

Carbon

C₂ in a Box: Determining Its Intrinsic Bond Strength for the X¹Σ_g⁺ Ground StateWenli Zou and Dieter Cremer^{*[a]}

Abstract: The intrinsic bond strength of C₂ in its ¹Σ_g⁺ ground state is determined from its stretching force constant utilizing MR-CISD+Q(8,8), MR-AQCC(8,8), and single-determinant coupled cluster calculations with triple and quadruple excitations. By referencing the CC stretching force constant to its local counterparts of ethane, ethylene, and acetylene, an intrinsic bond strength half way between that of a double bond and a triple bond is obtained. Diabatic

MR-CISD+Q results do not change this. Confinement of C₂ and suitable reference molecules in a noble gas cage leads to compression, polarization, and charge transfer effects, which are quantified by the local CC stretching force constants and differences of correlated electron densities. These results are in line with two π bonds and a partial σ bond. Bond orders and bond dissociation energies of small hydrocarbons do not support quadruple bonding in C₂.

Introduction

The C₂ molecule is one of the most investigated molecules, both experimentally and theoretically. It plays an important role in the catalyzed formation of fullerenes and carbonanotubes,^[1–3] is a frequent intermediate in combustion processes (the blue glow of hydrocarbon flames of Bunsen burners and gas hops results from C₂^[4,5]), and is found in interstellar space where it is emitted from comets and the atmospheres of carbon stars.^[6] The spectrum of C₂ varies with temperature, thus making it a helpful compound for studying the temperature of stars. C₂ undergoes simple reactions with hydrogen to form radicals and carbenes^[7,8] or is formed in combination–decomposition processes of radicals such as CH or CCl.^[9] Dicarbon exists only as a gas above 3600 °C (e.g., in electric arcs) below which it quickly condensates to graphite.^[10] Its properties are peculiar in so far as its first excited state, a³Π_u, is just 2.05 kcal mol^{−1} above the X¹Σ_g⁺ ground state,^[11] so that any metal catalyst facilitating intersystem crossing increases the reactivity of C₂. Several reviews have discussed the properties of C₂ and its higher homologues.^[10,12,13]

Theoretically, C₂ is important in two ways. The first has to do with its peculiar bonding properties, which, according to elementary molecular orbital (MO) theory, suggest a double bond made up of two π bonds (occupation of degenerate 1π_u orbitals) that are not supported by a σ bond, as the bonding effect of a doubly occupied 2σ_g⁺ orbital is formally annihilated by a doubly occupied 2σ_u⁺ orbital.^[14] A detailed analysis of the 2σ

orbitals reveals that the antibonding effect of the occupied 2σ_u⁺ is smaller than the bonding effect of 2σ_g⁺ MO. Accordingly, some partial σ-bonding results that increases the bond order (here, defined as the difference between bonding and antibonding contributions to the multiplicity of a bond) to a value somewhat larger than 2, but keeping it smaller than that in acetylene.^[14,15] Any orbital description of the C₂ bond has to consider its multireference character, which implies that the ground state wave function is better described by a linear combination of configuration state functions rather than by a Hartree–Fock (HF) single determinant wave function.

Because of its multireference character, C₂ has become a benchmark in connection with method development and high accuracy calculations, which establishes its second way of importance in theoretical chemistry. Studies on C₂ include density functional theory,^[16] coupled cluster,^[17–21] FCI (full configuration interaction),^[18,22–25] multireference configuration interaction,^[15,18,26,27] multireference perturbation theory,^[28,29] quantum Monte Carlo,^[30,31] variational reduced-density-matrix,^[32] valence bond (VB),^[24,25] and density matrix renormalization group calculations.^[33] There is no doubt that the character of the bond in C₂ should be described in terms of natural orbitals with fractional occupation numbers, rather than the MOs of the HF approach. This has also to be considered when calculated molecular properties, such as force constant, electron density, orbital populations, Wiberg or Mayer bond indices,^[34–37] and so forth, are used as tools for the description of bonding in C₂.

There are recent efforts to get an improved conceptual understanding of bonding in C₂, which were triggered in a somewhat uncommon way by means of a post in the chemistry blog of Rzepa. The post dealt with the cyonium cation CN⁺ and dicarbon as potentially quadruply bonded species.^[38] Since then, Shaik and co-workers have published three articles^[24,25,39] in which they postulate a quadruple bond for C₂ utilizing the results of VB and FCI calculations and combining them with

[a] W. Zou, Prof. D. Cremer

Computational and Theoretical Chemistry Group (CATCO)
Department of Chemistry, Southern Methodist University
3215 Daniel Ave, Dallas, Texas 75275-0314 (USA)
E-mail: dcremer@smu.edu

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201503750>.

a new interpretation of the two CH bond dissociation energies (BDEs) of acetylene. Their suggestion of a fourth, although weak ($15\text{--}20\text{ kcal mol}^{-1}$), bond in C_2 has triggered a wave of partly supporting and partly critical follow-up investigations.^[15,21,40–44] Especially, the critical comments by Frenking and Hermann on the postulate of a quadruple bond in C_2 as well as the counter-arguments by Shaik and co-workers^[15,45] reveal the bandwidth of interpretation possibilities based on the same experimental or computational facts.

The debate between quadruple bond believers and disbelievers centers on 1) the definition of an in situ bond energy of C_2 , which is essential for determining the energy equivalent of fourfold bonding, 2) the interpretation of the weights and nature of the components of the VB and FCI wave functions, 3) the stepwise dissociation of acetylene into C_2 as a measure for determining the CC bond strength, and 4) the descriptive value of a relatively low CC stretching force constant. This last point can be analyzed in connection with the Badger rule (the shorter bond length indicates a stronger bond)^[46–48] using acetylene as a reference, emphasizing an avoided crossing between the $X^1\Sigma_g^+$ ground state and the $B^1\Sigma_g^+$ doubly excited state of C_2 , and a partitioning of the force constant into σ - and π -contributions or, alternatively, HF and correlation contributions.^[15,24,25]

The current work does not make any attempt to interpret the VB and FCI results of the previous studies as these have already been excessively discussed using different bonding models.^[15,24,25,41,42] Instead we focus on the intrinsic bond strength of C_2 and possible experimentally verifiable descriptors so that the comparison between different CC bond types can be facilitated. In particular, the following objectives expressed in form of questions will be pursued:

- 1) Does a *clean* set of CC stretching force constants obtained for suitable reference molecules (ethane, ethylene, acetylene) lead to a different insight into bonding of C_2 ? Such a *clean* set of local CC stretching force constants is obtained by eliminating mode–mode coupling,^[49–51] which normally contaminates frequencies and force constants of normal vibrational modes (see Section 2).
- 2) Is there a possibility of obtaining a C_2 stretching force constant that is no longer affected by the avoided crossing between the C_2 ground and doubly excited state of $^1\Sigma_g^+$ symmetry?
- 3) What does the Badger rule give away about C_2 bonding? Or is this a dead-end as Shaik and co-workers^[25] pointed out?
- 4) Can a correlation corrected electron density $\rho(r)$ and/or energy density distribution $H(r)$ ^[52,53] in the bond region provide an insight into CC bonding?
- 5) Do electron-correlation-corrected bond orders support quadruple bonding?
- 6) Are there other means to probe CC bonding in C_2 in a non-destructive and electron-structure-conserving manner so that additional information on the nature of the bond can be gained? In this connection, we will apply a new way of

analyzing the electronic structure of C_2 , which is based on space confinement.

The results of this investigation and the answers to questions 1)–6) will be presented herein.

Computational Methods

Local CC stretching force constants and frequencies were calculated by solving the Wilson equation of vibrational spectroscopy^[54] and then using the normal vibrational modes to set up the kinematically decoupled Wilson equation, which directly leads to local vibrational modes and their properties.^[49–51] In this way, the local CC stretching force constants k_e^a and frequencies ω_e^a of the reference molecules ethane, ethylene, and acetylene in their equilibrium geometry (subscript e) have been obtained. In the case of measured vibrational frequencies, the corresponding local mode properties were calculated using the procedure described by Cremer and co-workers^[55] and utilizing normal modes from CCSD(T) (coupled cluster with all single and double excitations improved by a perturbative treatment of the triple excitations)^[56] calculations. In all normal mode calculations, the harmonic approximation was used. In some cases, anharmonically corrected CC stretching force constants were calculated numerically or, at lower levels of theory analytically employing vibrational perturbation theory at second order.^[57] These results suggested that the trends discussed in this work are only slightly affected by anharmonicity corrections and that the general conclusions drawn in this work are not changed. Therefore, the discussion will be preferentially based on harmonic stretching force constants.

Energy, geometry, and vibrational frequency calculations were carried out at the MR-AQCCSD (multireference averaged quadratic CCSD)^[58,59] and the MR-CISD+Q (multireference configuration interaction with all S and D excitations and a quadruple size-consistency correction) levels of theory,^[60–62] for both cases an (8,8) active space based on the 8 valence electrons and orbitals of C_2 was used. MR-CISD+Q(8,8) was applied to describe the potential energy curves for the $X^1\Sigma_g^+$ ground state and the $B^1\Sigma_g^+$ doubly-excited state in the range from 1.0 to 2.2 Å. Diabatic potential energy curves were obtained by using the theory of Cederbaum and co-workers^[63] in the simplified version of Werner and co-workers.^[64] For acetylene, ethylene, and ethane, the active space was extended to (10,10), (12,12), and (14,14), respectively, which includes also the 1s orbitals of the hydrogen atoms. Reference calculations were also carried out for N_2 in its $^1\Sigma_g^+$ ground state using MR-CISD+Q(10,8).

In the multireference calculations of ethane, the reference configuration state functions were selected according to a coefficient of ≥ 0.02 in the starting CASSCF(14,14) (complete active space self-consistent field with 14 electrons and 14 orbitals) wavefunction, that is, only those configuration state functions contributing to the wavefunction of the ground state with coefficients $\geq 0.04\%$ were included in the MR-AQCCSD(14,14) or MR-CISD+Q(14,14) calculations. Various single-determinant coupled cluster methods were also applied to obtain reference data for comparison: CCSD(T),^[56,65,66] BD(T) (Brueckner doubles with perturbative triples),^[65–67] CCSD(TQ),^[68] CCSDT,^[69] CCSDT(Q),^[70] and CCSDTQ.^[69]

Geometry optimizations and vibrational frequency calculations were carried out, where possible, with analytical gradients^[71] and analytical Hessian.^[72] Numerical calculations had to be carried out for MR-AQCC, MR-CI, BD(T), CCSD(TQ), and CCSDT(Q) for both vibrational frequency and force constant calculations. At all levels of

theory, Dunning's cc-pVTZ basis [4s3p2d1f/3s2p1d]^[73,74] was used to have a consistent description for both the hydrocarbons, C₂, the reference molecules X, as well as He-caged C₂ and X (see below). In the correlation calculations, the core electrons were frozen.

To determine molecular properties under the situation of space confinement, C₂ was caged up in an octahedron of six He atoms, in which two He atoms were positioned on the axis of C₂ (z direction) at a distance of 1.4 + 1.7 = 3.1 Å, corresponding to the sum of the van der Waals radii of He and C.^[75] The He atoms in the x and y directions were positioned so that O_h symmetry for the empty cage was fulfilled. A similar cage was constructed for acetylene and dinitrogen in their ground states (van der Waals distance of H: 1.2; N: 1.55 Å^[75]).

The confinement analysis was carried out by reducing the box in defined directions, always keeping D_{4h} symmetry for the endohedral complex. The increase of cage, X interaction energies (X = C₂, N₂, HCCH) during space confinement was kept within reasonable limits so that electron excitations could be excluded. The total electron density distribution ρ(r) of a confined molecule X always complied with the overall D_{4h} symmetry of the X@He₆ endohedral complex. Any change in the force constant contains two effects: 1) Compression of the bonding density (including all polarization effects) and 2) the charge transfer from the He atoms into a low-lying unoccupied orbital(s).

All confinement studies were carried out at the MR-CISD+Q/cc-pVTZ level of theory in which the noble gas cage was compressed in z direction by reducing the van der Waals distance between He and C by 10%, 20%, and so forth, and then optimizing the CC distance for a constant van der Waals distance in z direction and fixed (non-compressed) positions of the He atoms in the xy plane. For a compression in the x or y directions or xy plane by 10%, 20%, and so forth, the CC distance was reoptimized for fixed He-X van der Waals distances in z direction. Bond lengths and bond stretching force constants were calculated numerically. In the case of the HCCH confinement studies, the local CC stretching force constant was determined to exclude any HC-CC coupling effects. Results of the confinement studies were analyzed by calculating electron difference density distributions Δρ(r) = ρ(X@He₆, r) - ρ(He₆, r) - ρ(X, r), in which X corresponds to the confined molecule (C₂, N₂, HCCH). Since the CC bond length changes under the impact of compression, the difference density in the bond region was slightly flawed by position errors (as reference point the bond midpoint was used), which can be ignored in the bonding region but become larger at the nuclei.

All calculated properties obtained at the MR-CISD+Q level of theory for six different boxes are summarized in tables given in the Supporting Information. Additional X@He₆ cages with larger dimensions were also calculated to clarify at which van der Waals distance the confined molecule adopts the properties of the free molecule. There are slight differences at the reference van der Waals distance (0% space reduction); however, these are so small that they can be neglected for the discussion.

With the help of the calculated local CC stretching force constants, a bond strength order (BSO) *n* was determined by using a power relationship of the type^[48,76,77] $n(\text{CC}) = a k_e^a (\text{CC})^b$. For this purpose, the CC bond in ethane (*n* = 1.00) and that of acetylene (*n* = 3.00) were selected as suitable reference bonds. For a k_e^a value of zero, a BSO value of zero was imposed. In this way, the following values for constants *a* and *b* were obtained: 0.30673, 0.82091 (MR-AQCC), 0.30244, 0.82622 (MR-CISD+Q), 0.30801, 0.81747 (CCSD(T)), and 0.32968, 0.79943 (measured frequencies). All experimental geometries and frequencies of C₂H_{2*m*} (*m* = 0, 1, 2, 3) were taken from the NIST library.^[78,79]

Electron density and energy distributions were calculated either as response properties or were derived from natural orbitals and determined at the bond critical point *r_b* using the MultiWFN program.^[80] In addition, Wiberg^[34] and Mayer bond indices^[35,36] were calculated at the MR-AQCCSD, MR-CISD+Q, and CCSD(T) levels of theory.

CCSD(T) calculations were performed with the program package CFOUR,^[81] CCSDT, CCSDT(Q), and CCSDTQ with MRCC,^[82,83] CCSD(TQ) with ACES II,^[84] whereas the MR calculations were performed with MOLPRO.^[85] Local mode calculations were carried out with the program package COLOGNE2015,^[86] whereas bond order calculations were performed with the programs Molden2AIM and MOLBO of Zou and co-workers.^[87]

Results and Discussion

For C₂ in its X¹Σ_g⁺ ground state, measured bond length, and vibrational frequency have been converted to equilibrium values (Table 1) and therefore can be directly compared with the calculated data for which the theoretical value of the frequency is given in the harmonic approximation. The NIST tables^[78,79] contain a fairly complete data collection of calculated bond length and harmonic vibrational frequency values so that only a few comments are needed here. High accuracy results (MR-AQCC(8,8), MR-CISD+Q(8,8), and CCSDTQ) give the CC bond about 0.01 Å too long (larger basis sets lead to the expected contraction of the bond^[13]), which causes a 10–30 cm⁻¹ underestimation of the experimental vibrational frequency (1855 cm⁻¹, Table 2). Deviations become smaller if anharmonicity effects are considered. The calculated harmonic CC stretching force constants are in the range 11.784–12.063 (exception: CCSD(TQ): 12.244) and thereby smaller than the experimental value of 12.161 mdyne Å⁻¹ (Table 1). Anharmonically corrected CC force constants obtained at the MR-AQCC(8,8) and MR-CISD+Q(8,8) (adiabatically and diabatically) levels of theory are 12.176, 12.118, and 12.314 mdyne Å⁻¹ and thereby in better agreement with the experimentally based value.

For acetylene, ethylene, and ethane, agreement between theory and experiment is equally satisfactory confirming that target and reference molecules are reasonably described by the quantum chemical methods used for this study. If just the reference molecules ethane, ethylene, and acetylene are considered, bond length and local stretching force constant are related by a Badger relationship^[48,76] of the type $k_e^a = a(r_e)^b$ (MR-AQCC: *a* = 48.690, *b* = -5.775; MR-CISD+Q: 47.502, -5.667; exptl: 45.339, -5.633). The experimental bond length of C₂ is 0.021 Å shorter than predicted by the power relationship based on the reference CC bonds. Alternatively, one could say that the C₂ bond stretching force constant is too small by 1.199 mdyne Å⁻¹. Clearly, the Badger relationship is just qualitative and there have been many discussions why deviations are found therefrom.^[48,76,88–90] A bond shortening by 0.021 Å can be related to a decreased covalent radius in line with the increased electronegativity of a sp-hybridized C in C₂ that, contrary to the C atoms in acetylene, has not to accommodate charge obtained from a substituent atom. Alternatively, one could argue that a too small force constant reflects the avoid-

Table 1. CC bond properties: Bond length R , local stretching force constant and frequency, k_e^a and ω_e^a (CC), coupling frequency ω_e^{coup} , electron density and energy density at bond critical point, ρ_b and $H(\rho_b)$.^[a]

Molecule, symmetry	Method ^[a]	R(CC) [Å]	k_e^a (CC) [mDyn Å ⁻¹]	BSO n	ω_e^a (CC) [cm ⁻¹]	ω_e^{coup} [cm ⁻¹]	ρ_b [e Bohr ⁻³]	$H(\rho_b)$ [Hartree (Bohr ³) ⁻¹]
C ₂ , D _{∞h}	MR-AQCC(8,8)	1.2523	11.924	2.35	1837	0	0.324	-0.472
	MR-CISD + Q(8,8)	1.2527	11.784	2.32	1826	0	0.324	-0.471
	diabatic	1.2485	12.043	2.36	1846	0	0.327	-0.479
	CCSD(T)	1.2507	12.041	2.35	1846	0	0.329	-0.480
	BCCD(T)	1.2502	12.057					
	CCSD(TQ)	1.2472	12.244					
	CCSDT	1.2506	12.063					
	CCSDT(Q)	1.2531	11.816					
	CCSDTQ	1.2523	11.875					
C ₂ H ₂ , D _{∞h}	exptl ^[c]	1.2425	12.161	2.43	1855	0	-	-
	MR-AQCC(10,10)	1.2105	16.085	3.00	2133	-139	0.412	-0.651
	MR-CISD + Q(10,10)	1.2106	16.072	3.00	2132	-	0.411	-0.648
	CCSD(T)	1.2097	16.191	3.00	2140	-139	0.413	-0.654
C ₂ H ₄ , D _{2h}	exptl ^[c]	1.203	15.836	3.00	2217	-243	-	-
	MR-AQCC(12,12)	1.3379	9.137	1.89	1608	-	0.352	-0.464
	MR-CISD + Q(12,12)	1.3379	9.137	1.88	1608	-	0.353	-0.465
	CCSD(T)	1.3371	9.201	1.89	1613	58	0.353	-0.467
C ₂ H ₆ , D _{3d}	exptl ^[c]	1.339	8.924	1.90	1589	34	-	-
	MR-AQCC(14,14) ^[b]	1.5265	4.219	1.00	1092	-	0.246	-0.223
	MR-CISD + Q(14,14) ^[b]	1.5308	4.252	1.00	1097	-	0.246	-0.221
	CCSD(T)	1.5289	4.223	1.00	1093	-79	0.245	-0.221
	exptl ^[c]	1.536	4.007	1.00	1065	-243	-	-

[a] Basis set: cc-pVTZ. Core orbitals are frozen. [b] Threshold of reference configuration state functions (CSFs) selection: 0.02, that is, only the reference CSFs of CASSCF(14,14) with weight >0.04% are included in the MR-AQCC(14,14) and MR-CISD + Q(14,14) calculations. [c] All experimental values of C₂H_{2n} are taken from the NIST tables.^[78,79]

Table 2. Vibrational frequencies of molecules C₂H_{2n} ($n=0, 1, 2, 3$).^[a]

Molecule symmetry	Method	Frequency [cm ⁻¹] (IR intensity if IR active [km mol ⁻¹])
C ₂ , D _{∞h}	MR-AQCC(8,8)	1837 (σ_g^+)
	MR-CISD + Q(8,8)	1826 (σ_g^+)
	diabatic	1846 (σ_g^+)
	CCSD(T)	1846 (σ_g^+)
	exptl ^[b]	1855 (σ_g^+)
C ₂ H ₂ , D _{∞h}	MR-AQCC(10,10)	574 (π_g), 745 (π_u), 1994 (σ_g^+), 3410 (σ_u^+), 3509 (σ_g^+)
	CCSD(T)	578 (π_g), 746 (π_u ; 179), 2001 (σ_g^+), 3410 (σ_u^+ ; 83), 3511 (σ_g^+)
	exptl ^[b]	612 (π_g), 730 (π_u ; 195), 1974 (σ_g^+), 3295 (σ_u^+ ; 76), 3374 (σ_g^+)
C ₂ H ₄ , D _{2h}	CCSD(T)	823 (b_{2u}), 942 (b_{2g}), 967 (b_{1u} ; 89), 1047 (a_u), 1242 (b_{1g}), 1369 (a_g), 1479 (b_{3u} ; 8), 1672 (a_g), 3139 (b_{3u} ; 14), 3157 (a_g), 3219 (b_{1g}), 3246 (b_{2u} ; 21)
	exptl ^[b]	826 (b_{2u}), 943 (b_{2g}), 949 (b_{1u} ; 84), 1023 (a_u), 1236 (b_{1g}), 1342 (a_g), 1443 (b_{3u} ; 10), 1623 (a_g), 2989 (b_{3u} ; 14), 3026 (a_g), 3103 (b_{1g}), 3105 (b_{2u} ; 26)
	CCSD(T)	310 (a_{1u}), 821 (e_u ; 5), 1014 (a_{1g}), 1225 (e_g), 1407 (a_{2u}), 1427 (a_{1g}), 1511 (e_g), 1513 (e_u ; 15), 3038 (a_{2u} ; 53), 3040 (a_{1g}), 3097 (e_g), 3120 (e_u ; 121)
C ₂ H ₆ , D _{3d}	CCSD(T)	289 (a_{1u}), 822 (e_u), 995 (a_{1g}), 1190 (e_g), 1379 (a_{2u}), 1388 (a_{1g}), 1468 (e_g), 1469 (e_u), 2896 (a_{2u}), 2954 (a_{1g}), 2969 (e_g), 2985 (e_u)
	exptl ^[b]	

[a] Calculated vibrational frequencies in the harmonic approximation. Basis set: cc-pVTZ. Two C 1s orbitals are frozen. [b] All the experimental values of C₂H_{2n} are taken from the NIST tables.^[78,79]

ed crossing at 1.6 Å.^[24,25] This has to be clarified in the following discussion.

In those cases in which the normal and local mode frequencies have been calculated analytically, coupling frequencies^[50] can be given that measure the amount of kinematic coupling for the normal modes of a given molecule. For the reference molecules, the CC coupling frequencies range from 34 to 243 cm⁻¹, which corresponds to a 6–23% change in the frequency. Hence, the error in the local CC stretching force con-

stants based on measured frequencies is 0.3 mdyn Å⁻¹ (ethane) and <0.1 mdyn Å⁻¹ (acetylene), which implies a BSO error of 0.13 for ethane. This has to be considered when using normal mode force constants rather than the local stretching force constants to describe the intrinsic bond strength of C₂.

When the BSO values are determined with CC(ethane) and CC(acetylene) as suitable reference bonds ($n=1.00$ and 3.00), one obtains the intrinsic BSOs given in Table 1. For C₂, the BSO values are in the range 2.32–2.43, for which the largest value is

derived from the experimentally based local CC stretching force constant. On this scale, ethylene has a somewhat lower BSO than 2.00 (1.90; due to weakening by CH bond eclipsing), which suggests that the C_2 intrinsic bond strength is by 0.4–0.5 units larger than that of ethylene.

The electron density distribution in the bonding region should also provide a means for the intrinsic strength of a bond.^[91] Often it is assumed that electron density and energy density at the bond critical point (for the target and reference molecules of this work, always the midpoint of the CC bond) is representative of the density in the zero-flux surface and therefore an alternative means of the intrinsic bond strength. Cremer and Gauss^[91] emphasized that this can only be the case for non-polar bonds with similar density distributions in the non-bonding region and therefore a similar exponential decay in the directions perpendicular to the CC bond.

In this work, response densities were used to determine the electron and energy density at the bond critical point, $\rho_b = \rho(r_b)$ and $H_b = H(r_b)$ (see Table 1). BSO and ρ_b values of the CC bonds of the three reference molecules correlate according to a logarithmic relationship ($\rho_b = 0.350 \log(\text{BSO}) + 0.250$; $R^2 = 0.991$, MR-AQCC(8,8) calculations). Taking the C_2 value ($\rho_b = 0.324 \text{ eBohr}^{-3}$), a BSO much smaller than 2.0 results (1.7) indicating that the electron density at the bond critical point of C_2 is 0.05 eBohr^{-3} too small to indicate a bond stronger than a double bond. This confirms that the ρ_b values are just of qualitative value.^[91] A similar result is obtained when analyzing calculated energy densities H_b . We conclude that even highly correlated electron densities at the bond critical point are not suited to assess the intrinsic bond strength of C_2 , unless one integrates over the zero-flux surface or, better, the bond region, which is difficult to define.^[91]

The local stretching force constant provides so far the only direct measure for determining the intrinsic strength of the bond in C_2 . However, the reliability of the stretching force constant can be questionable in the case of diatomic molecules such as C_2 by the fact that an avoided crossing is possible, which changes the curvature of the potential energy function.^[24,25] In the following, we will determine changes in the force constant caused by an avoided crossing.

Impact of the avoided crossing on the properties of the ground state

In Figure 1, adiabatic (dashed) and diabatic (solid lines) representations of the C_2 dissociation curves of the $X^1\Sigma_g^+$ ground state and the $B^1\Sigma_g^+$ excited state as calculated at the MR-CISD+Q(8,8) level of theory are shown. There is an avoided crossing at 1.6 \AA , which changes the potential energy curve in such a way that, close to the equilibrium, it becomes broader and slightly flatter, thus invoking a somewhat smaller CC stretching force constant, which is in line with previous results.^[18,20,24,25,33] This implies that for diatomic molecules, in contrast to polyatomic molecules, stretching force constants have to be used with care when analyzing the intrinsic strength of a bond, because their values might be flawed by the effects of an avoided crossing. The observation made in

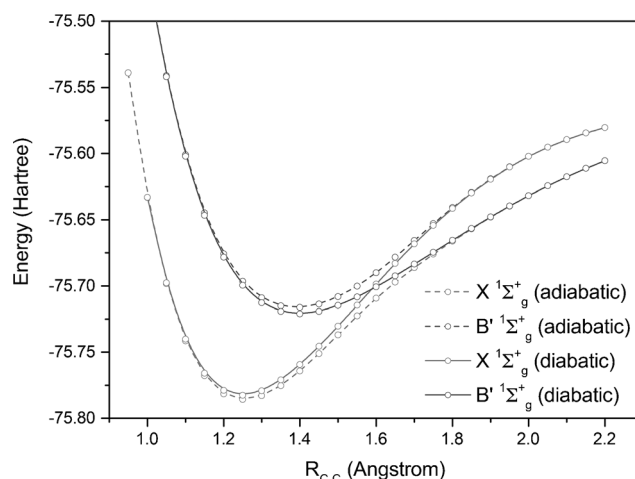


Figure 1. Adiabatic and diabatic representation of the C_2 dissociation curves of the $X^1\Sigma_g^+$ ground state (lower set, dashed line: adiabatic, full line: diabatic) and the $B^1\Sigma_g^+$ excited state (upper set, dashed line: adiabatic, full line: diabatic). The avoided crossing close to 1.6 \AA changes the value of the stretching force constant. MR-CISD+Q(8,8)/cc-pVTZ calculations.

this work is in line with the thorough investigations carried out by Shaik and co-workers^[24,25] or Sherrill and Piecuch.^[18] We have followed two different strategies to quantify the lowering of the CC stretching force constant: 1) carrying out diabatic MR-CISD+Q(8,8) calculations, which provide a potential energy curve no longer hampered by the avoided crossing,^[63,64] 2) confinement of the molecular space of C_2 , which can shift the position of the avoided crossing to higher energy values thus leading to a corrected stretching force constant. The latter approach can also be used to probe the electron density distribution of the caged molecule in different directions.

The diabatic calculations *correct* the potential energy function of the $X^1\Sigma_g^+$ ground state (Figure 1, solid curves). The dissociation curve becomes somewhat steeper, the equilibrium distance is shifted to a 0.04 \AA smaller value (1.248 \AA , Table 1), and the CC stretching force constant is corrected from 11.784 to 12.043 by $0.26 \text{ mdyn \AA}^{-1}$, which corresponds to a 0.04 increase of the BSO value to 2.36 at the MR-CISD+Q(8,8) level of theory. This implies that the experimentally based BSO value is 0.57 larger than that of ethylene, thus suggesting an intrinsic bond strength halfway between that of the CC bond in ethylene and that in acetylene. This confirms that bonding in C_2 is more complex than described by a simple MO picture, but still far away from the BSO value of a typical triple bond,^[76] let alone a quadruple bond.

Confinement of molecular space

A possibility of directly investigating the bonding situation in C_2 is given by a confinement analysis. A molecule changes its electronic structure and thereby its intrinsic bond strength under the impact of increasing space confinement. The changes in bonding can be quantitatively assessed via the local stretching force constant.^[92] Confining the space in either

z direction (σ direction: along the molecular axis) or x and y direction (π direction: perpendicular to the molecular axis, Figure 2a) leads to two basically different effects. 1) Any compression

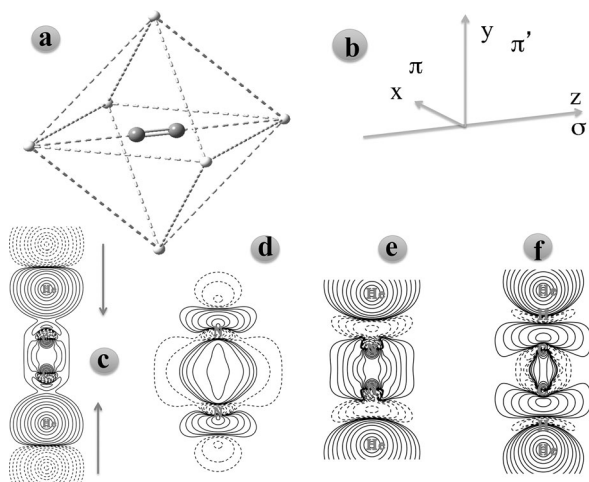


Figure 2. a) Helium cage He_6 with C_2 stretched along b) the z direction. He_6 is used to analyze electronic structure changes of C_2 , N_2 , and HCCH under the impact of space confinement. Difference density distribution $\Delta\rho(r)$ for a movement of the He-atoms in z-direction along the red arrows: c) C_2 ; e) N_2 ; f) HCCH. In the case of d) the difference density of the free N_2 molecule for a bond length reduction is shown. See text for details. Solid contour lines indicate an increase dashed contour lines a decrease of the electron density upon increased space confinement (reduced bond length). MR-CISD calculations.

sion of the electron density within the bonding region causes the bond to strengthen as the bond becomes shorter and a larger bond stretching force constant results.^[92] 2) Apart from density compression, there can be a charge transfer from the He atoms to the confined molecule where a low-lying unoccupied orbital(s) can accept negative charge. By analyzing the difference density distributions $\Delta\rho(r)$ shown in Figure 3, the orbital of X involved in the charge transfer can be identified, which is confirmed by the analysis of the fractional occupation numbers of the natural orbitals of the MR-CISD calculations.

By carrying out a confinement analysis for C_2 four objectives are pursued:

- 1) The avoided crossing is shifted as the $X^1\Sigma_g^+$ ground state and the $B^1\Sigma_g^+$ doubly excited state of C_2 are differently affected by space confinement. More information on a reliable stretching force constant is provided in this way.
- 2) Considering that up to four electron pairs are discussed in the bonding region of C_2 ground state,^[24,25,39,45] a z confinement of the CC bonding region should lead to an increase in the stretching force constant larger in magnitude than that for the NN stretching force constant of N_2 or the CC stretching force constant in HCCH.
- 3) Compression in x and y directions should move π density of C_2 from the outer into the inner bonding region. Through exchange repulsion, the σ density will be depleted, whereby the degree of depletion should provide a measure for the importance of the σ -electrons for bonding.

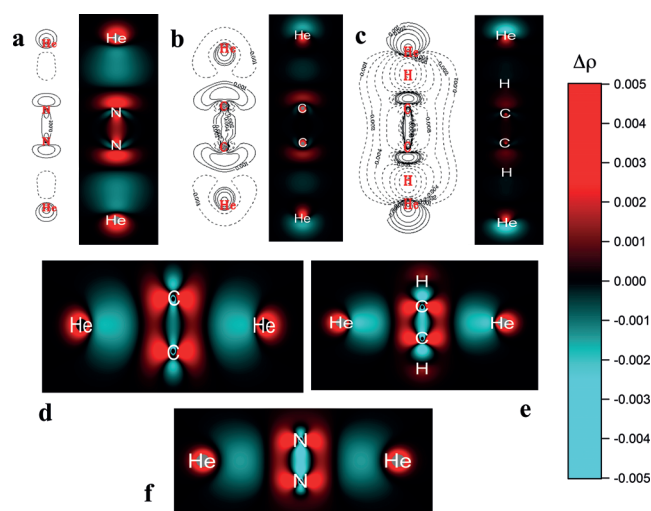


Figure 3. Calculated electron difference density distribution $\Delta\rho(r)$ showing charge transfer and polarization effects upon compression of the He_6 cage in the z direction (contour line on the left and colored diagram on the right): a) N_2 (20%), b) C_2 (20%), c) HCCH 20% and 40% and x, y directions (only colored diagrams): d) C_2 (20%), e) HCCH (20%), f) N_2 (20%). Blue color indicates a depletion of electron density, red accumulation, and black no density change (see color bar on the right). MR-CISD calculations.

- 4) Increasing space confinement should lead to a charge transfer from the He atoms to C_2 with the $3\sigma_g^+$ orbital being the suitable acceptor orbital. This should lead to a strong increase of the CC bond strength if a quadruple bond is given.

Hence, there are four reasons why space confinement can lead to improved insights into the bonding situation of the $X^1\Sigma_g^+$ ground state of C_2 .

Table 3 contains changes in geometry, stretching force constant, and charge transfer for the three confined target molecules $X = \text{C}_2$, N_2 , and HCCH. To discuss comparable values, the reduction of the van der Waals distance between the He-cage and X is given in percentage (to facilitate comparison) in cases in which an exact agreement was difficult to obtain, because bond length adjustments in the course of the geometry optimization of the confined molecule led to changes in the relative compression distances. However, relative confinement values for the analysis in Table 3 are close enough (about 40% in the z direction and 20% in the x and y directions) to make a meaningful discussion possible.

The $B^1\Sigma_g^+$ doubly excited state of C_2 has, due to the doubly occupied $3\sigma_g^+$ orbital, more density in the non-bonding region and accordingly is more sensitive to z confinement than the ground state, that is, its potential function increases more steeply for larger CC distances than that of the ground state, which shifts the avoided crossing to larger R values and reduces its influence on the value of the CC stretching force constant. At He–He distances that are 17–31% larger than the van der Waals distance, the C_2 bond length is identical to that outside the He_6 cage (1.253 Å), but its CC stretching force constant is 11.931 rather than 11.784 mdyn Å⁻¹ and thereby closer

Table 3. Changes in bond lengths ΔR , changes in stretching force constants Δk_e^a , charge transfer, and molecular orbital accepting the charge of confined N_2 , C_2 , and HCCH upon compressing the He_6 -cage in either the z or x, y directions.^[a]

Molecule	Compression direction: [value in %]	Bond	ΔR [Å]	ΔR [%]	Δk_e^a [mdyn Å ⁻¹]	Δk_e^a [%]	charge transfer [melectron]	MO accept. charge
N_2	z: 42.7	NN	-0.031	-2.8	6.712	29.8	5.5	$3\sigma_u^+$
C_2	z: 42.8	CC	-0.017	-1.3	1.710	14.3	42.6	$3\sigma_g^+$
HCCH	z: 40.2	CC	-0.008	-0.7	0.986	6.1	11.9 (-2.1)	$3\sigma_u^+$
	z: 40.2	CH	-0.020	-1.9	NA	NA	11.9 (-9.8)	$3\sigma_u^+$
N_2	x; y: 21.8	NN	-0.003	-0.3	0.205	0.9	0.5	$3\sigma_u^+$
C_2	x; y: 20.0	CC	-0.007	-0.6	0.178	1.5	2.1	$3\sigma_g^+$
HCCH	x; y: 20.0	CC	-0.004	-0.3	0.139	0.9	0.8 (7.5)	$3\sigma_u^+$
	x; y: 20.0	CH	-0.001	-0.1	NA	NA	0.8 (-8.3)	$3\sigma_u^+$

[a] MR-CISD + Q/cc-pVTZ calculations. Core orbitals are frozen.

to the diabatic value of 12.043 mdyn Å⁻¹, which confirms that the He-X interactions lead to a change in the avoided crossing.

Compression in σ direction

For 42.8% of space confinement in the z direction, the bond length of C_2 in its $^1\Sigma_g^+$ ground state shortens by 0.017 Å (1.3%) triggering an increase in the CC stretching force constant by 1.710 (14.3%) from 11.919 to 13.629 mdyn Å⁻¹ (see Supporting Information); 42.6 melectrons are transferred from each He atom in the z direction to C_2 thus increasing its density by 85.2 melectrons. The difference density plot in Figure 3 reflects the effects of charge transfer and charge polarization caused by the interaction between the He atoms and the confined molecule X. In Figure 2c–2f the effects of charge compression are illustrated in two different ways: 1) by reducing the van der Waals distance in z-direction by 40% the He atoms move toward the next atom of X as indicated by the arrows in Figure 2c, and 2) the difference density distribution $\Delta\rho(\text{cage}, r) = \rho(40\%, r) - \rho(0\%, r)$ for He atoms (depletion of density at the old He position: dashed contour lines; accumulation of density at the new He position: solid contour lines).

The increase of negative charge in the bonding region of C_2 because of space confinement is evident in Figure 2c, for N_2 in Figure 2e, or for HCCH in Figure 2f. For reasons of comparison, the difference density distribution $\Delta\rho(\text{free}, r) = [\rho(40\%, \text{free}, r) - \Sigma_i \rho(\text{atom}_i, 40\%, r)] - [\rho(0\%, r) - \Sigma_i \rho(\text{atom}_i, 0\%, r)]$ of the free N_2 molecule is plotted in Figure 2d (40% means a 40% reduction of the bond length). In this difference density, cage and geometrical effects are eliminated. One can identify regions (outer bond regions and outer lone pair regions) from where the density is moved into the inner bond and lone pair regions. As becomes evident from Figure 2e, the contraction of the bond density is stronger if the molecule is compressed in the cage as the density build up fills out a larger almost rectangular region. Accordingly, the stretching force constant is significantly larger for the confined molecule than for the free molecule.

The increase in the CC stretching force constant is connected with the bond length reduction, but also contains the ef-

fects of charge transfer from cage to endohedral molecule X. In the case of C_2 , this leads to the population of the $3\sigma_g^+$ orbital. It is evident that the He electron density is drawn into a more or less empty LUMO, so that the two He atoms in the z direction are polarized toward the inside of the cage (see, Figure 3b). The reference values calculated for the confinement and compression of N_2 , $^1\Sigma_g^+$, and HCCH, $^1\Sigma_g^+$, are listed in Table 3 and Table S1 (see Supporting Information), whereas the difference densities caused by charge transfer and polarization are shown in Figure 3. Compression in the z direction has a much stronger impact on the properties of N_2 than those of C_2 , although the charge transfer from the cage to N_2 is relatively low with $2 \times 5.5 = 11$ melectrons (into the $3\sigma_u^+$ NN antibonding MO, Figure 3). The bond length decreases by 0.031 Å (2.8%), whereas the stretching force constant increases by 6.712 from 22.504 to 29.216 mdyn Å⁻¹ (29.8%; Tables 3 and Table S1). The strong increase of the NN stretching force constant is a direct consequence of having an occupied $3\sigma_g^+$ orbital, the density of which is, to a large extent, outside the bond region and accordingly polarizes the He densities in the reverse way than C_2 does: The He density is pushed partly outside the cage, whereas N_2 density is pushed toward the N nucleus and into the bonding region (Figure 3), which leads to a substantial increase in its intrinsic bond strength. Compared to this effect, the partial population of the NN antibonding $3\sigma_u^+$ orbital plays only a small role. In the case of a compression of HCCH in z direction, the CH bonds function as puffers and a direct comparison with the situation of C_2 becomes more difficult (see Figures 2f and 3c and the Supporting Information).

There have been discussions that a third and a fourth bond in C_2 is established homolytically^[24,25,39,45] or by donor-acceptor interactions between a 2s electron pair at one C and the acceptor 2p σ orbital at the other C.^[15] The existence of significant σ -type bonding interactions increasing the C_2 bond multiplicity beyond three would lead to a density distribution in the σ region comparable to or larger than that of N_2 . Accordingly, z confinement of the CC bonding region should lead to an increase in the stretching force constant similar in magnitude to that found for the NN stretching force constant (29.8%). The relatively small increase of 14.3% for C_2 suggests that two ad-

ditional σ -bonding interactions, provided that they really exist, have little influence on the intrinsic bond strength. The correlated energy density at the CC bond critical point is in line with this result. The CC bond length of HCCH is shortened by 3.3%, but its ρ_b value is 25.5% larger than that of C_2 (CCSD(T) values; similar values are obtained for the other correlated densities of Table 1).

Compression in π direction

The π compression of all molecules investigated leads to charge transfer of just a few melectrons (4.2 for C_2 , 20% compression, Table 3) and therefore can be ignored. The CC or NN bond length decreases marginally (-0.003 to -0.007 Å, Table 3); this decrease is associated with a small increase in the stretching force constant (maximally 1.5%). Compression of the π density of C_2 leads to a shift of electron density toward the atoms (indicated by the red $2p\pi$ regions at the C atoms of Figure 3) and into the inner bond region where it leads to a depletion of σ density (blue regions in Figure 3d) as a result of exchange repulsion. Space confinement in the π direction should have the largest effects in regions in which the bond density is highest. There are six electrons in the CC bond region of acetylene and six in the bond region of N_2 . In both cases, π compression leads to comparable polarization toward the atoms as is indicated by the blue regions of charge depletion and red regions of charge accumulation. The depletion of electron density from the σ -bonding region of C_2 is significantly smaller as is indicated by the blackish-blue color in the $\Delta\rho(r)$ diagram for C_2 in Figure 3d.

For a quadruply bonded C_2 , the strongest of all π confinement effects should be expected, if there are two σ bonds besides the two π bonds. However, just a relatively weak change in the σ -electron density (indicated by a blackish-blue rather than blue color, Figure 3d to be compared with Figures 3e and 3f) is calculated for a 20% xy -compression, whereas the changes in the π region leading to an increase in the $2p\pi$ densities are comparable with those found for the π bonds of HCCH and N_2 . We conclude that the confinement analysis does not provide support for a quadruply bonded C_2 ground state with two significant σ bonds in addition to the two π bonds.

The nature of the C_2 bond

Different means have been used to describe the nature of the C_2 bond.^[15,21,24,25,39,41–43,45] In a simplified way, these can be considered as 1) orbital- or density-based, 2) (reaction) energy-based, or 3) PES (potential energy surface)-based (parameters connected with these three methods will be referred to as type 1, 2 or 3 parameters in the discussion below). Most common is the orbital-based approach where from the population of bonding and antibonding orbitals a bond order is derived.^[14] Since the electron density rather than the wavefunction (orbitals) of a molecule is an observable, various types of bond orders have been derived by using a density matrix formulation in terms of delocalized, localized, or natural orbitals^[34–37,93,94] or directly from the calculated electron density

distribution.^[95] Inherent to all bond order definitions is the attempt to distinguish between σ and π contributions to bonding and in this way predict the reactivity of a molecule (the higher the π character the more likely π additions are to occur). In the case of C_2 , a bond order of 2–3 would identify a molecule comparable in reactivity to that of acetylene, whereas a bond order of 4 would suggest extreme reactivity because breaking one of the weak σ bonds would lead to high biradical character. However, these considerations are of little use in view of a triplet state that is almost degenerate with the ground state, so that any means for intersystem crossing leads to a biradical anyway.

Martin^[21] has calculated bond orders of 3.65 to 3.99 using a single determinant approach. We calculate at the multireference level of theory significantly smaller Wiberg and Mayer bond indices of 2.799 and 2.667 (MR-CISD) as well as 2.794 and 2.663 (MR-AQCC), which underline the necessity of including both dynamic and static electron correlation effects in the calculation of any bond order.

The BDE (or the corresponding enthalpy, BDH) is a type 2 parameter to describe the nature of the chemical bond.^[96] For several decades, BDE values have been used to predict the weakest bonds in a reactant and the possible fragmentation patterns resulting therefrom. As a reaction index, the BDE value includes all changes accompanying bond cleavage, for example, the rehybridization and electron density reorganization of the fragments, spin decoupling and recoupling effects, energy changes resulting from avoided crossings, Jahn–Teller and pseudo-Jahn–Teller effects, or changes in spin-orbit coupling. It can happen that the bond order predicts multiple bonding, whereas the BDE value may be surprisingly small as a result of an avoided crossing between ground state and an excited state (see, for example, HgO, $^1\sum_0^+$ ground state^[97,98]). Since an avoided crossing is also encountered for the C_2 in its $X\ ^1\sum_g^+$ ground state, the BDE(CC) value of $144.0\text{ kcal mol}^{-1}$ (D_0 at 0 K), which has a ratio of 1.9:3 to the triple bond value of acetylene ($228.7\text{ kcal mol}^{-1}$, Table 4),^[99] might be too small because of its avoided crossing with the doubly excited state at 1.6 Å (Figure 1). Type 2 bond parameters are tools of limited value when attempting to get a deeper understanding of the nature of a chemical bond, as they focus on the dissociating molecule rather than the bond in the equilibrium situation of the molecule, which is at the focus of this and previous investigations.^[24,25]

Type 3 bond parameters are also energy-based, but in a more comprehensive manner as they relate to features of the PES in the vicinity of the global energy minimum of a given target molecule. Suitable response properties, such as the stretching force constant, can be derived by just determining the curvature of the PES in the desired direction.

Relationship between stretching force constant and intrinsic bond strength

If the PES of a polyatomic molecule in the direction of a specific bonding unit AB is modeled in an approximate way by a Morse potential as is usually done for diatomic molecules,^[100]

Table 4. Analysis of the BDE values of simple hydrocarbons.^[a]

Molecule	Bond A–B dissociated	BDE [kcal mol ⁻¹]	ΔBDE [kcal mol ⁻¹]	Predicted BDE(CC) [kcal mol ⁻¹]	ΔBDE(CC) [kcal mol ⁻¹]
C ₂ H ₆	H ₃ C–CH ₃	87.9			
	H ₃ CCH ₂ –H	99.2			
	[•] H ₂ CCH ₂ –H	34.9	64.3	152.2	–20.1
C ₂ H ₄	H ₂ C=CH ₂	172.3			
	H ₂ CCH–H	109.0			
	[•] HCCH–H	34.3	74.7	247.0	18.31
C ₂ H ₂	HC≡CH	228.7			
	HCC–H	131.7			
	[•] CC–H	112.9	18.8	247.5	103.5
C ₂	C=C, ¹ Σ _g ⁺	144.0			

[a] ΔBDE gives the difference between the first and the second CH BDE of a given hydrocarbon. Adding ΔBDE to the BDE value of the CC bond leads to a predicted BDE value of the CC bond with the next higher multiplicity, which differs by the amount ΔBDE(CC) from the measured BDE(CC) in column 3. All BDEs are measured values.^[99]

then we can formulate Equation (1), in which D_e^1 is the intrinsic BDE (IBDE) value that would be obtained if the fragments of a bond dissociation would be frozen in the geometry, orbital hybridization, and electron density distribution of the original molecule.^[101] The Morse constant a is given by Equation (2), which in turn leads to Equation (3), in which $X_e = \omega_e^a \chi_e$ is the anharmonicity constant. The local AB stretching frequency ω_e^a is related to the local stretching force constant k_e^a by^[49] [Eq. (4)], in which G_{nn} is an element of the Wilson's G-matrix for bond AB and c is the speed of light. Equations (3) and (4) can be used to derive an approximate relationship between the intrinsic bond strength and the local stretching force constant [Eq. (5)] in which $b = 1/(16\pi^2 c^2 X_e)$.

$$V(r) = D_e^1 [1 - e^{-a(r-r_e)}]^2 \quad (1)$$

$$a = \omega_e^a [2\pi^2 c G_{nn} / (D_e^1 h)]^{1/2} \quad (2)$$

$$D_e^1 = \omega_e^a / (4X_e) \quad (3)$$

$$4\pi^2 c^2 \omega_e^a = k_e^a G_{nn} \quad (4)$$

$$\text{IBDE} = D_e^1 = b k_e^a G_{nn} = b' k_e^a \quad (5)$$

The value of IBDE is significantly larger than that of the BDE, because the latter is lowered by geometry and density reorganization effects as well as other effects reducing its value. The change in the IBDE upon dissociation is easier to model by a Morse potential, because the anharmonicity effects are smaller and changes between the vibrational states are linear in the vibrational quantum number v for higher v than in the case of the potential energy $V(r)$ associated with the BDE.

The anharmonicity constant, which under normal conditions is sensitive to reorganization effects during the dissociation, is in the (geometry and electron density) frozen process for all bonds a constant as the type of interactions are now almost

electrostatic for increasing distance between the fragments. Therefore, its values can be absorbed by constant b . In the case that the same type of bonding is investigated, for example, the CC bond in ethane, ethylene, acetylene, and so forth, G_{nn} also becomes a constant^[49] and the linear relationship of [Eq. (5)] between the local stretching force constant k_e^a and the IBDE results that should be applicable for any polyatomic molecule which contains the same bond type.

In this connection, it has to be emphasized that the IBDE is not related to the in situ bond energy used by Shaik and co-workers in their investigations.^[24,25] The latter is based on a valence state of the fragment (atom), which models the electronic structure of the fragments (atoms) when bonded in a molecule. However, it does not consider the exact density distribution (polarization) that the fragments adopt in the molecule. Energetically, the electron density polarization leads to a large contribution to the IBDE that is not contained in the in situ bond energy.

The local stretching force constant describes the intrinsic bond strength and can be used instead of the so far inaccessible IBDE. Since it probes the bond for an infinitesimal change in the geometry it does not imply any electronic structure change and accordingly does not include any of the effects encountered for an increase of the bond length during dissociation. Therefore, it is directly related to the thermochemical stability of a molecule and can be used to compare the intrinsic strength of the same bond type occurring in different molecules. For C₂, it suggests an intrinsic bond strength of about 2.5, which is difficult to bring in line with a quadruply bonded molecule.

Evidence for quadruple bonding from CH bond dissociation energies

One major argument in favor of a quadruple bond in C₂ is the fact that the C–H BDE of acetylene is 131.7 kcal mol⁻¹, whereas that of the ethynyl radical is 112.9 kcal mol⁻¹ (Table 4 lists all relevant experimental BDE values^[99]) suggesting that a fourth bond in C₂ adds 18.8 kcal mol⁻¹ to its BDE.^[25] Following this line of argument, the available C–H BDE values listed in Table 4 would suggest that the π bond in ethylene adds 64.3 and the second π bond in acetylene 74.7 kcal mol⁻¹ thus leading to CC BDE values that are either too small (–20.1 kcal mol⁻¹ for ethane) or too large (18.3 kcal mol⁻¹ for acetylene). It is evident that the radicals generated in the first CH dissociation process are more (ethyl radical) or less stabilized by hyperconjugation (vinyl radical) or in the case of the ethynyl radical not at all.

Since the BDE values depend on the strength of the CH bond being broken (increasing from ethane to acetylene because of the increase in s character from sp^3 to sp) and the possibilities of the fragment to stabilize by electronic structure reorganization, the 18.8 kcal mol⁻¹ difference between the CH BDE values of acetylene can be either due to the stabilization of C₂ or the destabilization (lack of stabilization possibilities) of the ethynyl radical. In view of the fact that there is no simple relationship between BDE and IBDE values and reorganization

energies of the fragments cannot be measured or calculated, it is not useful to speculate on the intrinsic strength of any bond using BDE values or differences of BDE values.

Using Badger's rule to rationalize bonding in C₂

As mentioned in the previous section, C₂ does not fulfill the force-constant–bond-length relationship established for the reference CC bonds in ethane, ethylene, acetylene, and many hydrocarbons as shown in previous work.^[55,77,102] The force constant of C₂ is too small by 1.199 mdyn Å⁻¹, which could be associated with the avoided crossing between the X¹Σ_g⁺ ground state and the B¹Σ_g⁺ excited state (Figure 1), for which we disregard, for the moment, the results of the diabatic potential energy calculations presented in Table 1 and Figure 1. If the CC stretching force constant is increased by 1.199 mdyn Å⁻¹ to 13.360 mdyn Å⁻¹ so that it fulfills the $k_e^a = f(r_e)$ relationship for small hydrocarbons, the corresponding BSO value would raise to 2.62, which does not change the basic result of this work.

The question remains whether the Badger relationship (originally formulated for diatomic molecules^[46,48]) still holds for polyatomic molecules. Cremer and co-workers have formulated a generalized Badger rule, which is based on local stretching force constants and bond lengths.^[48,76] Here, we will show that a generalized Badger rule can be substantiated when introducing as suggested by Badger an effective bond length that measures the distance from atom to atom excluding impenetrable core regions.^[46,47,103] For this purpose, the Morse potential of Equation (1) has to be modified to fulfill the following conditions:

1) The potential energy V must approach infinity for $r \rightarrow 0$, which can be enforced by introducing a hard-sphere distance r_a , which leads to $V(r < r_a) = \infty$. 2) V , when measured relative to the separated atoms A and B, must approach zero for $r \rightarrow 0$. 3) V must approach the value of D_e for $r \rightarrow r_e$. The potential given in Equations (6) and (7) fulfills these conditions. One can use Equation (7) to derive a relationship between the local stretching frequency ω_e^a of a diatomic fragment AB and its bond length r_e [Eq. (8)]. Taking the derivative with regard to k_e^a leads to Equations (9) and (10):

$$V(r > r_a) = D_e^l (1 - e^{-a_e(r-r_e)})^2 - D_e^l \quad (6)$$

$$V(r_a) = V_a = D_e^l (1 - e^{-a_e(r-r_e)})^2 - D_e^l \quad (7)$$

$$(r_e - r_a)\omega_e^a = 2\hbar(D_e^l/2G_{nn})^{1/2} \ln \left[1 + (V_a/D_e^l + 1)^{1/2} \right] \quad (8)$$

$$\frac{\partial(r_e - r_a)}{\partial k_e^a} = \frac{\partial(r_e - r_a)}{\partial \omega_e^a} \frac{\partial \omega_e^a}{\partial k_e^a} = \frac{\omega_e^a}{k_e^a} \frac{\partial(r_e - r_a)}{\partial \omega_e^a} \quad (9)$$

$$\frac{\partial(r_e - r_a)}{\partial k_e^a} = \frac{(-V_a/\hbar)(2\mu X_e)^{1/2}}{(k_e^a)^2 [(4V_a X_e \mu / \hbar^2 k_e^a) + 1]^{1/2} \{ 1 + [(4V_a X_e \mu / \hbar^2 k_e^a) + 1] \}^{1/2}} \quad (10)$$

For the case that k_e^a is large, the derivative of Equation (10) varies with $(k_e^a)^{-2}$, if the force constant is small with $(k_e^a)^{-1}$, and otherwise with $(k_e^a)^{-p}$ for $1 < p < 2$. By this all possibilities of the generalized Badger equation^[48,76] [Eq. (11)] ($r_e - r_a$ is the effective bond length) are accounted for as becomes evident when calculating the derivative of Equation (11), which leads to Equation (12):

$$k_e^a (r_e - r_a)^p = \text{const} \quad (11)$$

$$\frac{\partial(r_e - r_a)}{\partial k_e^a} = (k_e^a)^{-(1+1/p)} \quad (12)$$

Again, the exponent is between -1 and -2 depending on the value of p . The lack of a predetermined exponent p depending on the atomic number and the charges of A and B indicates that the generalized Badger rule can only be quantitatively fulfilled for closely related bonds, whereas in other cases it is only qualitatively fulfilled. In the case of C₂, it may be used to determine an upper bound for its intrinsic bond strength, which turns out to be 2.62.

Conclusions

This work has presented different ways of determining the intrinsic strength of the chemical bond in C₂ in its ¹Σ_g⁺ ground state.

- 1) The intrinsic bond strength order of C₂ as measured by the (local) stretching force constants ranges from 2.35 to 2.43 depending on whether MR-AQCC(8,8), MR-CISD + Q(8,8), CCSD(T), or experimentally based force constants are used. The BSO values are reliable because all reference values (also the experimental ones) are based on mode-decoupled local vibrational modes, which lead to the correct local force constants.
- 2) The influence of the avoided crossing between the X¹Σ_g⁺ ground state and the B¹Σ_g⁺ excited state has been determined to increase the CC stretching force constant by just 0.259 mdyn Å⁻¹ from 11.784 to 12.043 mdyn Å⁻¹ according to diabatic calculations. Utilizing an empirical method based on the generalized Badger rule, the upper limit for the CC stretching force constants has been found to be 13.360 mdyn Å⁻¹, corresponding to a maximal BSO value of 2.61.
- 3) Wiberg and Mayer bond orders calculated at the multireference level of theory are significantly smaller (2.8 and 2.7, respectively) than those obtained at the single determinant level (3.7–4.0), thus underlining the necessity of including both dynamic and nondynamic electron correlation effects in the calculation.
- 4) A confinement analysis based on encaging C₂, N₂, and HCCH in He-cages and then reducing the available space along the molecular axis (z or σ direction) and perpendicular to it (xy , or π direction) provides no indication for CC triple or even quadruple bonding. For a comparable compression in the z direction, the local force constants ob-

tained by MR-CISD+Q calculations reveal a 29.8% increase for N_2 , but only 14.3% for C_2 despite the fact that the bonding $3\sigma_g^+$ orbital of the latter becomes populated by 86 melectrons, whereas 11 melectrons are transferred to the antibonding $3\sigma_u^+$ orbital of N_2 .

- 5) Difference density studies carried out for MR-CISD densities with and without space confinement in the π direction indicate that the σ -bonding region of C_2 is less densely populated as in the case of CC region of acetylene, which excludes the possibility of significant bonding by two σ -electron pairs (or donor-acceptor interactions^[15] between a 2s-electron pair at one C and an acceptor $2p\sigma$ orbital at the other C or, alternatively, two $2s^1-2p\sigma^1$ interactions).
- 6) The analysis of the CH BDE values for ethane, ethylene, and acetylene does not provide a convincing argument in favor of the existence of a quadruple bond with an intrinsic bond strength of 15–20 kcal mol⁻¹.
- 7) An analysis of correlated electron and energy densities based on MR-AQCC(8,8), MR-CISD+Q(8,8), and CCSD(T) calculations does not support a fully established triple or weak quadruple bond in the $X^1\Sigma_g^+$ ground state of C_2 .
- 8) A linear relationship between the intrinsic BDE and the local stretching force constants has been derived that is based on a Morse potential.
- 9) Application possibilities and limits of the generalized Badger rule for polyatomic molecules have been analyzed for the use of local stretching force constants and an effective bond length, which is based on suitable atomic core radii r_a .

Most results and arguments discussed in this work concern the intrinsic bond strength and the BSO-derived therefrom (apart from the Wiberg/Mayer bond order calculations). Such an analysis cannot confirm or exclude the possibility of a quadruple bond derived from the form of a VB or FCI wavefunction of C_2 . There may be a fourfold overlap in dicarbon and the arguments in favor of a quadruply bonded C_2 molecule might have their basic value in the light of bonding theory. The analysis carried out in this work considers the question whether the postulated quadruple bond has any relevance for the measurable bond properties, such as bond length, stretching frequency, and force constant; electron density; and BDE values. We come to the conclusion that this is not the case and that C_2 can be described as molecule with a bond halfway between that of ethylene and acetylene, which can be seen as a reflection of its multireference character.

The study of bonding in C_2 has led to interesting follow-up questions such as how the IBDE can be directly calculated or what is a systematic way of deriving effective bond lengths. Utilizing the methods of modern quantum chemistry we are able to answer these questions, which will be reported elsewhere.

One of the referees has given arguments in favor of a quadruple bond: 1) The electron density distribution in the bond region can underestimate the degree of σ bonding. 2) The Mayer bond order may be too small because of a too large influence of the $2\sigma_u^+$ orbital. 3) Reduced density matrix (RDM)

calculations obtained with the PNO5 functional suggest a bond order of 3.5.^[41] As for argument 1), we have analyzed the electron density and the energy density (see Table 1), which both suggest a bond order lower than 3. 2) The Mayer bond index has been calculated in this work for natural orbitals and a correlation corrected density matrix at the MR-AQCC and MR-CISD levels of theory. This should correct an improper balance of bonding and antibonding MOs at the HF level. 3) Any approximate functional based on the RDM methodology has the problem of including both dynamical and non-dynamical correlation in a well-specified manner. So far it is not clear how this is accomplished by the PNO5 functional.^[41]

Acknowledgements

We thank G. Frenking, University Marburg, for useful comments. This work was financially supported by the National Science Foundation, Grant CHE 1152357. We thank SMU for providing computational resources. We acknowledge useful comments on our manuscript given by two unknown referees.

Keywords: ab initio calculations · bond strength · carbon · force constants · quadruple bonds · space confinement analysis

- [1] R. F. Verner, C. Benvegna, *Handbook on Fullerenes: Synthesis Properties, Applications*, Nova Science, New York, 2012.
- [2] T. Yamada, T. Namai, K. Hata, D. N. Futaba, K. Mizuno, J. Fan, M. Yudasaka, M. Yumura, S. Iijima, *Nat. Nanotechnol.* **2006**, *1*, 131–136.
- [3] P. W. Dunk, N. K. Kaiser, C. L. Hendrickson, J. P. Quinn, C. P. Ewels, Y. Nakanishi, Y. Sasaki, H. Shinohara, A. G. Marshall, H. W. Kroto, *Nat. Commun.* **2012**, *3*, 855.
- [4] A. S. King, R. T. Birge, *Astrophys. J.* **1930**, *72*, 19–40.
- [5] A. Brockhinke, M. Letzgus, S. Rinne, K. Kohse-Höinghaus, *J. Phys. Chem. A* **2006**, *110*, 3028–3035.
- [6] O. Sorkhabi, V. M. Blunt, H. Lin, M. F. A'Hearn, H. A. Weaver, C. Arpigny, W. M. Jackson, *Planet. Space Sci.* **1997**, *45*, 721–730.
- [7] P. S. Skell, J. H. Plonka, *J. Am. Chem. Soc.* **1970**, *92*, 5620–5624.
- [8] P. S. Skell, F. A. Fagone, K. J. Klabunde, *J. Am. Chem. Soc.* **1972**, *94*, 7862–7866.
- [9] K. J. McDonald, A. D. Buettner, B. J. Petro, R. W. Quandt, *Chem. Phys. Lett.* **2008**, *464*, 26–30.
- [10] A. Van Orden, R. J. Saykally, *Chem. Rev.* **1998**, *98*, 2313–2357.
- [11] K. P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure, IV: Constants of Diatomic Molecules*, Van Nostrand, New York, 1979.
- [12] W. Weltner, R. J. Van Zee, *Chem. Rev.* **1989**, *89*, 1713–1747.
- [13] M. Martin, *J. Photochem. Photobiol. A* **1992**, *66*, 263–289.
- [14] T. A. Albright, J. K. Burdett, M. H. Whangbo, *Orbital Interactions in Chemistry*, Wiley, New York, 1985.
- [15] G. Frenking, M. Hermann, *Angew. Chem. Int. Ed.* **2013**, *52*, 5922–5925; *Angew. Chem.* **2013**, *125*, 6036–6039.
- [16] P. R. T. Schipper, O. V. Gritsenko, E. J. Baerends, *Theor. Chem. Acc.* **1998**, *99*, 329–343.
- [17] J. D. Watts, R. J. Bartlett, *J. Chem. Phys.* **1992**, *96*, 6073–6084.
- [18] C. D. Sherrill, P. Piecuch, *J. Chem. Phys.* **2005**, *122*, 124104.
- [19] D. I. Lyakh, V. V. Ivanov, L. Adamowicz, *J. Chem. Phys.* **2008**, *128*, 074101.
- [20] D. Datta, L. Kong, M. Nooijen, *J. Chem. Phys.* **2011**, *134*, 214116.
- [21] J. M. L. Martin, *Mol. Phys.* **2014**, *112*, 785–793.
- [22] M. L. Abrams, C. D. Sherrill, *J. Chem. Phys.* **2004**, *121*, 9211–9219.
- [23] L. Bytautas, K. Ruedenberg, *J. Chem. Phys.* **2005**, *122*, 154110.
- [24] S. Shaikh, D. Danovich, W. Wu, P. Su, H. S. Rzepa, P. C. Hiberty, *Nat. Chem.* **2012**, *4*, 195–200.

- [25] D. Danovich, P. C. Hiberty, W. Wu, H. S. Rzepa, S. Shaik, *Chem. Eur. J.* **2014**, *20*, 6220–6232.
- [26] A. D. Pradhan, H. Partridge, C. W. J. Bauschlicher, *J. Chem. Phys.* **1994**, *101*, 3857–3861.
- [27] T. Müller, M. Dallos, H. Lischka, Z. Dubrovay, P. G. Szalay, *Theor. Chem. Acc.* **2001**, *105*, 227–243.
- [28] U. S. Mahapatra, S. Chattopadhyay, R. K. Chaudhuri, *J. Chem. Phys.* **2008**, *129*, 024108.
- [29] W. Jiang, A. K. Wilson, *J. Chem. Phys.* **2011**, *134*, 034101.
- [30] G. H. Booth, D. Cleland, A. J. W. Thom, A. Alavi, *J. Chem. Phys.* **2011**, *135*, 084104.
- [31] D. Cleland, G. H. Booth, C. Overy, A. Alavi, *J. Chem. Theory Comput.* **2012**, *8*, 4138–4152.
- [32] G. Gidofalvi, D. A. Mazziotti, *J. Chem. Phys.* **2005**, *122*, 194104.
- [33] S. Sharma, *J. Chem. Phys.* **2015**, *142*, 024107.
- [34] K. Wiberg, *Tetrahedron* **1968**, *24*, 1083–1096.
- [35] I. Mayer, *Chem. Phys. Lett.* **1983**, *97*, 270–274.
- [36] I. Mayer, *Int. J. Quantum Chem.* **1986**, *29*, 477–483.
- [37] I. Mayer, *J. Comput. Chem.* **2007**, *28*, 204–221.
- [38] H. S. Rzepa, accessed on 2011-06-04. See <http://www.ch.imperial.ac.uk/rzepa/blog/?p=3065> (Archived by WebCite at <http://www.webcitation.org/5zBSjBjhm>).
- [39] S. Shaik, H. S. Rzepa, R. Hoffmann, *Angew. Chem. Int. Ed.* **2013**, *52*, 3020–3033; *Angew. Chem.* **2013**, *125*, 3094–3109.
- [40] J. Grunenberg, *Nat. Chem.* **2012**, *4*, 154–155.
- [41] J. M. Matxain, F. Ruiperez, I. Infante, X. Lopez, J. M. Ugalde, G. Merimo, M. Piris, *J. Chem. Phys.* **2013**, *138*, 151102.
- [42] L. T. Xu, T. J. Dunning, *J. Chem. Theory Comput.* **2014**, *10*, 195–201.
- [43] D. Cooper, F. E. Penotti, R. Ponec, *Comput. Theor. Chem.* **2015**, *1053*, 189–194.
- [44] M. Hermann, G. Frenking, *Chem. Eur. J.* **2016** 10.1002/chem.201503762.
- [45] D. Danovich, S. Shaik, H. S. Rzepa, R. Hoffmann, *Angew. Chem. Int. Ed.* **2013**, *52*, 5926–5928; *Angew. Chem.* **2013**, *125*, 6040–6042.
- [46] R. M. Badger, *J. Chem. Phys.* **1934**, *2*, 128–131.
- [47] R. M. Badger, *J. Chem. Phys.* **1935**, *3*, 710–715.
- [48] E. Kraka, J. A. Larsson, D. Cremer in *Computational Spectroscopy: Methods, Experiments and Applications* (Ed.: J. Grunenberg), Wiley, New York, **2010**, pp. 105–149.
- [49] Z. Konkoli, D. Cremer, *Int. J. Quantum Chem.* **1998**, *67*, 1–9.
- [50] W. Zou, R. Kalescky, E. Kraka, D. Cremer, *J. Chem. Phys.* **2012**, *137*, 084114.
- [51] W. Zou, D. Cremer, *Theor. Chem. Acc.* **2014**, *133*, 1451.
- [52] D. Cremer, E. Kraka, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 627–628; *Angew. Chem.* **1984**, *96*, 612–614.
- [53] D. Cremer, E. Kraka, *Croat. Chem. Acta* **1984**, *57*, 1259–1281.
- [54] E. B. Wilson, J. C. Decius, P. C. Cross, *Molecular Vibrations*, McGraw-Hill, New York, **1955**.
- [55] D. Cremer, E. Kraka in *Theoretical and Computational Chemistry, Vol. 5, Theoretical Organic Chemistry* (Ed.: C. Parkanyi), Elsevier, Amsterdam, **1998**, pp. 259–327.
- [56] K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479–483.
- [57] V. Barone, *J. Chem. Phys.* **2005**, *122*, 014108.
- [58] P. G. Szalay, R. J. Bartlett, *Chem. Phys. Lett.* **1993**, *214*, 481–488.
- [59] H.-J. Werner, P. J. Knowles, *Theor. Chim. Acta* **1990**, *78*, 175–187.
- [60] H.-J. Werner, P. Knowles, *J. Chem. Phys.* **1988**, *89*, 5803–5814.
- [61] P. Knowles, H.-J. Werner, *Chem. Phys. Lett.* **1988**, *145*, 514–522.
- [62] S. R. Langhoff, E. R. Davidson, *Int. J. Quantum Chem.* **1974**, *8*, 61–72.
- [63] T. Pacher, L. S. Cederbaum, K. Köppel, *J. Chem. Phys.* **1988**, *89*, 7367–7381.
- [64] H. J. Werner, B. Follmeg, M. H. Alexander, *J. Chem. Phys.* **1988**, *89*, 3139–3151.
- [65] C. Hampel, K. Peterson, H.-J. Werner, *Chem. Phys. Lett.* **1992**, *190*, 1–12.
- [66] M. J. O. Deegan, P. J. Knowles, *Chem. Phys. Lett.* **1994**, *227*, 321–326.
- [67] K. Raghavachari, J. A. Pople, E. S. Replogle, M. Head-Gordon, N. C. Handy, *Chem. Phys. Lett.* **1990**, *167*, 115–121.
- [68] R. J. Bartlett, J. D. Watts, S. A. Kucharski, J. Noga, *Chem. Phys. Lett.* **1990**, *165*, 513–522.
- [69] M. Kállay, P. R. Surján, *J. Chem. Phys.* **2001**, *115*, 2945–2954.
- [70] Y. J. Bomble, J. F. Stanton, M. Kállay, J. Gauss, *J. Chem. Phys.* **2005**, *123*, 054101.
- [71] G. E. Scuseria, *J. Chem. Phys.* **1991**, *94*, 442–447.
- [72] J. Gauss, J. F. Stanton, *Chem. Phys. Lett.* **1997**, *276*, 70–77.
- [73] T. H. Dunning, *J. Chem. Phys.* **1989**, *90*, 1007–1023.
- [74] D. Woon, T. J. Dunning, *J. Chem. Phys.* **1994**, *100*, 2975–2988.
- [75] *Handbook of Chemistry and Physics*, 90th ed. (Ed.: D. R. Lide), CRC, Boca Raton, **2009**.
- [76] R. Kalescky, E. Kraka, D. Cremer, *J. Phys. Chem. A* **2013**, *117*, 8981–8995.
- [77] W. Zou, R. Kalescky, E. Kraka, D. Cremer, *J. Mol. Model.* **2013**, *19*, 2865–2877.
- [78] M. E. Jacox in *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69 (Eds.: P. J. Linstrom, W. G. Mallard), National Institute of Standards and Technology, Gaithersburg MD, 20899, <http://webbook.nist.gov>.
- [79] NIST Computational Chemistry Comparison and Benchmark Database, NIST Standard Reference Database Number 101, Release 16a (Ed.: R. D. Johnson III), August **2013**, <http://cccbdb.nist.gov/>.
- [80] T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580–592.
- [81] CFOUR, Coupled-Cluster techniques for Computational Chemistry, a quantum-chemical program package by J. F. Stanton, J. Gauss, M. E. Harding, P. G. Szalay with contributions from A. A. Auer, R. J. Bartlett, U. Benedikt, C. Berger, D. E. Bernholdt, Y. J. Bomble, L. Cheng, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W. J. Lauderdale, F. Lipparini, D. A. Matthews, T. Metzroth, L. A. Mück, D. P. O'Neill, D. R. Price, E. Prochnow, C. Puzzarini, K. Ruud, F. Schiffrmann, W. Schwabach, C. Simmons, S. Stopkovicz, A. Tajti, J. Vázquez, F. Wang, J. D. Watts and the integral packages MOLECULE (J. Almlöf, P. R. Taylor), PROPS (P. R. Taylor), ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, J. Olsen), and ECP routines by A. V. Mitin, C. van Wüllen. For the current version, see <http://www.cfour.de>.
- [82] Z. Rolik, L. Szegedy, I. Ladjászki, B. Ladóczki, M. Kállay, *J. Chem. Phys.* **2013**, *139*, 094105.
- [83] MRCC, a quantum chemical program suite written by M. Kállay, Z. Rolik, J. Csontos, I. Ladjászki, L. Szegedy, B. Ladóczki, G. Samu. See <http://www.mrcc.hu>.
- [84] ACES II is a program product of the Quantum Theory Project, University of Florida. Authors: J. F. Stanton, J. Gauss, S. A. Perera, J. D. Watts, A. D. Yau, M. Nooijen, N. Oliphant, P. G. Szalay, W. J. Lauderdale, S. R. Gwaltney, S. Beck, A. Balková, D. E. Bernholdt, K. K. Baeck, P. Rozyczko, H. Sekino, C. Huber, J. Pittner, W. Cencek, D. Taylor, R. J. Bartlett. Integral packages included are VMOL (J. Almlöf, P. R. Taylor); VPROPS (P. Taylor); ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, J. Olsen, P. R. Taylor); HONDO/GAMESS (M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. J. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, J. A. Montgomery).
- [85] H. J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz et al., MOLPRO, version 2010.1, a package of ab initio programs. **2010**, see <http://www.molpro.net>.
- [86] E. Kraka, W. Zou, M. Filatov, J. Grafenstein, D. Izotov, J. Gauss, Y. He, A. Wu, V. Polo, L. Olsson, Z. Konkoli, Z. He, Cremer, D. COLOGNE2015. **2015**, Southern Methodist University, Dallas, TX.
- [87] W. Zou, D. Nori-Shargh, J. E. Boggs, *J. Phys. Chem. A* **2013**, *117*, 207–212.
- [88] J. Cioslowski, G. Liu, A. M. Castro, *Chem. Phys. Lett.* **2000**, *331*, 497–501.
- [89] R. Kalescky, E. Kraka, D. Cremer, *Int. J. Quantum Chem.* **2014**, *114*, 1060–1072.
- [90] R. Kalescky, W. Zou, E. Kraka, D. Cremer, *J. Phys. Chem. A* **2014**, *118*, 1948–1963.
- [91] D. Cremer, J. Gauss, *J. Am. Chem. Soc.* **1986**, *108*, 7467–7477.
- [92] R. Kalescky, E. Kraka, D. Cremer, *J. Phys. Chem. A* **2014**, *118*, 223–237.
- [93] J. Cioslowski, S. Mixon, *J. Am. Chem. Soc.* **1991**, *113*, 4142–4145.
- [94] E. D. Glendening, J. K. Badenhop, F. Weinhold, *J. Comput. Chem.* **1998**, *19*, 628–646.
- [95] R. F. W. Bader, T. S. Slee, D. Cremer, E. Kraka, *J. Am. Chem. Soc.* **1983**, *105*, 5061–5068.
- [96] Y.-R. Luo, *Comprehensive Handbook of Chemical Bond Energies*, Taylor & Francis, Boca Raton, FL, **2007**.
- [97] M. Filatov, D. Cremer, *ChemPhysChem* **2004**, *5*, 1547–1557.

- [98] K. Peterson, B. C. Shepler, J. M. Singleton, *Mol. Phys.* **2007**, *105*, 1139–1154.
- [99] B. Ruscic, *J. Phys. Chem. A* **2015**, *119*, 7810–7837.
- [100] G. Herzberg, *Molecular Spectra and Molecular Structure, I: Spectra of Diatomic Molecules*, Van Nostrand, New York, **1950**.
- [101] D. Cremer, A. Wu, A. Larsson, E. Kraka, *J. Mol. Model.* **2000**, *6*, 396–412.
- [102] A. Humason, W. Zou, D. Cremer, *J. Phys. Chem. A* **2015**, *119*, 1666–1682.
- [103] D. J. Swanton, B. R. Henry, *J. Chem. Phys.* **1987**, *86*, 4801–4807.

Received: September 17, 2015


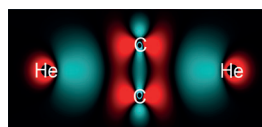
Revised: November 20, 2015

Published online on ■ ■ ■, 0000

FULL PAPER

Carbon

W. Zou, D. Cremer*

 **C₂ in a Box: Determining Its Intrinsic Bond Strength for the X¹Σ_g⁺ Ground State***Quadruple or not
to quadruple
the bond*

The C₂ conundrum—a never-ending story: Multireference-coupled cluster calculations of free and confined dicarbon, C₂, lead to a bond strength order of 2.5 relative to that of ethane according to adiabatic/diabatic calculations and local stretching force constants.

Electron density and energy density together with Wiberg and Mayer bond indices, all determined at the multireference level, suggest a bond multiplicity lower than 3 in line with the bond strength order.