled with the MO diagram in Scheme 1, displaying a pair of occupied MOs of the σ type, one bonding ($2\sigma_g$) and one possibly antibonding ($2\sigma_u$)? As argued in the Introduction, this can be interpreted by the shapes of the respective orbitals and by the natural orbital occupation numbers obtained from two-configuration MCSCF or CASS-CF(8,8) wave functions. If the $2\sigma_g$ and $2\sigma_u$ MOs are clearly bonding and antibonding, respectively, then this argues in favor of the absence of σ bonding, and therefore in support of the bonding mode displaying two "suspended" π bonds, i.e., group 2. If, on the other hand, the $2\sigma_u$ orbital is only weakly antibonding, then structures displaying σ bonding, i.e., group 1 and group 3, are favored.

Figure 2 displays the shapes of the $2\sigma_g$, $2\sigma_u$, and $3\sigma_g$ MOs, as they arise from a two-configuration MCSCF calculation involving the two most important configurations, $|(\text{core})2\sigma_g{}^2 2\sigma_u{}^2 1\pi_u{}^4\rangle$ and $|(\text{core})2\sigma_g{}^2 1\pi_u{}^4 3\sigma_g{}^2\rangle$. It appears very clearly that $2\sigma_g$ is strongly bonding, as is $3\sigma_g$, albeit to a somewhat lesser extent than $2\sigma_g$. On the other hand, the $2\sigma_u$ MO is an out-of-phase combination of two outward-directed hybrids and has therefore very little antibonding character. It follows that the two most important configurations in the $X^1\Sigma_g{}^+$ ground state both display some important contribution from σ bonding, in agreement with the predominant weights of group 1 and group 3 structures arising from the VB calculations, and ruling out group 2.

Diabatic Potential Energy Curves. Figure 3 shows the diabatic potential energy curves (PECs) for each individual
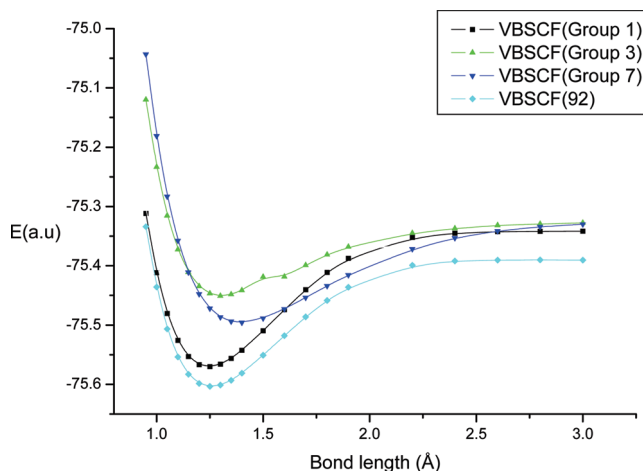
Figure 3. The VBSCF calculated PECs for the ground states of the C₂ molecule with the 6-31G* basis set.

group of VB structures, shown above in Scheme 3, calculated at the VBSCF/6-31G* level. For each group, the VBSCF calculation is performed in the space of all of the VB structures that belong to this group, and this time the orbitals are reoptimized for each group, so as to get the lowest possible energies for the diabatic curves (VDC method, see Theory and Methodology section). Groups 4−6 that are included in the calculation of the ground state for completeness but do not represent chemically meaningful bonding modes are not considered in Figure 3. Moreover, we encountered some computational difficulties with the diabatic energy curve of group 2, which was found to lie between group 1 and group 3 at the equilibrium distance, in contradiction with the results displayed in Table 4 (group 2 lying above group 3). However, examination of the VB wave functions showed that some of the orbitals optimized for group 2 alone are exceedingly different from the corresponding orbitals in the ground state. For example, the overlap between orbitals p_{1z} and p_{2z} (Scheme 2) is 0.70 in the ground state, vs only 0.30 as optimized for group 2 alone. It was therefore concluded that the result of the VBSCF calculation of group 2 alone has little to do with group 2 as a component of the ground state. For this reason, Figure 3 is restricted to the diabatic curves of groups 1, 3, and 7, together with the adiabatic ground state.

It is seen that the lowest diabatic curve in the region near the equilibrium geometry is that of group 1, which represents the triply bonded bonding mode. Group 3 and group 7 curves lie significantly higher than those of group 1 at the equilibrium geometry, but group 7 (the 6-σ−2-π bonding mode) becomes the lowest one at 1.7 Å, in agreement with the full CI study in the MO framework that predicts that determinants

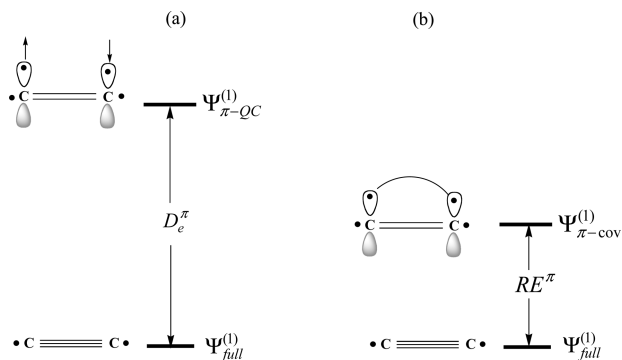**Figure 4.** (a) Definition of in situ bond energy for a π bond of structure **1** based on the quasiclassical state (QC) reference. (b) Definition of the covalent-ionic resonance energy for a π bond of structure **1**.

of the type $|(\text{core})2\sigma_g^2 2\sigma_u^2 1\pi_u^2 3\sigma_g^2\rangle$ become dominant from this distance onward.

Characteristics of the Individual σ and π Bonds. As has been shown above, the VBCIS calculation with a restricted set of 78 structures yields an accurate total bond dissociation energy (BDE), calculated as a difference between the molecular energy and the sum of atomic energies. However, this global quantity does not give us much information on the individual σ and π bonds that participate in the overall bonding. Two questions of interest are as follows: (i) What are the relative strengths of the π and σ bonds as contributors to the overall bonding? (ii) What are the natures of these individual bonds: classical covalent or, rather, charge-shift bonds (see the definition below)? These features of the σ and π bonds were investigated by restricting attention to the major VB structure (**1**).

In multiple bonds, like in C_2, it is not simple to experimentally determine separate bond energies for σ and π bonds. In double bonds (e.g., ethylene), one can roughly estimate the π bonding energy as the rotational barrier; however, this quantity also involves relaxation of the σ bond and hyperconjugation in the twisted form. The problem gets even worse with triple bonds, since these species do not have rotational barriers. However, as we have shown amply before,[13,40−43] these difficulties can be bypassed by defining *a nonbonded reference state* for one π bond, in which the two electrons maintain opposite spins but do not exchange. For example, if one wants to estimate the strength of one of the two π bonds in the triply bonded structure **1**, one may define a nonbonded state, called the "quasiclassical state" $\Psi_{\pi\text{-QC}}^{(1)}$ in Figure 4, in which the electrons of a given π bond have only one spin arrangement pattern (only $\alpha\beta$), and therefore this structure by itself has no bonding due to the resonance with the second spin arrangement pattern that is required to form a singlet pair. In such a state, the interactions across the unpaired π bond in $\Psi_{\pi\text{-QC}}^{(1)}$ involve only classical electron−electron repulsion, nuclear repulsion, and electron−nuclear attraction, and since the fragments are neutral, these terms sum to approximately zero. Thus, the difference between the energy of $\Psi_{\pi\text{-QC}}^{(1)}$ and that of the fully bonded structure **1** gives the "in situ" π-bonding energy D_e^π at a given interatomic distance, i.e., the bonding energy that effectively stabilizes the electronic interaction of the considered π bond

without any other relaxation or reorganization term arising from other bonds. The in situ π-bonding energy in structure **1** is expressed in eq 9:

$$D_e^\pi = E(\Psi_{\pi\text{-QC}}^{(1)}) - E(\Psi_{\text{full}}^{(1)}) \tag{9}$$

where $\Psi_{\text{full}}^{(1)}$ is the fully optimized wave function for structure **1**, calculated by a VBSCF calculation involving the 21 VB structures of group 1.

An important point to note is that the QC state remains nonbonding only at distances equal to or longer than the optimal bonding distance[12] but becomes repulsive at shorter distances and therefore ceases to be a good reference state for measuring the in situ bonding energy in such a case. Moreover, one expects the repulsive wall of the QC state to be basis set dependent: the more flexible the basis set, the less repulsive the QC state. Accordingly, the method can be applied for the π components of multiple bonds but will be much less accurate for the σ component, since at a length of 1.25 Å, the latter is "compressed" relative to the optimal distance for a single σ bond ($\sim$1.50 Å for a C−C σ bond between sp hybrids). Thus, we will only get a rough estimation for the σ bond strength.

Equation 9 has been applied for structure **1** with the 6-31G* basis set, yielding an in situ bonding energy of 93.3 kcal/mol for the π bond, very close to the value 92.25 kcal/mol that was found with the same technique by Ploshnik[44] for the π bond of acetylene. Interestingly, these values are significantly larger than the in situ π bonding energy of 72.0 kcal/mol calculated by Galbraith et al.[6] for ethylene, in agreement with the principle that π bonds prefer short bond lengths.

The same technique has been used to estimate the in situ bonding energy of the σ bond in **1**, yielding an in situ bonding energy of 99.4 kcal/mol in 6-31G* basis set, and only 64.1 kcal/mol in the larger cc-pVTZ one, thus confirming the expected basis set dependency and the lack of accuracy of the "in situ" estimation of the σ bond strength of C_2.

Summing up the σ and π in situ bonding energies, one would arrive at a total of 251−286 kcal/mol for structure **1**, a value that is of course much larger than the true dissociation energy because the fragments enjoy some demotion energy from their local high spin states in the molecule to their triplet states at infinite distance. This high value can be compared to the estimated bond strength of acetylene relative to the high spin fragments, as calculated by Frenking.[45] In this approach, which is also that of Trinquier and Malrieu,[46,47] Carter and Goddard,[48] and others,[49] the acetylene molecule is considered as the product of interactions between two $^4\Sigma^-$ CH fragments, yielding a triple bonding energy of 270.9 kcal/mol,[45] before the final dissociation energy is obtained after adding the demotion energy of the fragments from $^4\Sigma^-$ to their ground states $^2\Pi$. From this comparison between acetylene and the triply bonded structure (**1**) of C_2, it seems that our window of 64−99 kcal/mol for the in situ σ bond strength of structure **1** is reasonable.

In the VB framework, any two-electron bond is described as a superposition of one covalent and two ionic forms, even

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Table 5. In Situ π-Bonding Energies and Covalent-Ionic Resonance Energies for the π and σ Bonds of the Triply Bonded Structure **1**, As Calculated by the VBSCF Method (Energies in kcal/mol)

basis set	D_e^π	D_e^σ	RE$^\pi$	RE$^\sigma$
6-31G*	93.3	99.4	44.2	15.1
cc-pVTZ	88.1	64.1	36.1	12.2

in the homonuclear case.[13] Generally speaking, whenever the covalent structure has the largest weight, which is always the case for homonuclear molecules,[50] the bond dissociation energy BDE of any of the σ or π bonds in structure **1** will be given in eq 10:

$$BDE = BDE_{cov} + RE_{cov\text{-}ion} \qquad (10)$$

Here, BDE$_{cov}$ is the covalent spin-pairing energy of the bond, and RE$_{cov\text{-}ion}$ is the covalent-ionic resonance energy due to the mixing of the ionic structures into the covalent one(s). Both quantities are variational within the subset of VB structures. In classical covalent bonds (e.g., H$_2$, H$_3$C−CH$_3$, etc.), the covalent term is the major one; however, there exists a category of bonds, termed "charge-shift" (CS) bonds, where it is the resonance energy term, RE$_{cov\text{-}ion}$, that is the major one, in eq 10, and responsible for most of the bonding.[50,51]

The covalent-ionic resonance energy of a π bond in structure **1** can be estimated by means of eq 11, as schematized in Figure 4b:

$$RE^\pi = E(\Psi^{(1)}_{\pi\text{-cov}}) - E(\Psi^{(1)}_{full}) \qquad (11)$$

where $\Psi^{(1)}_{\pi\text{-cov}}$ is a variational combination of all of the VB structures in group 1 in which the considered π bond is purely covalent, and $\Psi^{(1)}_{full}$ is defined as in eq 9. The calculated values are displayed in Table 5. The 6-31G* value for RE$^\pi$, 44.2 kcal/mol per π bond, is seen to be slightly smaller than 50% of the in situ π-bonding energy (93.3 kcal/mol), showing that the π bonds in **1** have a strong charge-shift character and lie between classical covalent bonds and charge-shift ones, according to our classification.[50] The same conclusion is reached with the calculation in the cc-pVTZ basis set.

The charge-shift character of the σ bond in structure **1** can be estimated in an analogous way, by means of eq 12:

$$RE^\sigma = E(\Psi^{(1)}_{\sigma\text{-cov}}) - E(\Psi^{(1)}_{full}) \qquad (12)$$

where $\Psi^{(1)}_{\sigma\text{-cov}}$ now involves the VB structures in group 1 in which the σ bond is purely covalent. The RE$^\sigma$ values, 12−15 kcal/mol (Table 5), are now much smaller than the estimated in situ σ-bonding energy, clearly classifying the σ bond in **1** as a classical covalent bond.

Conclusion

The electronic structure of the C$_2$ molecule in the ground state was described herein using the ab initio VB calculations. While this molecule is known to require very sophisticated computational methods in the MO−CI framework, owing to its strong multireference character, the VB method encounters no particular difficulties with this challenging

molecule. Thus, a simple VBSCF calculation involving 78 VB structures, selected on the basis of chemical criteria, is followed by configuration interaction with single excitations (VBCIS). Such a calculation provides spectroscopic parameters that are very close to experimental values in the largest basis set, and also close to full CI calculated values in the smallest one.

According to the VB results, the electronic structure of the C$_2$ ground state is more complex than that of acetylene and is described in terms of three interacting bonding schemes. A triply bonded structure, analogous to the bonding scheme of acetylene, is the major one in terms of weights, and the lowest in energy at the equilibrium distance. The second structure in terms of weights is an ethylene-like structure, displaying a $\sigma + \pi$ double bond. The structure with two suspended π bonds but no σ bond contributes only marginally to the ground state.

The natures of the π and σ bonds are investigated in the triply bonded bonding scheme. The "in situ" strength of each of these bonds is estimated, defined as the effective strength of the bonding interaction at the equilibrium distance without the geometrical relaxation and fragment reorganization that occur at large distances. The π bond is found to be stronger than the π bond of ethylene, but as strong as the π bond of acetylene with an in situ bond strength of 93.3 kcal/mol. The σ bond strength could not be estimated accurately by the "in situ" technique; however the estimated order of magnitude shows that this bond strongly contributes to the overall bonding in C$_2$. This probably explains why the structure with suspended π bonds cannot be the major one in the ground state of C$_2$.

The VB calculations also allow for specification of the contribution of the covalent-ionic resonance energy to bonding in each of the π and σ bonds. While the σ bond is found to be a perfectly classical covalent bond, the π bonds have significant contribution from the covalent-ionic resonance energy, which classifies them as intermediate between classical covalent and charge-shift bonds.

Finally, the bonding picture of C$_2$ that emerges from this study is that of a mixture of a major triply bonded structure, •C≡C•, with rather strong σ and π bonds, perturbed by a less important $\sigma + \pi$ doubly bonded structure :C=C:, which accounts for the bond length being intermediate between that of ethylene and that of acetylene, but closer to the latter molecule.

Note Added in Proof. We thank one of the referees for pointing out the results of some unpublished CASSCF (8,8) calculations in support of the triply bonded structure **1**. The occupation numbers of the natural orbitals from this calculation indicate that although the π bonds (x and y) are very important, with occupation numbers of 1.89 for the bonding orbitals vs 0.12 for the antibonding ones, the σ orbitals also contribute to bonding, with cumulated occupa-

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tion numbers of 2.38 for the bonding σ_g orbitals vs only 1.61 for the antibonding $2\sigma_u$ which, we recall, is only slightly antibonding

Supporting Information Available: These five schemes show all 92 VB structures in groups 1−7. This information is available free of charge via the Internet at http://pubs.acs.org/.

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