

How to Estimate the Number of Bonds in 2nd row Diatomic Molecules from Excited State Potential Energy Curves: A Theoretical Treatise



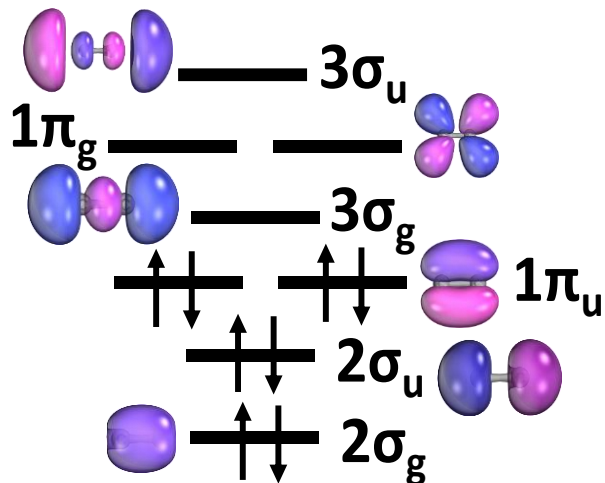
Indian Association for the
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Kolkata, India

Ishita Bhattacharjee
School of Chemical Sciences

Bonding Nature of Dicarbon: C₂

Multiple Bonding in C₂

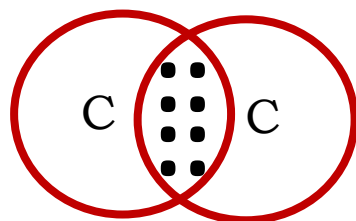
Molecular Orbital Diagram



Bond order=2.0

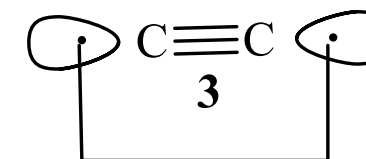
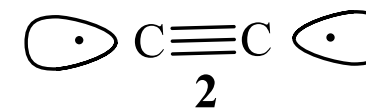
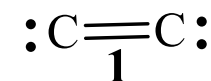
Two π bonds,
 no σ bonds

Lewis Pairing



Four Bonds

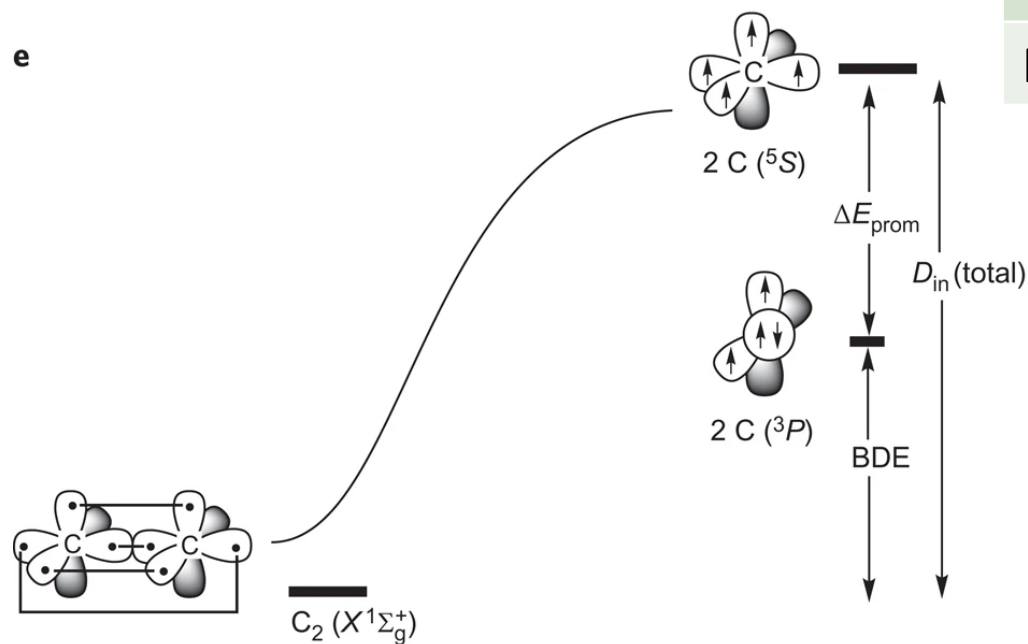
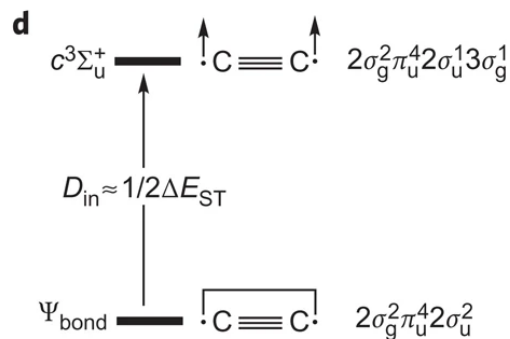
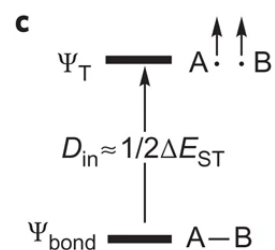
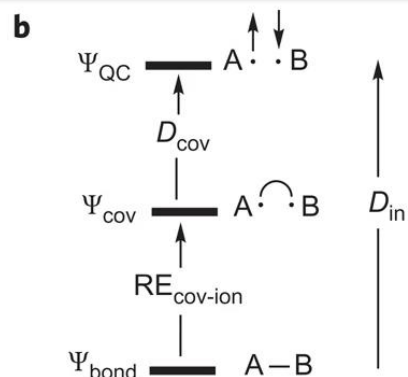
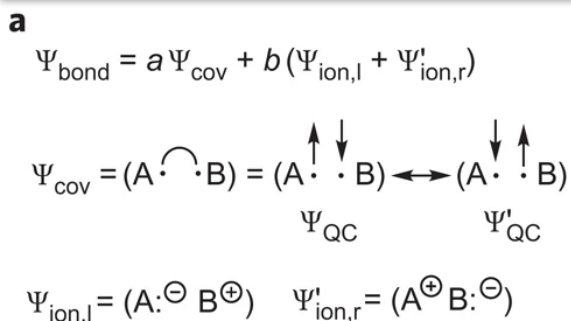
VB Picture sp hybridization



Outwardly pointing
 electrons results in
 the fourth bond

Bonding Nature of Dicarbon: C₂

The Case of Quadruple Bonding in C₂



Values of in situ bond energies for the fourth bond in kcal/mol

Method	C ₂
VBSCF/6-31G*	14.30
VBSCF/6-31G* (1/2ΔE _{ST})	11.64
FCI/6-31G*	14.80

BN and CN⁺
 isoelectronic to C₂ were
 predicted to have the Q
 Bond


The Quadruple Bonding Conundrum of C_2

An Ongoing Debate

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OPINION

The name's (quadruple) bond?

BY PHILIP BALL | 13 MAY 2013

Philip Ball discusses the contentious issue of C_2 bonding. [Drew's draw](#)
four lines ?

“This seems unlikely to be the last word. It makes one wonder about the current understanding of chemical bonding that there is not even a consensus about this apparently simple molecule. That is not to say that the tools are inadequate; rather, they merely have different virtues.”

Why “Quadruple Bonding in C₂” is Counterintuitive

	Quadratic force constant (mdyn Å ⁻¹)	Vibrational frequency of C-C stretching mode (cm ⁻¹)
C ₂ (ground state)	12.18	1855
Acetylene	15.80	1974

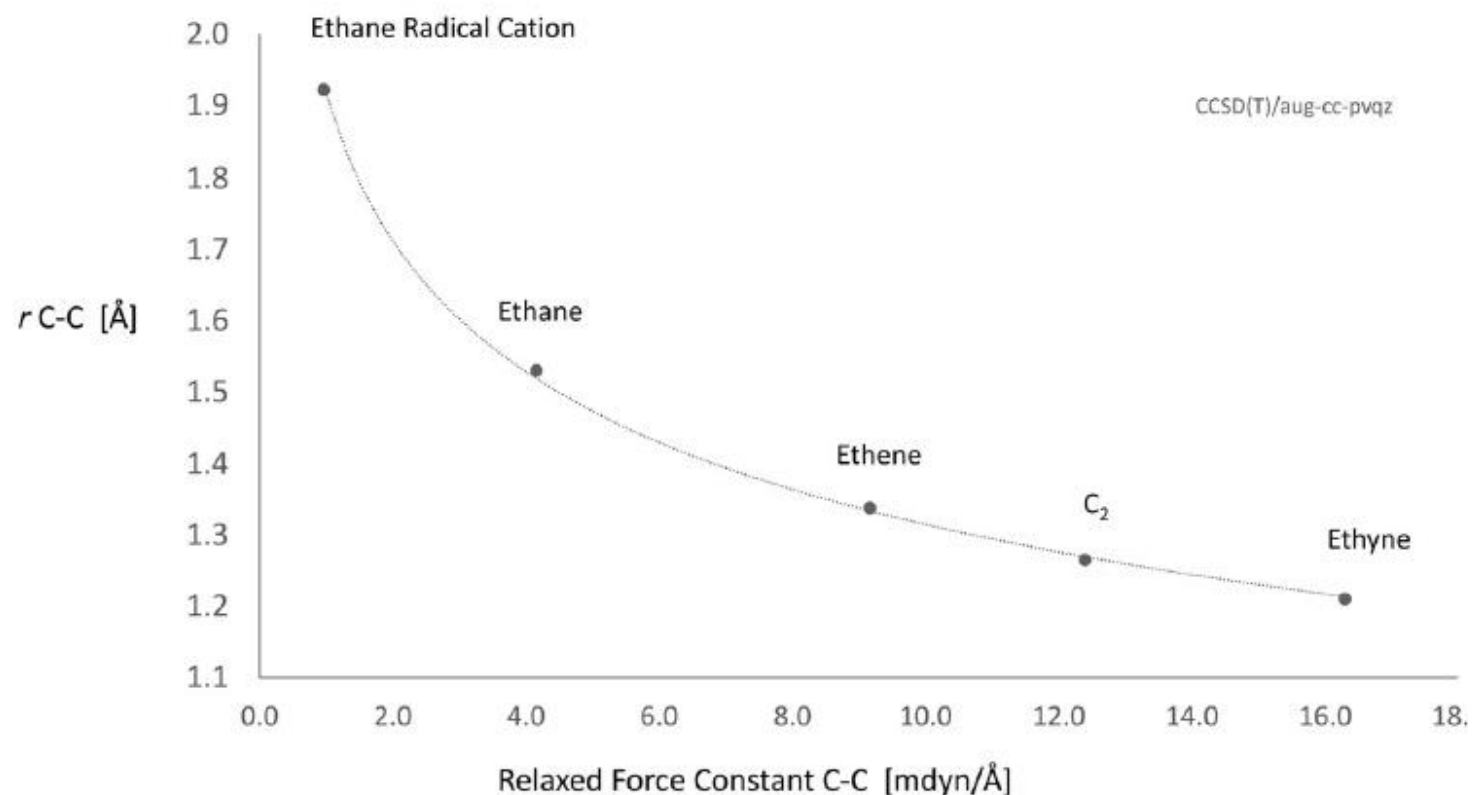
The values indicate bonding in C₂ is weaker compared to acetylene



Frenking, G. et al. *Angew. Chem. Int. Ed.* **2013**, 52, 5922; Piris, M. et al. *Chem. Eur. J.* **2016**, 22, 4109

[https://www.chemistryviews.org/details/ezone/9017541/Why Does C2 Cause so Many Problems.html](https://www.chemistryviews.org/details/ezone/9017541/Why_Does_C2_Cause_so_Many_Problems.html)

Why “Quadruple Bonding in C₂” is Counterintuitive



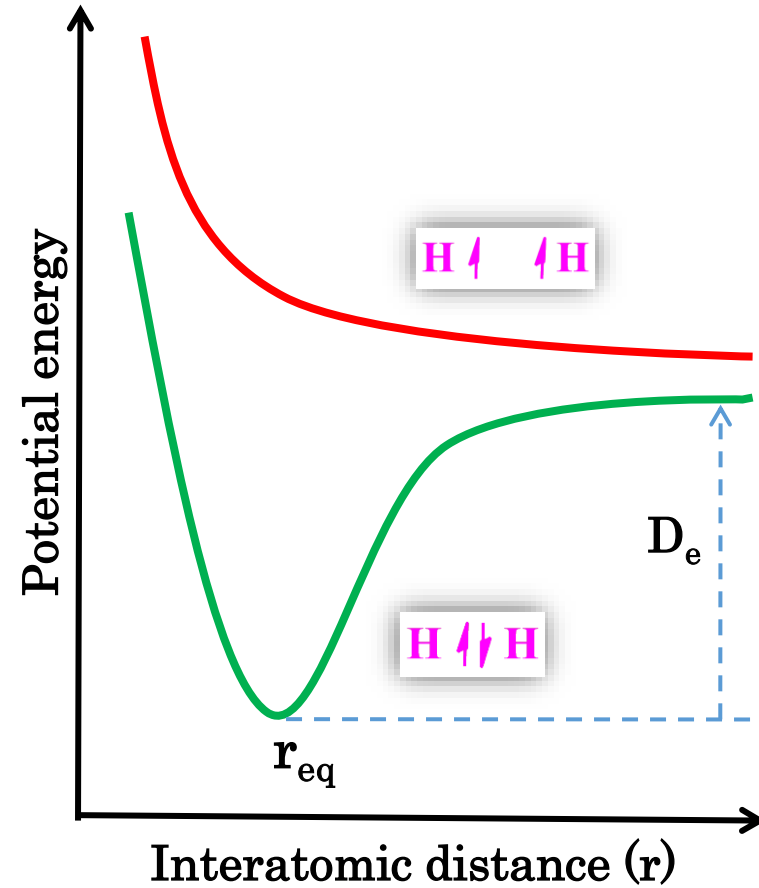
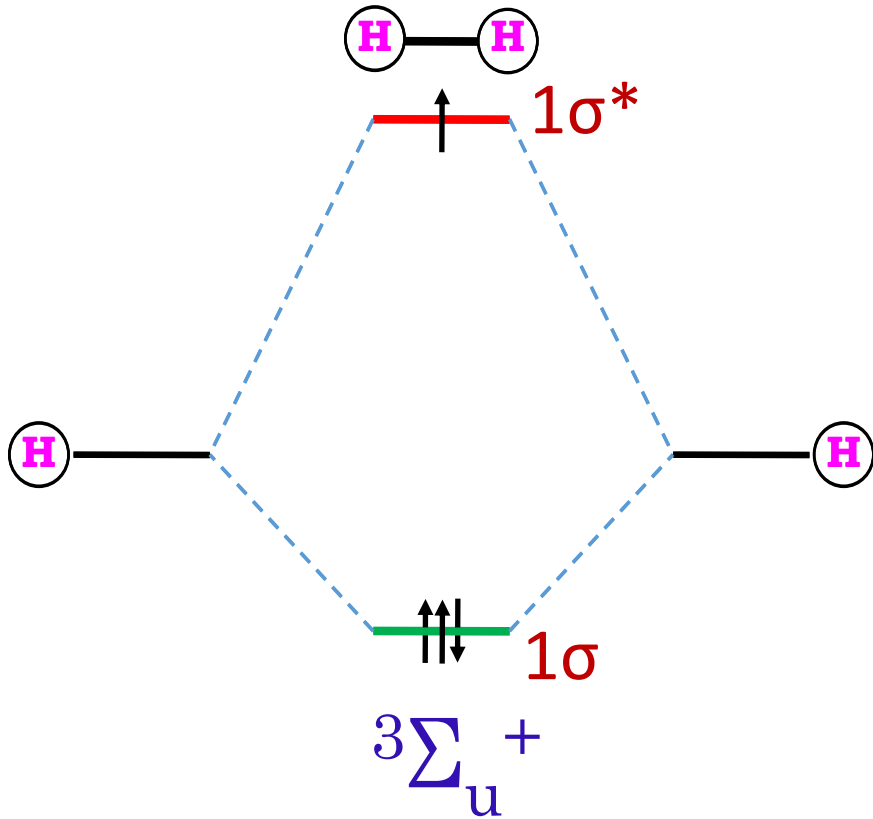
Molecule	Effective Bond Order (EBO)
Acetylene	2.86
C ₂	2.16
Ethylene	1.93

Frenking, G. et al. *Angew. Chem. Int. Ed.* **2013**, 52, 5922; Grunenberg *Chem. Eur. J.* **2016**, 21, 17126

https://www.chemistryviews.org/details/ezone/9017541/Why_Does_C2_Cause_so_Many_Problems.html

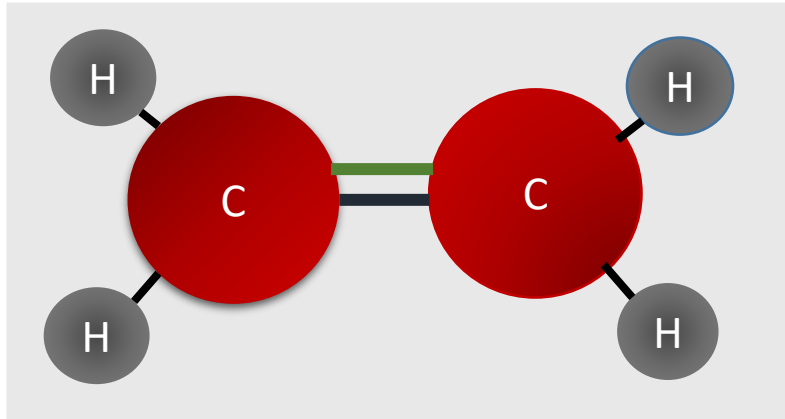
Bonding from Excited State Perspective

“The Return to Innocence”: Potential Energy Curves

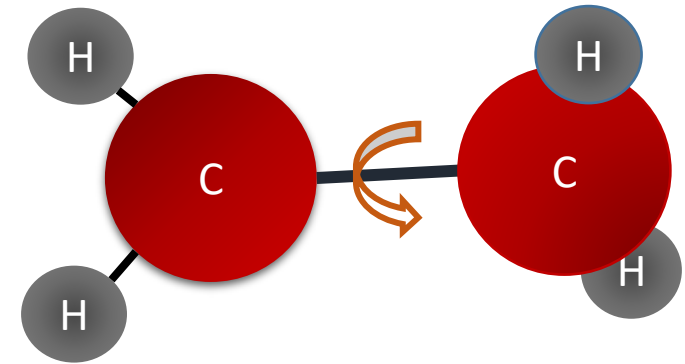
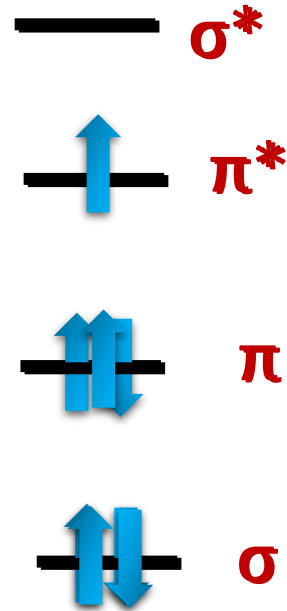


How does this apply to Two Multiply Bonded Atoms

Multiple Bonding in Molecules



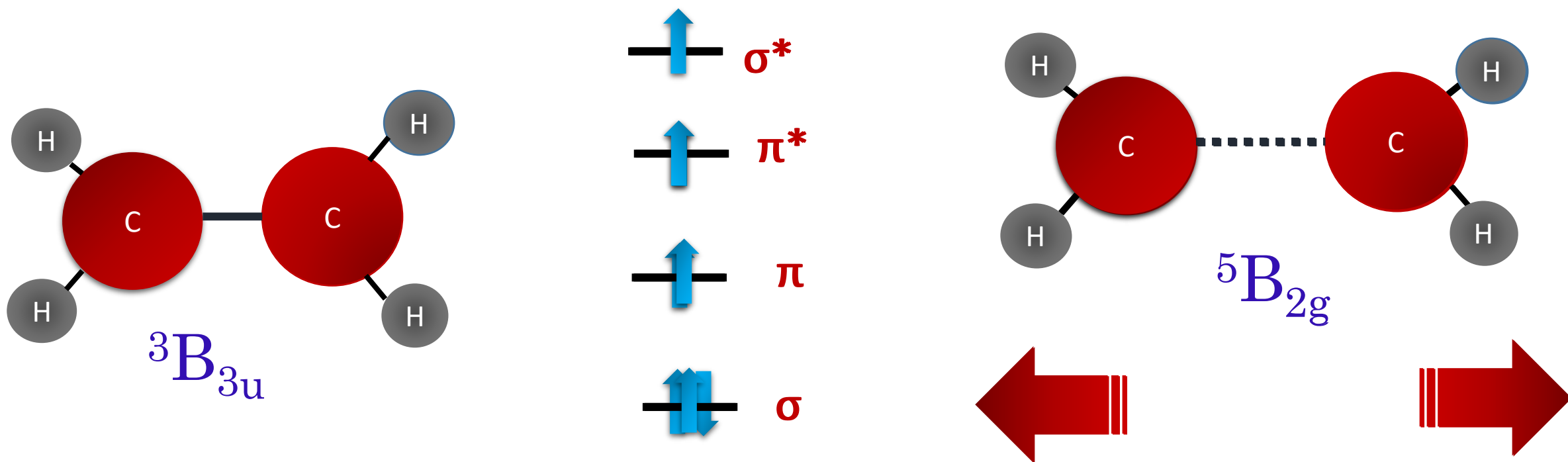
1A_g



$^3B_{3u}$

How does this apply to Two Multiply Bonded Atoms

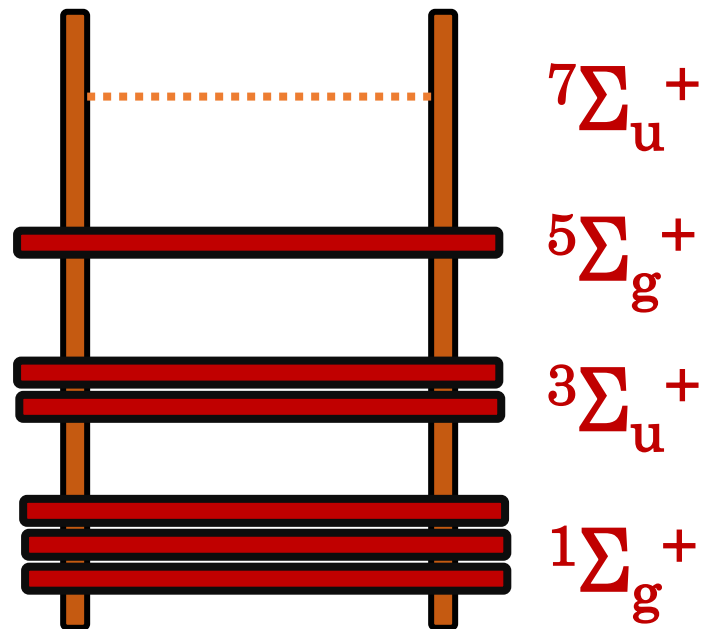
Multiple Bonding in Molecules



Higher Bond Order Means One has to reach higher Spin State to decimate Bonding

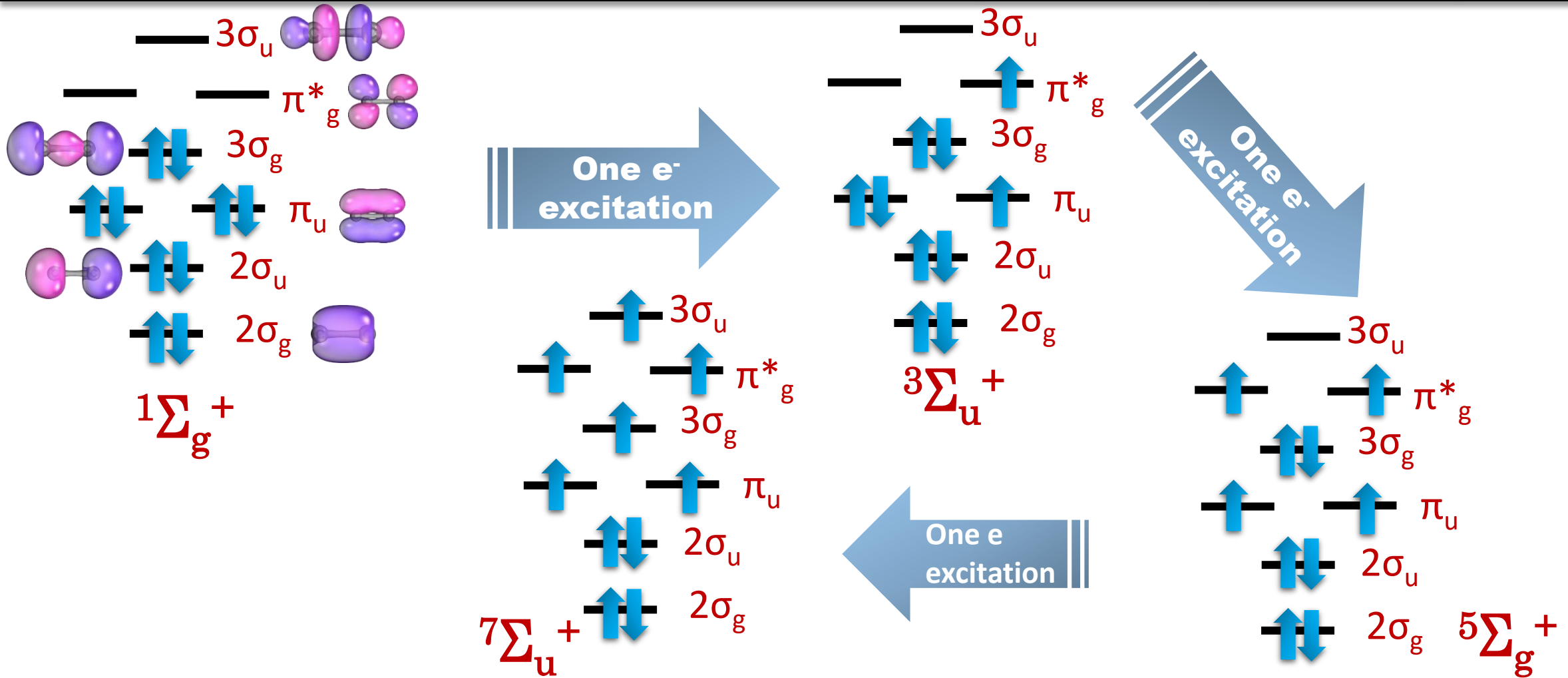
Understanding Multiple Bonding from an Excited State Perspective

- High spin states can be created by breaking bond pairs through excitation of electrons from bonding to respective antibonding orbitals. It will lead to high spin sigma states within the valence space.
- Lowest Energy **High Spin Σ States** will have lesser number of bonds compared to that of the ground state



Bonding from Excited State Perspective

Excited States: An avenue to inspect multiple bonding

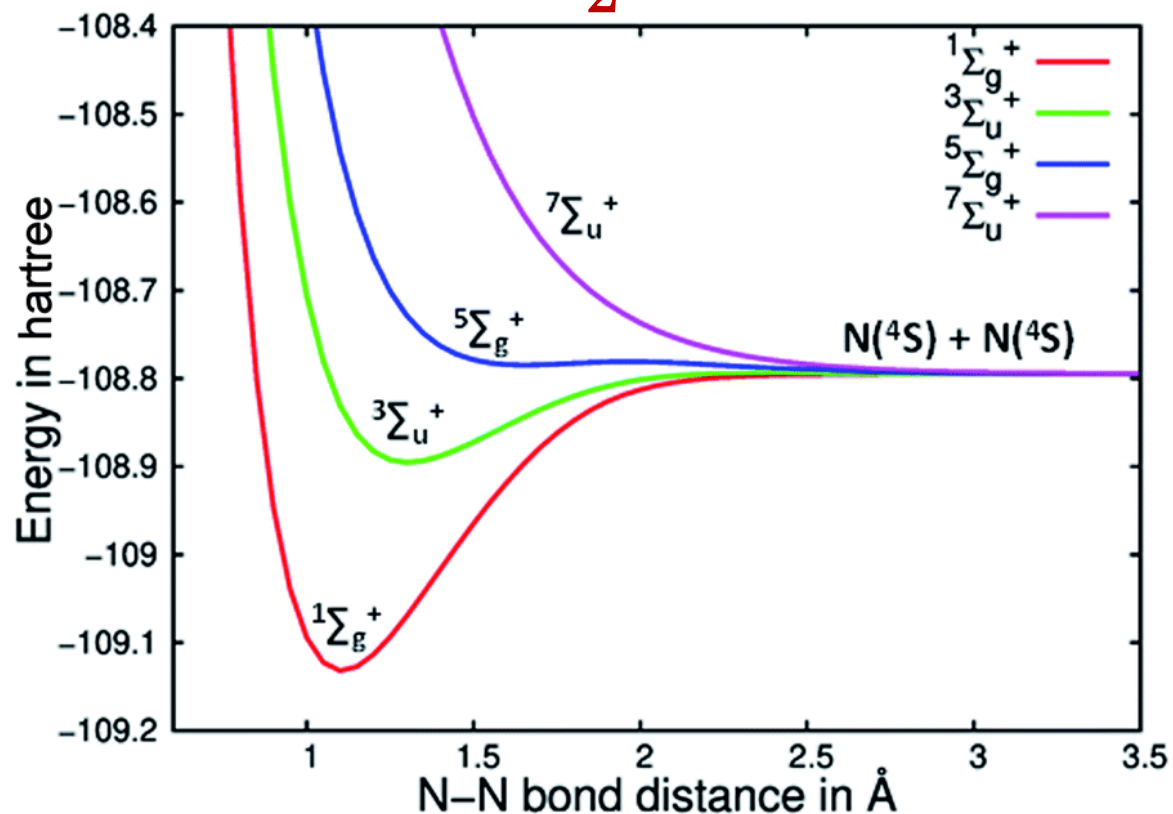


Computational Details

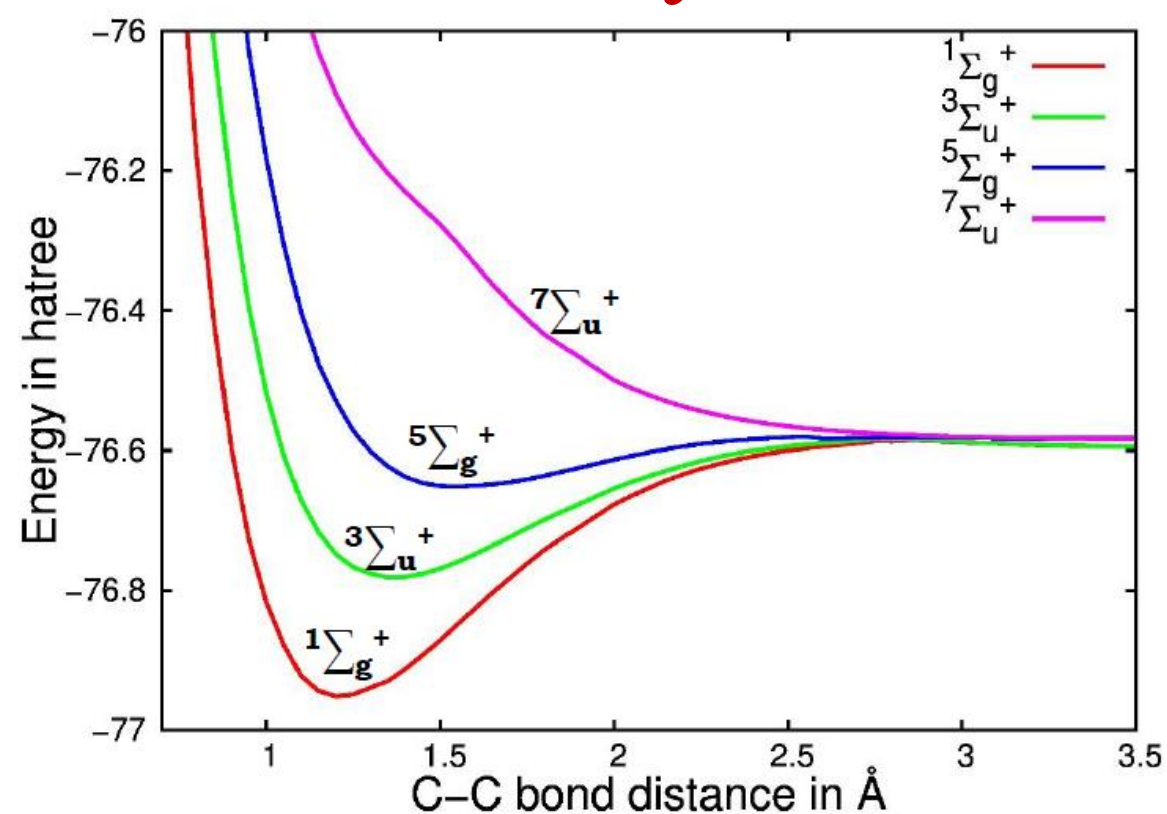
- All computations were conducted at the CASSCF level, using cc-pvqz basis set.
- For the diatomic N_2/C_2 molecule, we used [10,8]/[8, 8] CAS.
- For acetylene, we used [10,10] CAS.
- All the values we had taken correspond to state averaged calculations.

Potential Energy Curves (PECs) of N₂ and Acetylene

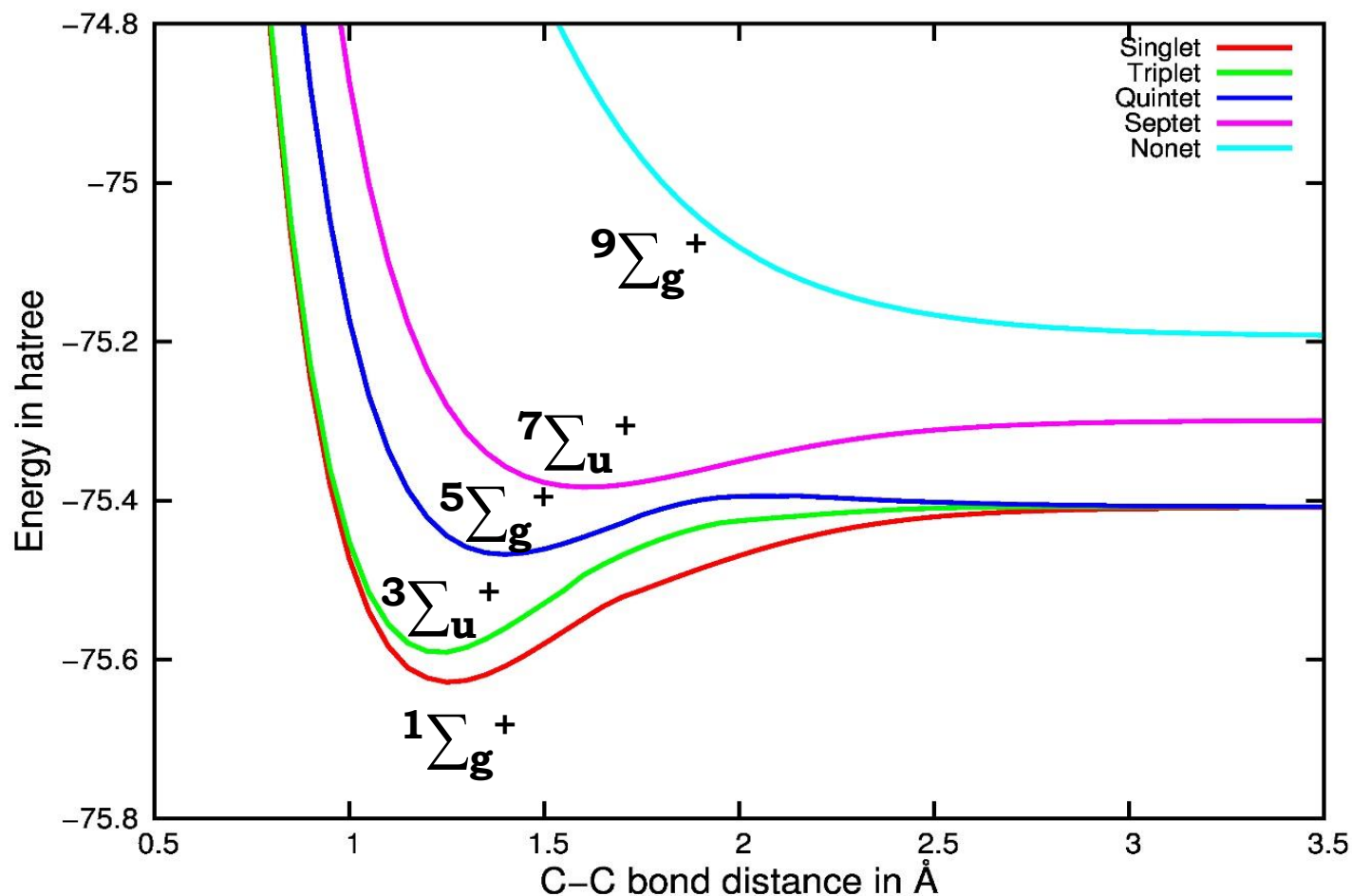
N₂



Acetylene

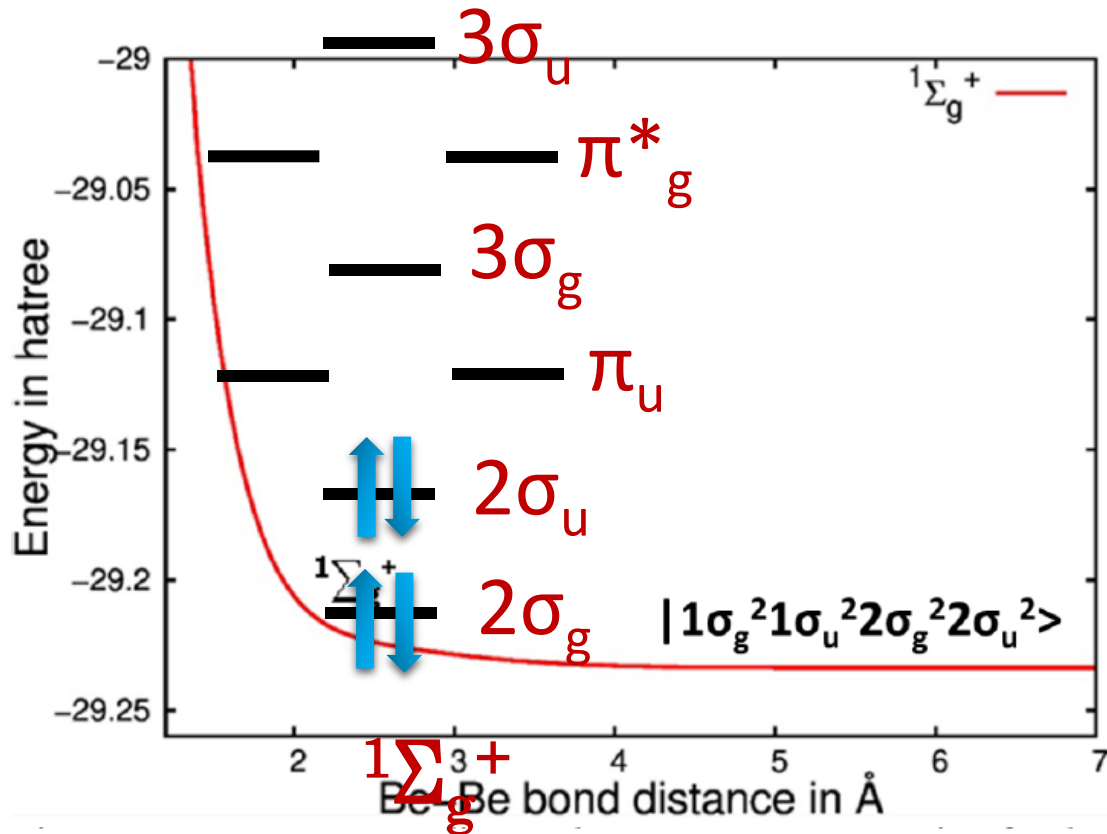


Potential Energy Curves (PECs) of the Five Spin States of C₂

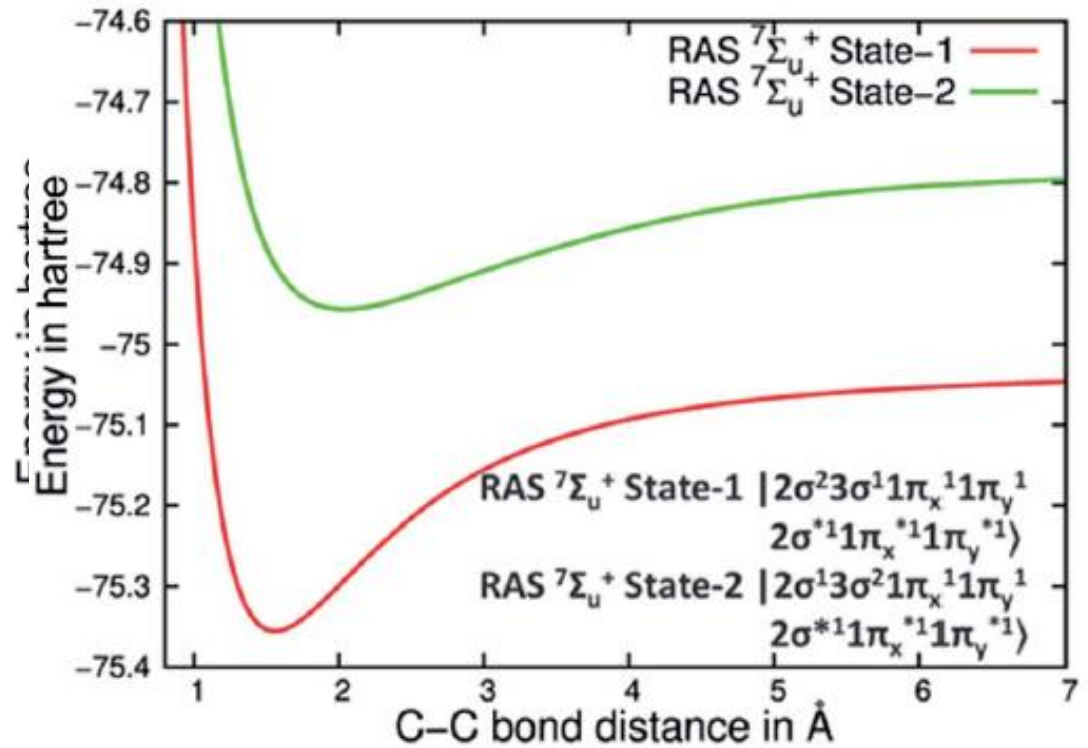


Comparison: C₂ with Be₂ (RASSCF)

Why 4σ Electrons Can lead to 2 bonds in C₂ but not in Be₂



Be₂



C₂ $7\Sigma_u^+$

Accidental Quasi-Degeneracy of $2\sigma_u$ and $3\sigma_g$ in C₂ assists in forming 2 Bonds

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NEWS

Excited state potential energy curves reignite diatomic carbon's bond order conundrum

BY RUTH ZADIK | 7 JULY 2020



A new theoretical study by scientists in India claims to provide overwhelming evidence that the simplest carbon compound, diatomic carbon (C_2), has a quadrupole bond. The researchers propose that their findings could be experimentally verified. Unsurprisingly for such a contentious field, some experts in the field remain unconvinced.

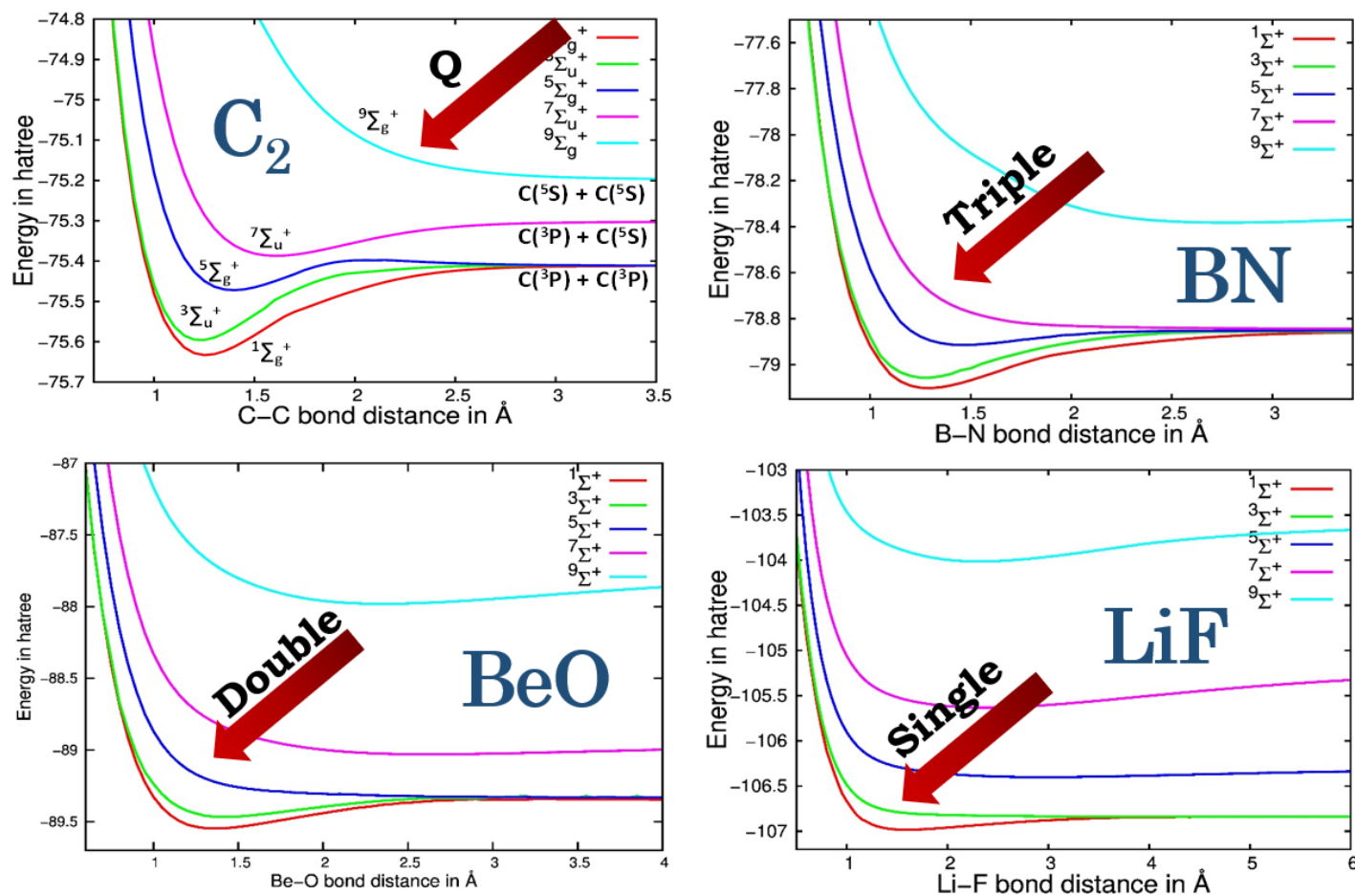
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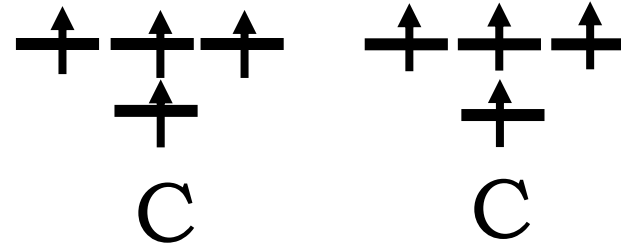
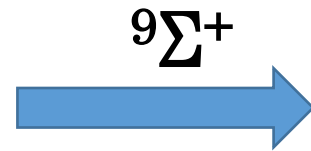
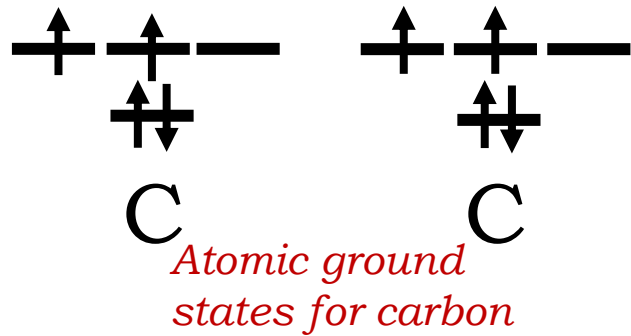
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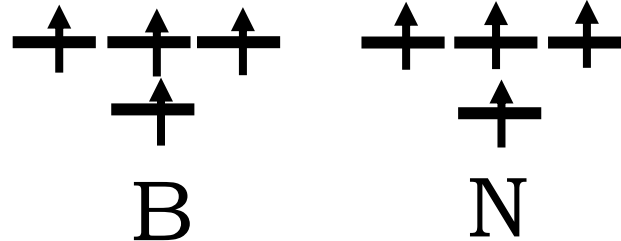
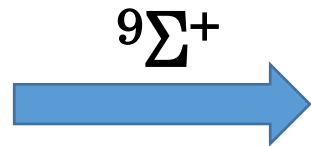
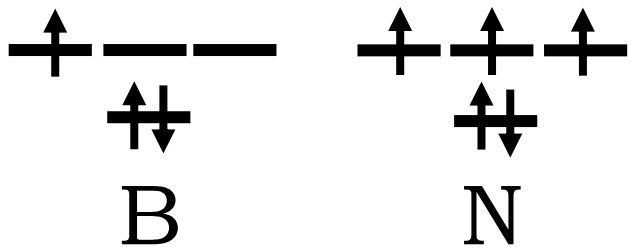
Lowest Lying Dissociative Spin State : Determiner of No. of Bonds ?



Bonding reappears after the dissociative state



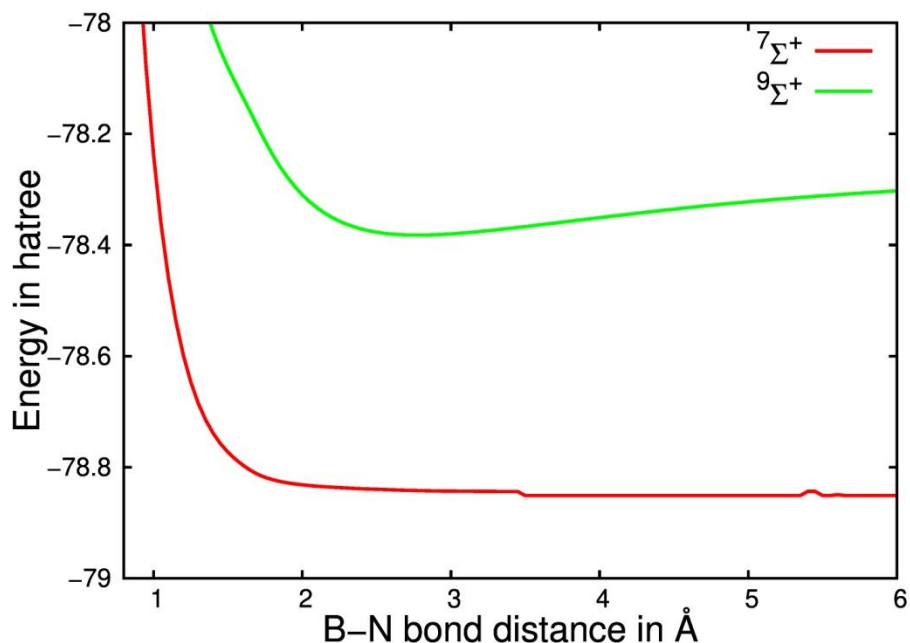
$9\Sigma^+$ state is achieved by simple unpairing of electrons



Complete transfer of an electron from nitrogen to boron is mandatory to reach a state with all unpaired electrons

Atomic ground states for boron and nitrogen

Bonding reappears after the dissociative state



B-N distance	2.75 Å	7.00 Å
Spin Multiplicity	(Boron, Nitrogen)	(Boron, Nitrogen)
$1\Sigma^+$	(+0.1, -0.1)	(0.0, 0.0)
$3\Sigma^+$	(0.0, 0.0)	(0.0, 0.0)
$5\Sigma^+$	(0.0, 0.0)	(0.0, 0.0)
$7\Sigma^+$	(0.0, 0.0)	(0.0, 0.0)
$9\Sigma^+$	(-1.0, +1.0)	(-1.0, +1.0)

- Our analysis supports the fact that Bond Order of $C_2 >$ Bond Order of N_2
- From Purely Dissociative PECs bond order of 2nd row Diatomic Systems can be predicted and they have integral values
- The diatomic isoelectronic species of C_2 exactly follows Lewis concept of bonding and bond order.
- As we go to higher spin states, after complete cleavage of all bonds, a complete transfer of electron takes place resulting in formation of ionic bonds. The PECs indicate that Coulomb attraction are the only stabilising forces present.

Thank you!