



One Molecule, Two Atoms, Three Views, Four Bonds?*

Sason Shaik,* Henry S. Rzepa,* and Roald Hoffmann*

What could be simpler than C_2 , a well-known diatomic molecule that has the second strongest homonuclear bond (with respect to atomization)? Well, this molecule turns out to be a microcosm of the bonding issues that bother (creatively) chemists, as this trialogue shows. It began when one of the authors published two lively papers on the bonding in C_2 . A second author became involved when he commented in a blog (a new thing in chemistry) on an isoelectronic molecule. The several studies of the third author, whose favorite molecule this has been for decades, were ignored in those two papers—as you can imagine, at some point he complained. In the spirited conversation that ensued, the authors roam through multi-configurational states, a quadruple bond between main-group elements, Mulliken's foresight, the utility of VB viewpoints, inorganic structures containing this small organic piece, what makes a diradical, the irrelevance of atomization energies to reactivity and thermodynamic stability, and much more. It's amazing how much heat (and light) can be generated by a simple molecule whose spectrum we've all seen, yet which you will not hold in a vial.

Roald: C_2 is one of my favorite molecules, for this diatomic epitomizes many of the fundamental questions of chemistry.

Not one of us has held a bottle of C_2 . But... every one of us has seen C_2 in action—the lovely blue color of hot hydrocarbon flames is due in large part to emission from excited C_2 molecules on their way to soot or CO_2 (OH and CH emissions contribute to the color).

Anyway, my eyes are wide open to anything new about C_2 . I saw a paper from my friends, Sason Shaik and Philippe Hiberty, with four collaborators.^[1]

Sason: I never realized that such a small molecule could arouse so much passion, Roald. We entitled the paper “Bonding Conundrums in the C_2 Molecule: A Valence Bond

Study”. It always intrigued me that C_2 was supposedly bonded by two suspended π -bonds, like two levitating halves of a sandwich with nothing in it. You can still see this description, which is based on naïve bond order calculations, in textbooks.^[2]

Henry: Wait, Sason, you're jumping into the problem, and no one knows what the hell you're talking about!

Roald: Can I set the stage?

Sason: How could I stop you?

Roald: I love doing simple things. The states of C_2 come from occupying the so-called canonical orbitals of the molecule.

Sason: It's not so simple.

Roald: You will get your chance, Sason, to tell us why it isn't. Here are the MO's of any homonuclear diatomic molecule; everyone knows them (Figure 1).

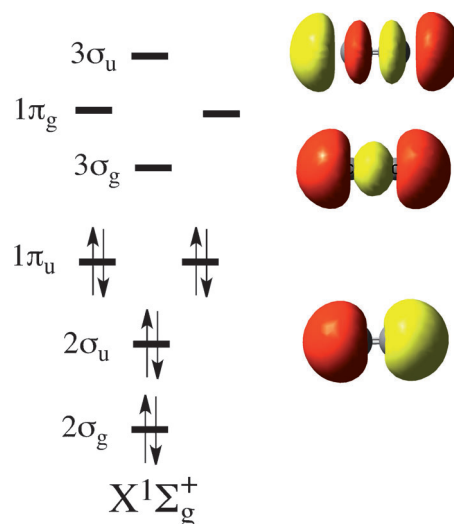


Figure 1. Valence molecular orbitals of C_2 . The energy scale is schematic; in particular the $3\sigma_g/1\pi_u$ gap is small; $1\sigma_g$ and $1\sigma_u$, omitted from this diagram, are 1s combinations.

In C_2 eight valence electrons occupy the four lowest MOs. Though... the $3\sigma_g$ and $1\pi_u$ must be very close to each other in energy^[3]—the lowest lying triplet state of the molecule, arising from promoting one electron from $1\pi_u$ to $3\sigma_g$ is only 716 cm^{-1} (2 kcal mol^{-1}) above the ground state.^[4]

Henry: The bonding picture that bothered Sason comes from assuming that $2\sigma_g$ is bonding, $2\sigma_u$ is antibonding, occupying them both gives no net bond. And with four electrons in π_u , one has a net double π bond. With no σ bond.

Sason: Intrigued, not bothered. And there are an awful lot of assumptions behind that “promotion” of an electron from $1\pi_u$ to $3\sigma_g$.

Roald: We'll find out, won't we? But at least now the stage is set. And I've got my bit of teaching in.

[*] Prof. Dr. S. Shaik

Institute of Chemistry and The Lise Meitner-Minerva Center for Computational Quantum Chemistry
Hebrew University of Jerusalem, 91904, Jerusalem (Israel)
E-mail: sason@yfaat.ch.huji.ac.il

Prof. Dr. H. S. Rzepa

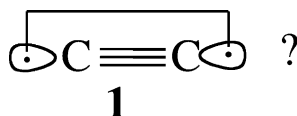
Department of Chemistry, Imperial College London
South Kensington Campus, London, SW7 2AZ (UK)
E-mail: h.rzepa@imperial.ac.uk

Prof. Dr. R. Hoffmann

Baker Laboratory, Department of Chemistry and Chemical Biology
Cornell University, Ithaca, New York 14853-1301 (USA)
E-mail: rh34@cornell.edu

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Sason: To get back to my story—in that first paper, as VB aficionados we joined forces with Wei Wu to test whether VB calculations retrieves those levitating π bonds. And also straighten out weird things in kinky potential energy curves, supposedly coming from some good ab initio calculations. From looking at 78 VB structures, we concluded the molecule is best described as a triply bonded structure. Even though we got a singlet ground state wherein all the eight electrons were paired, in this 2011 paper we overlooked the presence of the 4th electron pair. So, let me draw it below (**1**), for now, with a question mark.



We also focused too much on papers with high-level calculations of C_2 and therefore missed many interesting papers. For example, we missed Roald's work on C_2 and solid-state carbides, and we missed a paper by Paul Schleyer and co-workers, thinking about a possible quadruple bond in C_2 . I will get to Paul's paper again later.

At some moment, our attention turned back to the 4th electron pair and its potential contribution to bonding in C_2 . As we began this more exciting study of C_2 , we were ushered to a blog by Henry Rzepa,^[5] Henry is with it, he writes blogs. He also feels that blogs are important ways of communicating science in the future, and I still didn't (ironically, I am now on the board of editors of the blog journal *Computational Chemistry Highlights*^[6]). But, as we both love bonding, Henry never gave up on wooing me to look at his blog. In this instance, he was arguing with his fellow bloggers about quadruple bonding in CN^+ .

Henry: I am in the wonderful position of each week meeting groups of up to eight young and receptive minds for what we here call undergraduate tutorials. They tend to ask questions from "out of the left field." So it was on December 16, 2010. I had to try to explain to them why the nitronium cation, NO_2^+ was a common reagent used for aromatic electrophilic substitution, but that the "cyonium" cation, CN^+ was not. One starts the interaction (these were "fresher" students, just two months into their university experience) with asking for a volunteer to draw a valence bond structure for the species under discussion. NO_2^+ quickly emerged, but as a group we pondered rather longer upon CN^+ .

Roald: CN^+ ? Henry, how did you ever get to such a weird molecule?

Henry: It's not as weird as you think. CN^+ is implicated in some organic reactions^[7] and you can find it in the tails of comets.^[8]

That night I decided to try to collect some thoughts on my blog, the intention being that the more inquisitive students might have a follow up to the tutorial (I had cut my teeth in this by speculating upon the Finkelstein reaction, which has proven my most popular post to date).^[9]

Roald: The special thing about Henry's blogs is they're not just words. First, he does what I keep telling my graduate students to do—you have a program, for God's sake use it,

play with it, do a calculation on any small problem related to your problem. Let the calculations teach you. They are so easy! Henry does just that. And he also delights in graphics, so his blogs are *Gesamtkunstwerke*, in which one is invited to dip into a graphic, often one on several levels, or an animation.

Henry: Thank you, Roald! When I got home on Dec 16th, I did just that, and put CN^+ into the playpen (sorry, program). And thought about a quadruple bond in that molecule. The HOMO of that molecule, from what is of course a rather naïve molecular orbital calculation, is a degenerate π type.

Roald: I'm happy, that MO diagram of Figure 1 is good for something.

Henry: Even for heteronuclear molecules! The MO that caught my attention was the HOMO-2 (I show it in Figure 2 left), being the anti-bonding combination resulting from end-on overlap of the 2s AOs, with substantial admixture of the 2p_z AOs (z being the molecular axis).

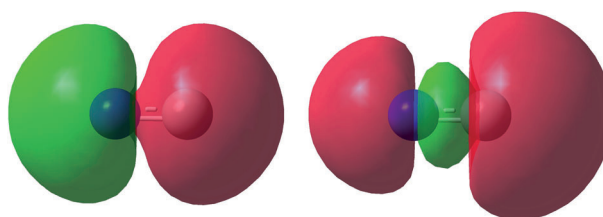


Figure 2. The HOMO-2 (left) and the LUMO (right) for CN^+ in a simple MO picture.

Sason: It's derived from the $3\sigma_g$ of the homonuclear diatomic (see Figure 1).

Henry: Yes. The mandatory node for this combination appears to have crept from the center of the bond to embedding itself onto the nitrogen atom. Since the sense of this can be difficult to perceive from a (static) diagram such as that in Figure 2 left, I introduced rotatable orbital surfaces on my blog to facilitate exploration and the reader is encouraged to try this out (I also gave the calculation itself a DOI-like identifier^[10] if you wished to seek access to the details of the calculation itself).

Well, this orbital did not look very anti-bonding to me. It seemed possible that it might not fully overcome the positive contribution of the in-phase combination, the consequence being an elevation of the total bond order beyond two. The LUMO (Figure 2 right) results from the in-phase overlap of the 2p_z AOs, and any (multi-reference) contribution from occupancy of this orbital must also tend to increase the bond order.

Sason: It turned out to be a lucky marriage of prepared minds. While our gang was continuing its study of C_2 , now looking at the 4th bond, Henry's blog made it clear that there may be many more molecules that are isoelectronic to C_2 and that all of them are potentially bonded by quadruple bonds. It was a relief to know that we were not so lonely with this "crazy" idea, and so it made sense to include him in this second study.

Roald: This is the way science should work—someone brings a good idea to you, you include him as a coauthor.

Sason: We did include Henry, and we never had a second thought about doing so.

Henry: Collaborative science often includes people coming in from “left field,” or an unexpected direction that you might not try yourself. I had been investigating other methods of exploring bonds such as the ELF technique. But it had become apparent that these did not really allow the individual components of a bond to be dissected. I emailed Sason (he and I had previously exchanged emails about his concept of charge shift bonds as applied to [1.1.1] propellane^[11]), knowing his group were experts in VB theory, and asking him for a response to my blog post.^[5] I had entirely failed to make a connection between CN^+ or C_2 and [1.1.1] propellane, my thoughts were compartmentalized into two quite separate boxes (to use the modern parlance, I was clearly not thinking out of either of these two boxes). Little did I know that Sason and his group were already there! But that is why one contacts colleagues, to make connections.

Roald: Henry, I love your blogs, but...is that just your way of avoiding the oh so friendly comments of referees?

Henry: There are two ways of looking at that. Referees of articles are anonymous, and in truth one does not really have any way of knowing what the factors are influencing their comments. Blogs can also attract comments; a number of my posts have attracted far more comments than any refereed article does. Most commentators are indeed friendly (not unconnected to also not being anonymous) and the nature of the ensuing dialog is often more constructive and positive than the anonymous system.

Roald: Interesting, that's *not* what one finds in comments on You-Tube videos or on internet threads. There a lot of venom spills out; maybe because people's identity is disguised. But you're right—blogs start conversations, papers in our journals often don't.

Sason: Guys, you are indulging in digression... Let's get back to our molecule. In our second paper^[12] (the one that included Henry), we in fact found that the carbon atoms in the C_2 ground state were bound in its ground state by a 4th bond, a weak “inverted” bond, with a strength of 12–17 kcal mol⁻¹. This was a victory for the Lewis model of electron pairing. Let me also mention that I have been teaching chemistry to humanities students, and last year one came to the whiteboard and drew C_2 with four bonds. When he did that, I thought to myself, “go learn from the children.”

Roald: You're paraphrasing Matthew 21:16.

Henry: Who quoted Psalms 8:3.

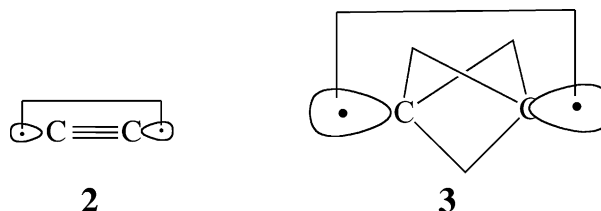
Sason: I doubt the student read Matthew or Psalms, but for sure, he applied the Lewis idea, which is so easy to apply! It makes the notion of bonding so clear.

So, now I remove the question mark from structure 1.

Roald: Wait, wait. There was not a whisper of a 4th bond in your first paper on the molecule.

Put yourself for a moment into the situation of an outside observer—an organic chemist trying to understand. Here are three masters of modern valence bond theory—Sason Shaik, Philippe Hiberty, and Wei Wu. They do a thorough paper on C_2 and only see a triple bond. Then they do a second paper and all of a sudden they see a 4th bond. If experts can't see a bond before their eyes the first time, how are ordinary chemists supposed to see one?

Sason: You are right. We overlooked it because we were hung up on the question of the levitating double bond, and on the technical difficulties of getting a reasonable potential energy curve for C_2 . I guess the reason the 4th bond was initially ignored was the “inverted” relationship between the sp lobes on carbons (see 2). However, the story^[11] of the inverted bond in [1.1.1] propellane taught us a great lesson, that inverted bonds (see 3) can have a substantial bonding energy.



The [1.1.1] propellane story started me thinking about the possibility of quadruple bonding and I suggested to my co-authors that we calculate the bond energy of the inverted bond in C_2 . Valence bond (VB) theory can give you this nice quantity, which we call in-situ bonding, and it can do so for any electron-pair bond. But the trouble is that few people believe VB theory, so I told David, my co-worker; let's do a Full Configuration Interaction (FCI). I am not sure if you ever looked at a FCI output. It looks like a telephone directory. I learned from Roald to read outputs.

Roald: Oh, those were the good old days, Sason. Today nobody knows how to draw an orbital from the wave function.

Sason: You're always interrupting Roald; a teacher is always a teacher I guess. Anyway, after a close look it was clear to me that we can transform the FCI wave function to a GVB one having 4 bond-pairs. Lewis must be very happy, wherever he might be now. The student of humanities who drew a quadruply bonded C_2 would have been excited to know that his application of the electron-pairing idea he wrote on the whiteboard is actually correct and exciting/bothersome for many chemists.

Roald: OK, but how I wish you had just “fessed” up by saying it in plain words, like “We have published a study of C_2 . But we had missed something in that study, the potential of a fourth bond. We should not have missed it for Henry had been talking about it, and Paul Schleyer had an interesting paper on it. Now we have looked at the molecule again, and by golly, these guys have a point. Or rather, it's more complicated than we or they thought...”

Sason: Roald, I think your hypothetical introduction for our paper undermines the achievement and twists somewhat what actually transpired. Let me give you an alternative and more realistic description. In the first paper (Ref. [1]), which was a massive work, we slaved to tackle computational difficulties in the calculations of C_2 , and showed that the conclusions based on the bond order index were wrong. After publication, we looked again at the VB data and we realized that we missed a jewel—the 4th bond in C_2 was hiding in the VB calculations. And despite the weakness of this bond, it was very important; it had the potential of changing a fundamental view of bonding, and not just in that molecule. The discussions

with Henry further convinced us that the discovery was not limited to C_2 and that there were more molecules out there, which potentially possessed quadruple bonds between main elements. The excitement of the discovery was reflected, as it should have, in the introduction to the second paper (Ref. [12]). I still recall vividly this excitement. And this is how science proceeds when one feels he/she made a discovery. Isn't it so?

Incidentally, one might think one could use bond orders to gauge the strength of that bond. Henry and we used bond orders, of different kinds, which change all over the place—I will be happy to send you a table where you can pick any bond order you like for C_2 . Bond orders may be quantitative, but they do not count bonds properly.

Henry: I've had this experience too. The trouble with a bond order is that it's not easy to find an experiment that measures it directly.

Roald: Me too! In a recent study of H_2 under pressure, we calculated Mulliken Overlap Populations, Wiberg and Meyer bond indices...

Sason: Just the fact that there are so many different indices with the names of ingenious people attached to them tells you something.

Henry: Eugen Schwarz and H. Schmidbaur mention more representatives in this human zoo of charge and bond definitions, in a wonderful, thoughtful article asking theoreticians to be cautious about denying chemical intuition.^[13]

Roald: ... and got widely different results. I like to show these to people who claim there is a good way to define a bond. Of course they'll tell me that I should do a QTAIM analysis.

Sason: Better define that.

Henry: Quantum Theory of Atoms and Molecules, QTAIM, a method based on the topology of the electron density ρ ,^[14] has its uses.

Roald: I was saying that tongue-in-cheek, Henry. I am no great fan of QTAIM—in the hundreds of QTAIM papers that crowd the literature, I have yet to see one that makes a chemical prediction, or suggests an experiment.

Sason: You're digressing, as always. So, there was no way to get a 4th bond in C_2 from an MO or DFT calculation. None whatsoever! What we did was a tour de force, starting from VB and from FCI ends and getting the two pictures to converge. I am very proud of the achievement and I am sure Henry is with me on that. Even Paul, whose paper we neglected to cite initially, defined it as a "breakthrough" in his interview in *Chemistry World*.^[15]

Maybe a good word for all our co-authors is in order here Roald.

Roald: Indeed, a masterly job. One doesn't often see a full CI, especially not one made with understanding in mind.

Sason: Now, let me say something about Paul Schleyer's paper.^[16] I admire Paul, and am *truly* sorry we missed his paper, and so glad we managed to cite his paper in "notes added in proof."^[12] Having said that, reading his paper carefully makes it clear that Paul raised the idea of a quadruple bond only to conclude that there is nothing like that in C_2 ("Some ideas will survive. Quadruple CC bonding does not"). He repeated this conclusion in a comment on Henry's blog on January 25, 2012.

Roald: Paul was wrong. You found that 4th bond.

Sason: So you agree with us?

Roald: Got me. I do and I don't. But go on.

Sason: Anyway, the final version of our paper does not cite a lot of papers on C_2 , which we reluctantly had to omit to conform to the maximum allowed number of references in *Nature Chemistry*.^[12] One of these is the Jemmis, Pathak, King and Schaefer paper.^[17] Jemmis and his co-authors are good friends and I deleted the reference to their work quite unhappily.

With C_2 being such a small and popular molecule, it would have been a miracle had we not missed many computational papers.

In fact, you should have also admonished us for neglecting to cite Christine Wu and Emily Carter, who used correlation-consistent CI calculations based on a GVB wave function,^[18] and even though they do not address the 4th bond in C_2 in such detail, still they describe the molecule with four electron pairs holding the two carbon atoms.

We also missed Frank Weinhold and Clark Landis, who in their book^[19] discussed a new type of diatomic bonding, v -bonding. If you consider the σ -bonding in C_2 , then initially you have single electrons in 2s and 2p_z on each carbon. You can make two bonds, by pairing 2s of one carbon with 2p_z on the other carbon, and vice versa, i.e., two v -sigma bonds, which together with the π -double bond yield a quadruple bond. I think this idea is very appealing, and if you accept it, you will have to abandon the use of MO-bond orders in terms of bonding and anti-bonding orbitals. Having said that let me add a less happy note. We have tried out the Weinhold and Landis wave function using VB theory. Alas, it is unstable, collapsing to the quadruply bonded picture with identical hybrids. At the moment, we have to give up this pretty picture.

Roald: You know what? The first person to write down a quadruple bond for a state of C_2 was... Robert S. Mulliken. Here (Figure 3) is a Table from a paper by him in 1939, two years after I was born.^[20] He's analyzing the bond lengths in the excited states of C_2 , and comes up with an empirical formula...

Henry: No bond indices yet in 1939, but the original Lewis dot-notation^[21] has now settled down to expressing the idea of four bonds as four lines connecting two atoms.

Roald: ... relating the bond lengths to the occupation of bonding (strongly or weakly) and antibonding orbitals. He then decides to apply the same formula to the configurations of C_2 in organic molecules (I will come back to that).

And there it is, right above acetylene! But not a word in the text about it, not a word...

Can I dream? I wish Mulliken had spoken up about C_2 (more than the entry in this table). And that Linus Pauling would have joined in and pointed out that even in the ground state of C_2 there could be a weak 4th bond.

Henry: A quick regression to Figure 1. Mulliken's quadruple bond surely corresponds to a double excitation in the simple single-reference MO Scheme from what he calls $y\sigma_u$ and what we would call $2\sigma_{gu}$ into his $x\sigma_g$, our $3\sigma_g$.

Roald: Yes, Mulliken knows that the quadruply bound C_2 is a high-lying excited state.

TABLE I. Approximate energy and r_0 values for low energy electron configurations of C_2 and C_2^+ .

$\gamma\sigma_u$	$\pi\pi_u$	$\pi\sigma_g$	$\pi\pi_g$	EST. MEAN ENERGY* (eV)	STATES	NO. OF C—C BONDS	r_0 VALUES (Å)	
							CALC.	OBS.
2	4			0	$1\Sigma_g^+$	2	1.24	1.243
2	3	1		0	$3\Pi_u, 1\Pi_u$	2	1.32	1.313, 1.318
2	2	2		0	$3\Sigma_g^-, 1\Delta_g, 1\Sigma_g^+$	2	1.40	
1	4	1		3	$3\Sigma_u^+, 1\Sigma_u^+$	3	1.18	1.240
1	3	2		3	$3\Pi_g, 1\Pi_g$	3	1.26	1.266, 1.257
2	3	0	1	6	$3, 1\Sigma_u^+, 3, 1\Delta_u, 3, 1\Sigma_u^-$	1	1.46	
2	2	1	1	6	$3, 1\Phi_g, 5, 3, 3, 3, 3, 1, 1, 1\Pi_g$	1	1.54	1.541
2	1	2	1	6	$3, 1\Sigma_u^+, 3, 1\Delta_u, 3, 1\Sigma_u^-$	1	1.62	
0	4	2		6	$1\Sigma_g^+$	4	1.12	
0	4	2			$C \equiv C$	4	1.12	
(1)	4	(1)			$-C \equiv C -$	3	1.18	1.20
(1)	2+(1)	(1)	(1)		$> C = C <$	2	1.40	1.34
(1)	(2)	(1)	(2)		$\geq C - C \leq$	1	1.62	1.54
2	3			0	$2\Pi_u$	$1\frac{1}{2}$	1.35	
2	2	1		0	$4, 2\Sigma_g^-, 2\Delta_g, 2\Sigma_g^+$	$1\frac{1}{2}$	1.43	
2	1	2		0	$2\Pi_u$	$1\frac{1}{2}$	1.51	
1	4			3	$2\Sigma_u^+$	$2\frac{1}{2}$	1.21	
1	3	1		3	$4, 2, 2\Pi_g$	$2\frac{1}{2}$	1.29	
1	2	2		3	$4, 2\Sigma_u^-, 2\Delta_u, 2\Sigma_u^+$	$2\frac{1}{2}$	1.37	
2	2	0	1	6	$2\Phi_g, 4, 2, 2, 2\Pi_g$	$1\frac{1}{2}$	1.57	
2	1	1	1	6	$4, 2, 2(\Sigma_u^-, \Delta_u, \Sigma_u^+)$	$1\frac{1}{2}$	1.65	
2	0	2	1	6	$2\Pi_g$	$1\frac{1}{2}$	1.73	
0	4	1		6	$2\Sigma_g^+$	$3\frac{1}{2}$	1.15	
0	3	2		6	$2\Pi_u$	$3\frac{1}{2}$	1.23	

Figure 3. A table from a 1939 paper by R. S. Mulliken.^[20]

Sason: Roald, I wish this was clearer... But frankly, I think you are using a Talmudic strategy to reconstruct a new text from Mulliken's paper. He is trying to solve a spectroscopic problem and assigns the 2300 Å band to a $\Sigma_g^+ \rightarrow \Sigma_g^+$ transition, but his Σ_g^+ excited state is not the one you are referring to.

In his paper, Mulliken also tries to propose an equation that competes with Pauling's equation for predicting equilibrium bond distances, and hence he makes use of different electronic configurations with their predicted and observed distances to construct the equation. Since he uses the bond order formula for counting bonds, he shows all the possible bonding multiplicities C_2 can have in its various configurations. The "quadruply bonded C_2 configuration" in Table 1 is not meaningful in his eyes, so he does not discuss it.

Anyway, I wouldn't call it an excited state because it will be highly mixed with other Σ_g^+ configurations (there are more than 140 such configurations). The 1979 calculations of Kirby and Liu^[22] show that the $3^1\Sigma_g^+$ state, nascent from this "quadruply-bonded" configuration, lies ≈ 7 eV above the ground state and its BDE is merely ≈ 33 kcal mol⁻¹. In fact, as the authors conclude using Herzberg's data, this state might be a Rydberg state; it has nothing to do with quadruple bonding. This is a multi-reference problem and one cannot look at single configurations and count the number of bonds.

There is, in fact, a lower Σ_g^+ configuration, labeled $B'\Sigma_g^+$ by Varandas.^[23] This state mixes substantially into the ground state of C_2 at 1.6 Å, due to avoided crossing, but it contains less π -bonding than the ground state. We discussed this in our

first paper,^[1] and we used it to explain^[12] why, despite the quadruple bond in the ground state of C_2 , the corresponding force constant is nevertheless smaller than that of the triple bond in acetylene. As I keep saying, MO-based bond orders are not a good measure of bonds, especially in multi-reference situations.

Roald: Sason, I think you are unfair to Mulliken—it was 1939, and while one already knew about CI improving wave functions, the idea of multiconfigurational wave functions was not yet in the wind.

Sason: I do not think so, Roald. I am in fact giving Mulliken all the credit he well deserves; he knew the rules of CI in and out. Because the "quadruply bonded configuration" was not by itself a real state, he did not say anything about it, other than using it to calibrate the bond-order/bond-length equation. I am sure you are thinking now, "he blamed me for using Talmudic reading and now he is doing it himself."

Roald: No, no. I agree entirely with the way you describe Mulliken's use of that structure. And I was wrong to say that he thinks of it as a true excited state.

Henry: Sason, your calculations show here that my simple-minded analysis is but an approximation to a deeper one. The Wiberg bond order for the stable singlet state had indicated ≈ 3.6 , Weinhold and Landis's NBO analysis had pointed to four bonding orbitals, but we now see such solutions as perhaps unstable in VB theory or misleading.

Sason: The Wiberg index of the SCF wave functions is close to 4 indeed. It may be that the ν -bonding is responsible for that,

as suggested by Weinhold and Landis.^[19] But as you move on to correlated wave functions, the bond order (BO) drops to 3 and in some cases (using Mayer's bond order) even to smaller values. This is perfectly understandable—a number of the configurations you mix in to improve the wave function populate antibonding orbitals. Hence the bond order, as defined, decreases compared with the SCF value.

Having said that, I still believe that generally the bond order is useful as a qualitative concept, e.g., comparing ethane, ethylene and acetylene, gives you a good picture of the relative bonding. BO will work wonderfully in many cases, but will fail in molecules like C_2 which has a multi-reference character, that being the root cause of the 4th inverted bond. In fact, our friend Philippe Hiberty calculated the bond dissociation energy (BDE) of the single MO configuration for $C_2 \rightarrow 2C$. It is only 11 kcal mol⁻¹! By contrast, his calculations for the BDE in acetylene and N_2 , both of which are largely well described by a single configuration, give values that are reasonably close to the experimental BDEs. For C_2 you cannot argue from a lower level of theory. You have to go to higher levels, e.g., FCI and VB.

Roald: I love it, a small molecule that is more complicated for theory than its larger relatives.

Sason: Well, atoms are sometimes the most difficult to calculate properly...

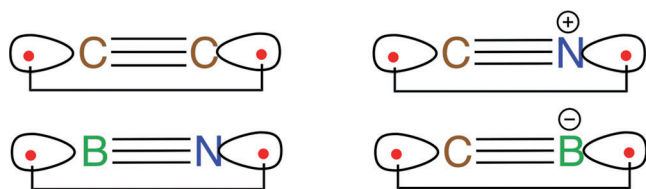
Henry: But am I correct in asserting that there is no fundamental reason (based on symmetry alone) why the AOs in singlet C_2 could not combine to give a bond order greater than 3? I have thought that one could summarize Lewis^[21] and also Langmuir's^[24] ideas by arguing that the maximum bond order deriving from MOs of σ and π symmetry was two each, making a maximum main group chemical bond order of four.

Sason: Sure, Henry. This is what we found in C_2 and its isoelectronic series shown below in Figure 4; the quadruple bond arises from a Lewis pairing of the eight valence electrons. Still we must not forget that bonds that occupy the same space, like the internal and inverted σ -bonds of C_2 , repel one another and so we'll end up with one bond being strong and the other weak. In retrospect, this is so simple!

Roald: Amazing, where wondering about an electrophilic reagent can lead you!

Sason: Maybe we should all read more of Henry's blogs, and more VB theory..

Roald: Or, as I've said before, make use of that wonderful software in our hands. Sorry, in our computers. On the



Quadruple bonding !

Figure 4. Cartoons representing the quadruple bonding in isoelectronic main group diatomic molecules. Adapted with permission from Ref. [12].

maximum bonding that you can get out of a set of orbitals, Henry, I recall here the fascinating story of diatomic Cr_2 , with contentions of a hextuple bond in the molecule.^[25]

Can I switch the discussion to mysteries of C_2 that we haven't yet touched on? For instance there is a form of C_2 that, if not possessed of a 4th bond, has more bonding in it, in one way of measuring that bonding, than the ground state.

Henry: This brings to mind this famous exchange^[26]

Oscar Wilde: "I wish I had said that"

Whistler: "You will, Oscar, you will."

I think I know which state you mean, it is actually a pair of states, $^{1,3}\Sigma_u^+$; the triplet is known with a CC bond length shorter by a hair than the ground state separation. It's the fifth state up in this theoretical picture (Figure 5) of the potential energy curves of C_2 .

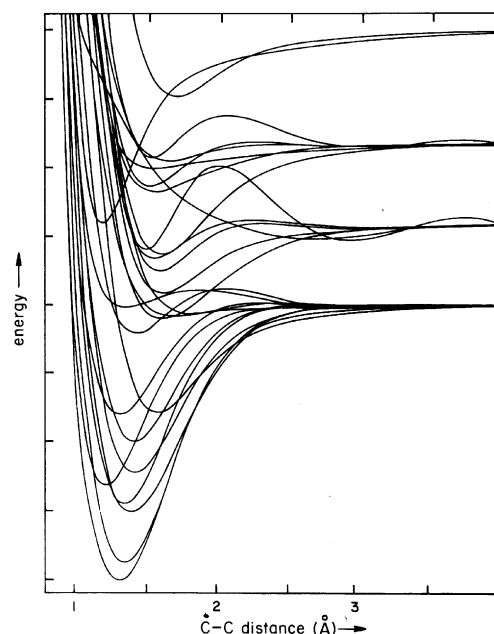


Figure 5. Theoretical potential energy curves for the ground and various excited states of C_2 . The curves were drawn by R. Hoffmann after early calculations by Fougere and Nesbet.^[27] The vertical axis markings are 1.36 eV apart.

Roald: Yes. A classical violation of Badger's rule—the old regularity relating short bonds with strong ones and with higher quadratic force constants. This state has a shorter bond length than the ground state, but is definitely weaker energetically.

Henry: Another digression along the same lines, but Sason and his co-workers^[28] famously convinced everyone that the π -bonds in benzene are distortive, as manifested by the depression of the wavenumber of the Kekulé normal vibrational mode (the one that shifts the double bonds in the manner of the two Kekulé resonance forms). And I might add that the lowest quintet excited state of benzene, although its C-C bond lengths are longer than in benzene, shows the frequency of the same Kekulé mode to be elevated compared to the ground state.^[29]

Sason: Henry, now this is a digression I love, and you are making an excellent point. Benzene is a good story, since as

you said, the C=C stretching frequency, $\omega(b_{2u})$, is lower than the same frequency in the excited states, and famously in the first excited state ($^1B_{2u}$). The ground and the first excited states have D_{6h} geometries, and the excited state has longer CC distances and less C=C bonding.^[30] I think one can find many cases where the three-fold connection of bond length-bond energy-force constant (frequency) is violated.^[31] It is from these cases that we learn about the fragility of our rules and the need to improve them.

Roald: To get back to C_2 —pretty remarkable, a bond in an excited state of a molecule that is shorter than the ground state equilibrium separation! And do you want to know why?

Sason: Go ahead, my friend. You are just looking for another way to demonstrate the superiority of MO theory to VB. And in all friendship, I will disagree with you...

Roald: No doubt you will. $^{1,3}\Sigma_u^+$ has one $2\sigma_u$ electron (ever so slightly antibonding; see Figure 1) promoted to a $3\sigma_g$ lone pair combination, slightly bonding. One can in fact get the right trends for the equilibrium distances in most of the 22 or so excited states of C_2 ,^[4] by looking at the population of the MO's and thinking about their bonding or antibonding character. That's what Mulliken did for the fewer states known in 1939. I think the ability to do so really impressed the spectroscopic community. But organic chemists were not yet ready for it...

Sason: Even if the states are not described well by a single configuration? Not one, but many of the C_2 states are inherently multiconfigurational. In the ground state the mixing between the fundamental MO configuration and the one doubly excited ($2\sigma_u \rightarrow 3\sigma_g$) brings about 53 kcal mol⁻¹ as calculated by David Danovich, while the fundamental configuration is barely bound (11 kcal mol⁻¹). How can one ignore such a huge resonance energy quantity? It's not for nothing that I looked through that FCI telephone directory. Just remember, that this seemingly simple argument fails for the ground state, which is quadruply bonded.

Roald: I don't understand it, myself, but even if the states are multiconfigurational, as you say, the simple MO argument works. Perhaps because a single configuration makes the greatest contribution. Perhaps... well let me quote here a wonderful passage from a remarkable inorganic spectroscopist of my generation, Chr. Klixbüll Jørgensen:

"[We draw attention to] the propensity of preponderant electron configurations suitably chosen to *classify correctly* the symmetry types of the groundstate and the lowest excited levels... The paradoxical situation is that this classification works even though we know that Ψ of many-electron systems do not correspond to well-defined configurations... The whole theory of such configurations is a masquerade played by Nature; it is *as if* the preponderant configurations are taxologically valid." [italics in original]^[32]

You will have to read Jørgensen's book to find out what he meant by his neologism "taxonomy".

Sason: He sounds an interesting person. I wish I had known him, Roald. Anyway, I am not against your bonding/antibonding arguments, but if the argument fails for one state, shouldn't we reflect whether it is valid for other states? I don't disagree that the $^{1,3}\Sigma_u^+$ states are really interesting. In fact, I might also have an explanation for the short bond

length in these states based on VB for these excited states... For example, the $^1\Sigma_u^+$ state is ionic, $\cdot\text{C}\equiv\text{C}^+\leftrightarrow^+\text{C}\equiv\text{C}\cdot$. The Coulomb attraction will shorten the bond, but the ionic character will raise the state energy which becomes an excited state with a shorter bond length compared with the ground state. Isn't this a useful physical insight?

One feature that should bother you is that these states are higher in energy than the ground state, so they cannot really have "more bonding"... I think we should not use BO-bond/energy relationships for the C_2 states.

Roald: Oh, Sason. Chemistry is not mathematics, and even if it bothers some people like hell, there are no theorems of chemistry.^[33] Chemical arguments are not falsified by an exception. Or a qualification, which is what I view the multiconfigurational argument to be. That Mulliken could make sense, easily, of bond lengths in many excited states of C_2 , that stands. And that this kind of thinking could make more sense in all of organic and inorganic chemistry—that bond length trends on ionization and excitation could be easily understood—that has really moved the science forward.

There are many measures of bonding—distances, energies, force constants, coupling constants, electron densities, difference densities, various magnetic and spectroscopic criteria. I prefer to concentrate on the equilibrium bond length as the prime experimental criterion for bonding.

Sason: You are my teacher, Roald, and you know I share many of your scientific values. I for example, feel as you do that an important role of theory is to paint from the numerical results lucid trends and open new windows. For this reason, I fail to see your objection to doing higher-level calculations, and then obtaining lucid pictures. Isn't this the same goal? Anyway, I am glad you accepted my suggestion and removed the bond energy connection in dealing with these excited states.

Roald: And it sure does give me pause that the $^{1,3}\Sigma_u^+$ state has a shorter bond length but does seem by the dissociation energy criterion to have a smaller dissociation energy value. Is that due to an avoided crossing, that is, mixing in another configuration at long distances?

Sason: Yes. At least the $^1\Sigma_u^+$ state undergoes avoided crossing with $B'^1\Sigma_u^+$. Just look at Figure 1 in the Kirby and Liu paper.^[22] There are in fact many $^1\Sigma_u^+$ states that mix with one another. The $^3\Sigma_u^+$ state seems not to be plagued by this extensive configuration mixing. I still do not have a simple VB understanding of its short equilibrium bond length. It will come eventually... But I do not deny that I may eventually have to agree that these VB-derived solutions will not be so portable as the bonding/antibonding rationale you have been teaching all of us. It is OK. Alternative explanations coming from higher theories are important, since they broaden our understanding of molecules.

Roald: There is another excited state that is really very interesting, and this is the $^3\Pi_g$ (there should also be a corresponding singlet) with the long 1.535 bond length. You can see in Mulliken's table^[20] that this state was known over 70 years ago. The long bond comes from occupation of the antibonding π_g^* MO.

Why do I think this one is interesting? Because the range of CC bond length in the ground and excited states of C_2 is 1.23–1.54 Å. That is about the bond length range of CC bonds in organic molecules, from the 1.21 of triple bonds to 1.53 of ethane.

Sason: But, as you know, it is simple to understand this state based on VB theory. I am sure you thought about all these states before and saw that VB can elucidate many of these trends.

Roald: Yes! VB is the way to explain simply how the small C_2 molecule plays out in its excited states the gamut of all CC bond length in 60 million organic compounds. Here is how it goes: Let's form ethane, ethylene, acetylene from C_2 plus six, four, or two hydrogens. To bond with the hydrogen in the various ways, different hybrids are needed. To get those hybrids you will need a mixture of spectroscopic states (some observed, some not) of C_2 . I bet that the configuration of C_2 that mixes in strongly into the six hybrids needed to form ethane will have electrons in it that are promoted to π_g orbitals.

One reason I know this is that I have looked at the HOMO of ethane (so back to MO's, I love moving back and forth, as does Sason). I show the e_g HOMO of staggered ethane in Figure 6. And at the carbons it is π -like, and CC antibonding. A piece of the CC antibonding π_g MO of C_2 is in the ethane HOMO!

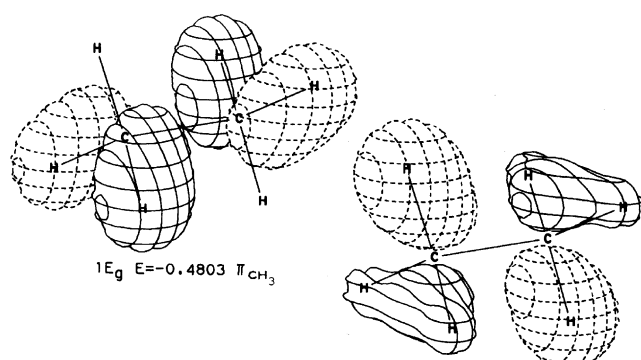


Figure 6. Staggered ethane HOMO from Jorgensen and Salem.^[34]

Sason: Roald, you are succeeding so well with all this Lego piecing *because* you are moving back and forth between MO and VB thinking modes. That is great fun, because each method has its own specific insights. I still remember you deriving the isolobal analogy on the blackboard (now we have only whiteboards) by starting from canonical MOs, then plucking off ligands, and getting localized hybrids, and subsequently re-blending them to form symmetry adapted orbitals capable of different bonding patterns. I wish we could teach all chemists this art of crossing through mirrors. I just returned from the VB workshop in Paris where all participants, including DFT, MO and MRCI aficionados, used VB and local reading of wave functions.

Roald: It turns out that there is another set of molecules, now very inorganic, in which C_2 appears. Solid state carbides contain carbon in just three forms—as atomic (ionic, formally

C^{4-}) interstitials in refractory materials, such as WC, as diatomic C_2 units, and (just a few) as C_3 's. The C_2 carbide familiar to all of us is CaC_2 .

Henry: I remember it! There is a characteristic odor of wet acetylene in a carbide lamp which I encountered myself whilst caving in Mexico once. Wikipedia informs me it is due to $\approx 20\%$ contamination of the industrial grade material with CaO , Ca_3P_2 , CaS , Ca_3N_2 , SiC , and the smell is due to PH_3 , NH_3 , and H_2S generated from these.

Sason: I recall as a child, we use to use calcium carbide to send tin-can rockets. A little water on the carbide, a tin can over it, and we ran away like madmen to hide. The tin can will fly in the air. One time it fell on someone's head.

Roald: Indeed, a number of C_2 -containing carbides are available, especially from the work of Wolfgang Jeitschko.^[35] You will never find them in an introductory chemistry text—neither teacher nor student wants to see this wondrous complexity. Nor in the usual inorganic chemistry course, dominated as these are by molecular chemistry. Table 1,

Table 1: CC distances in some extended carbides containing C_2 units. This is a selection from longer tables in W. Jeitschko et al.^[35] and J. Li and R. Hoffmann.^[36] The crystal structures vary in quality; they have all been arbitrarily reduced to 3 significant figures.

Compound	CC distance [Å]	Compound	CC distance [Å]
CaC_2	1.19	$U_2Cr_2C_5$	1.34
Ho_2C_3	1.24	$DyCoC_2$	1.37
Sc_3C_4	1.25	$CeRhC_2$	1.39
$ScCoC_2$	1.26	$CeNiC_2$	1.41
YbC_2	1.29	U_2NiC_3	1.43
$Gd_{24}Ru_{15}C_{40}$	1.31	$Th_2Ru_6C_5$	1.46
Er_2FeC_4	1.33	$UCoC_2$	1.48

shows a selection of those carbides. The C_2 units are not naked; they form polyanions of varying dimensionality with the transition metals in the structure.

Note the range of CC bond lengths, 1.19–1.48 Å. Pretty close to the range of bond lengths in all organic molecules, and to the range of CC separations in the ground and excited states of C_2 .

Sason: The carbides you are showing are indeed marvelous. Many C_2 units. C_2 chemistry, and a universe made from C_2 units! I hope this is taught somewhere...

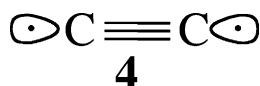
Henry: I think of the C_2 unit in CaC_2 as C_2^{2-} , isoelectronic with nitrogen, explaining the very short CC separation. Probably the other C_2 unit's bond lengths can be explained as C_2 bearing 4^- or 6^- charges, like deprotonated ethylene and ethane.

Roald: Yes, but note the continuity of bond lengths, not just 1.21, 1.34, 1.40, 1.53 Å. A detailed analysis (we have examined some of these)^[36] shows that there is electron transfer to C_2 , and also occupation, full or partial, of bands formed from specific C_2 states.

Sason: This looks like a mixture of valence states ending with fractional charge transfer.

Roald: I agree; that's a good VB way to look at these negatively charged C_2 's, stuck in a sea of cations.

There is one more matter I would like to take up on C_2 , a matter of disagreement between Sason and me. Sason, you say C_2 is not a diradical. I used to think of it as singlet-coupled diradical, 4:



That helped me to come to peace with the reactivity and kinetic lability of C_2 . Organic di(bi)radicals (e.g. methylenes, cyclobutadiene, trimethylenemethane, *m*- and *p*-benzyne) have certain characteristic reactions, a consequence of their more or less unpaired electrons (depends on spin state), and their low-lying and high-lying partially filled, partially empty orbitals. Typically a) they exist in a spin balance—two spin states not too far in energy from each other. Sometimes the singlet is higher (methylene) than the triplet, sometimes lower (*p*-benzyne); b) they are prone to often highly exothermic dimerization or polymerizations, that is, the activation energies for such reactions are small; c) they are reactive, with characteristic reactions being H or Cl atom abstractions, or low-activation insertion into C–H bonds.^[37]

I see C_2 in its simple valence structure I drew above (I am choosing to see the 4th bond as not a bond, but a singlet coupling of interacting orbitals, I know) as a diradical. So why do you say that C_2 is not a diradical?

Sason: A fair question, Roald. Let me just remark that you are not using MO theory any more. How do you get this triply bonded structure with the diradical character? For sure from VB!

Roald: Touché. That diradical came from my muddled VB-MO mind. I look at C_2 and I see in it three clear bonds, whose MO representation is the $2\sigma_g$ and the π_u . I think of $3\sigma_g$ and $2\sigma_u^*$ as being the delocalized equivalent of two localized lone pairs. Both are occupied in N_2 . In a single configuration description of C_2 only one lone-pair combination is occupied, and that's how I come to a diradical.

Sason: It is simpler to start here from VB: you form sp hybrids at each carbon, then you make an internal triple bond between the carbon atoms and you are left with the two inverted sp hybrids, each having one electron, and you couple them to a singlet pair.

Roald: I think the only difference between us is that you choose to call that coupling a 4th bond. And I don't: I look at C_2 's reactivity, and I see a diradical at work.

Sason: And I don't. Why do I say C_2 is not a diradical? If you look at Figure 4 in our paper,^[12] you will see that the overlap between the GVB orbitals of the 4th inverted bond ranges between 0.44 for C_2 to 0.53 for BN. These are very significant overlaps (for the π -bonds the respective overlap is 0.77), which mean that in addition to the spin coupling in the covalent “diradical structure”, the inverted bond enjoys a significant resonance energy (RE) due to ionic-covalent mixing. This RE is 33 % for C_2 and reaching 47 % for BN. This is quite similar to many homopolar covalent bonds, e.g., $\approx 29\%$ for the C–C bond of cyclopropane,^[38] and it may be starting to converge to the percentages found in charge-shift bonds, for example, in [1.1.1]-propellane. Finally, the strength

of the bond in the series we calculated is 12–17 kcal mol^{−1}, quite significant, and more than most of the δ and bonds ϕ bonds in transition metals, and at par with the bent π bonds of the *trans*-bent higher row analogues of acetylene.^[39]

With these features, the 4th bond of C_2 is not a diradical, even though the definition of the border is fuzzy. Let me give you an example of a “diradical bond”; this is the δ bond of $Re_2Cl_8^{2-}$, so referred to by many in the community. The GVB pair overlap here is 0.130, the CI coefficients are similar for the fundamental MO configuration ($\sigma^2\pi^4\delta^2$) and the doubly excited one ($\sigma^2\pi^4\delta^{*2}$). These very similar coefficients make the δ bond a singlet-coupled diradical, without much covalent-ionic resonance energy. In fact, the occupation numbers, of the δ and δ^* orbitals are 1.39 and 0.68, which reveal a high diradical character.^[40,41]

Roald: And in C_2 ?

Sason: If one uses just a two-configuration wave function, the populations of $2\sigma_u$ and $3\sigma_g$ are 1.73 and 0.27, respectively.

But back to $Re_2Cl_8^{2-}$. The singlet triplet excitation, as far as I could estimate from the literature is 9.2–10.6 kcal mol^{−1}, which makes the bond energy of the δ bond 4.6–5.3 kcal mol^{−1}, 50 % lower than the values for the inverted 4th bond in C_2 and its isoelectronic series. What should we call then the 4th bond? It is a bond, albeit a weak one. In fact, as I shall immediately convince you, the *experimental* bond energy of the 4th bond in C_2 is ≈ 17 kcal mol^{−1}. This is a value not to dismiss but to grapple with!

Of course, this does not mean that I expect C_2 to be rock stable. It is not. But the best ways to gauge its reactivity are, a) the barrier for dimerization process, $2C_2 \rightarrow C_4$, compared with that in radical dimerization where the barrier is zero; and b) compare the H-abstraction reactivity of C_2 with a radical like CH_3 for reactions having the same thermodynamic driving forces. The barrier difference can be directly converted to bond energy of the 4th bond.

Roald: Since both C_2 and C_4 are pretty well-known in the vapor phase, one has their heats of formation. This dimerization ($2C_2 \rightarrow C_4$) is exothermic by no less than 169 kcal mol^{−1}.^[42] The reason for the large exothermicity I think is that the central bond in linear C_4 is substantially stronger than a CC single bond.

Sason: C_4 cannot be formed by a simple dimerization of two singlet C_2 molecules! It has a cumulenic structure, $:C=C=C=C:$, and a triplet ground state. This triplet-state C_4 product does not originate from the singlet state of C_2 . This means that the process of coupling two singlet C_2 molecules to yield a singlet C_4 diradical is likely to have a non-negligible barrier and a less favored exothermicity, which accounts for the strength of the 4th bond.

Henry: I've already started playing with the $2C_2 \rightarrow C_4$ transformation.

Sason: I would like to suggest that one needs a multi-reference study of the two singlet C_2 molecules reacting to singlet C_4 .

Roald: It should be done. Meanwhile, we do have some experimental information. Because of its intermediacy in flames, and astrochemical interest, people have studied many reactions of both the $^1\Sigma_g^+$ ground state and the $^3\Pi_u$, the low-lying triplet of C_2 ,^[43] lying just 718 cm^{−1}, a little more than

2 kcal mol⁻¹ above the ground state. They react readily with just about everything in sight. To be specific: The triplet has an activation energy of 5.6 kcal mol⁻¹ for reaction with CH₄.^[44] The C₂ ground state reaction with methane (and with H₂ or ethane) is much faster;^[45] these reactions, run down to 24 K, are close to the collisional limit.^[46] C₂ reacts readily with alkenes at 77 K, to give what seems to be an initial diradical.^[47] C₂ in both low-lying electronic states reacts barrierlessly with vinyl acetylene in crossed molecular beam experiments.^[48]

Do you need more evidence that C₂ in its ground state has the reactivity of a radical or diradical?

Sason: Chemists are amazing in how they manage to probe the reactivity of so many transients! The evidence you bring here Roald is indeed very interesting. It shows that the 4th bond is weak, as we had it. But does it really prove that you have a diradical? I think not. Let me give you some counter arguments:

Reading the paper of Pasternack and McDonald^[45] shows that the pathways of the ¹Σg⁺ ground state reaction are different than those of the ³Π_u state; they may differ in the trajectory, in whether the product is a ground state CCH radical or an excited state, and in the reaction exothermicity. The most recent paper by Páramo et al.,^[46] further shows that the reactions can be complex, sometimes involving insertion reactions like carbenes, other times H-abstraction, and some disagreements between different experimental studies. Other studies by Skell et al.^[47] argue for cycloaddition reactions to multiple bonds, with diradical intermediates. I think these studies are great, but not mechanistically conclusive yet. They reveal perhaps the weakness of the 4th bond, but they certainly do not probe the “diradical” character of the ground state.

It is not easy to tell what reactivity probes and what it doesn't. Fluorine atom cleaves easily the H–H bond—is the H–H bond a diradical? Of course not, this reaction is very fast because it is very exothermic. Another example to ponder is that of the singlet methylene that has only electron pairs, and is nevertheless much more reactive than the triplet methylene, which is a diradical. Doublet CH is a monoradical, but it reacts fast as a singlet carbene (inserting into C–H bonds), while the quartet CH, which is a tri-radical, is long lived. The reasons are clear, but they have nothing to do with the initial state of the reactive species. There is also a transition state to think about...

Let's take another example, silaethylene and disilene have a π-bond (albeit weak, but stronger than the 4th bond of C₂). Nevertheless, these molecules dimerize with hardly any barrier, presumably via diradicals, because the reaction is formally forbidden. The same applies to the triply-bonded molecules with heavy atoms. Does the very high reactivity of silaethylene or the presence of diradical intermediates during the cycloaddition prove that it is a diradical in the ground state? I think not. If every reactive molecule will be defined as a diradical, you may be left with very few bonds...

To sum up: while I think the reactivity studies of C₂ you found are fascinating, they do not reveal the “diradical” character of the molecule. Reactivity depends not only on the nature of the ground state but also on the nature of the

excited state that correlates to the product state, as I have been saying for years.

The best way to probe the effect of the 4th bond on reactivity is by comparing the H-abstraction reactivity of C₂ and CH₃ in identity processes, from HCC and CH₄, respectively. Using my latest VB modeling of this reaction,^[49] and using the lowest value for the BDE of the 4th bond (12 kcal mol⁻¹), I can predict that the barrier for C₂ abstracting of H atom will be 4.4 kcal mol⁻¹ higher than that for the abstraction by CH₃.

Roald: One final thing that I want to say about C₂: it is the finest example I know of the *unimportance* of atomization energies in chemistry. Here we have the world's second most stable—with respect to atomization—homonuclear diatomic molecule, second only to N₂. It takes ≈150 kcal mol⁻¹, 6.5 eV mol⁻¹ecule, to take C₂ into two atoms of C. But the heat of formation of C₂ is^[42] +200 kcal mol⁻¹! To put in another way, it takes 150 kcal mol⁻¹ to break C₂ into two C atoms. But carbon (diamond or graphite) is so stable that C atoms going to C (graphite) is far further downhill (350 kcal mol⁻¹ per two C atoms) in enthalpy.

Friends, there are too many papers written by theoreticians in the literature in which *sub voce* or explicit claims to stability (in the sense of the compounds existing in a bottle) are made on the basis of atomization energies being large. C₂ illustrates just how silly such claims are. What matters in chemistry, if you are going to have a coelenterate in the sea or a lab chemical in a bottle is kinetic persistence.

And kinetic persistence C₂ does not have.

Sason: I agree, and this is unfortunate, that just that carbon molecule that possesses a quadruple bond is also kinetically unstable.

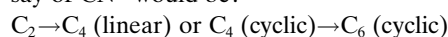
Roald: Live with it. Just as we live with the fact that dark, slippery graphite is more stable than brilliant, expensive diamond.

Sason: Still, I bet that CH₃· is less stable, but we know so much about its properties, and even the barrier for the CH₃ + CH₄ exchange reaction has been determined.^[50] And cyclobutadiene...!^[51] Being unstable does not mean less interesting.^[52] Unstable molecules cause aging. Others (like H₂O₂) may cause stem cells to evolve to neuron cells in our aging brains. Still others are utilized by our immune systems. Would you consider these molecules/species do not matter for us?

Roald: You're right, Sason—catalysts and intermediates, and much of tuning of reactivity play off thermodynamic metastability and kinetic lability.

Sason: C₂ is important despite its kinetic instability because it teaches us something new about bonding; something that evaded us for years!

Henry: I agree that neutral C₂ itself is a highly transient species, probably only amenable to spectroscopic study in the gas phase. But one might ask if the prospects are more enticing for any of its ionic isoelectronic relatives such as CN⁺ partnered perhaps with for example, a non-coordinating/non-oxidizing anion^[53] such as B₁₂Cl₁₂²⁻? I thought I might calculate energies for the following reactions to see what the prospects of isolating slightly more persistent oligomers, say of CN⁺ would be:



$\text{CN}^+ \rightarrow \text{C}_2\text{N}_2^{2+}$ (acyclic) or $\text{C}_2\text{N}_2^{2+}$ (cyclic) $\rightarrow \text{C}_3\text{N}_6^{3+}$ (cyclic)

The results (see Figure 7 for optimized structures for CN^+ , those for C_2 are more symmetrical) may give us an approx-

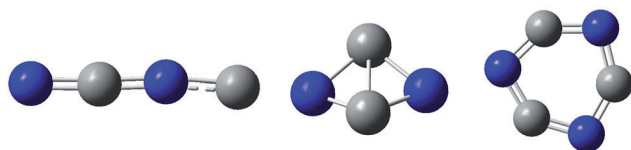


Figure 7. Possible dimers and trimers of CN^+ . Carbon is blue, nitrogen gray.

imate indication of viability.^[54] Thus (at the coupled-cluster CCSD(T) level and a 6-311G(d) basis set) the dimerization of C_2 is *exothermic* to a linear C_4 ($\Delta G_{298} = -114.7 \text{ kcal mol}^{-1}$) or a cyclic isomer (-125.3). And the trimerization is exothermic by $-255.6 \text{ kcal mol}^{-1}$. In contrast, CN^+ is *endothermic* with respect to an acyclic ($+43.5$) or cyclic ($+79.5$) dimer and trimer ($+182.7$). But the real test for the persistence of, for example, CN^+ may be whether its electron affinity is not so large that it does not abstract electrons immediately from any neighboring counterion.

Roald: The great difference between C_2 and CN^+ oligomerization is what one would expect from electrostatics. I also note that your exothermicity of the C_2 dimerization is way off from the experimental value (though we need to take a careful look where the NIST tables got their values from).

Henry: Yes, the NIST tables can have errors; Stewart^[55] has teased out 34 (a very small proportion of the entries, it has to be said) using semi-empirical calculations of thermodynamic quantities, and at the high end of computation, the so-called W1-4 theories^[56] are routinely predicting molecules for which “re-measurement may be in order.” The NIST tables reveal^[57] ΔG_{298} for the dimerization of C_2 as $-156.2 \text{ kcal mol}^{-1}$, which is $30.5 \text{ kcal mol}^{-1}$ more exothermic than my first stab at calculating this quantity as noted above. This implies that either C_2 is calculated to be $15.2 \text{ kcal mol}^{-1}$ too stable, or that C_4 is calculated to be $30.5 \text{ kcal mol}^{-1}$ too unstable. A variational calculation cannot achieve the first condition, so we are left with two possibilities: 1) that the calculation of C_4 in particular is in error or 2) that the experimental dimerization measurements of ΔG_{298} are in error. The former could arise from two basic effects; lack of proper extrapolation to the basis set and single-reference correlation limit, coupled with neglect of the multi-reference character of both C_2 and C_4 . We can bracket the first of these by re-calculating using the W1 theory noted above,^[58] which gives a slightly greater exothermicity of $-136.8 \text{ kcal mol}^{-1}$ for C_2 dimerization, better than the previous value, but still insufficiently exothermic by $19.6 \text{ kcal mol}^{-1}$.

Roald: All that uncertainty, Henry, and you give us figures to a tenth of a kcal mol^{-1} !

Henry: You tease me Roald, but with calculations, others may try to reproduce them, and quoting that extra decimal place can come in useful for this!

Sason: Henry, these exploratory calculations are great, and your point about experimental errors in the NIST database is

intriguing. But as I said above, C_2 has a multiconfigurational ground state. C_4 is likely to be in the same boat. Furthermore, to get the strength of the 4th bond one has to calculate the energy for the transformation of 2C_2 to singlet C_4 , which may reveal the strength of the 4th bond. But there is a simpler way. Wait and see...

Henry: It turns out that Massó and co have looked at this problem.^[59] It appears the missing link might be that C_4 is not a singlet, but a triplet ground state, and that this result is indeed only recovered from a multi-reference study. According to them, at the cc-pVTZ/MRCI+Q level, a linear triplet state for C_4 is some $24.1 \text{ kcal mol}^{-1}$ lower than the cyclic singlet. This more than accounts for the discrepancy noted above. It reinforces what Sason says, that a properly balanced multi-reference study for both singlets and triplets of C_2 and C_4 will be required; non-trivial even for such small molecules! But at least we have identified one experimental handle against which the properties of these diminutive molecules might be tested.

Sason: Let me say my last words about the bonding in C_2 . I promised you an experimental value for the bond dissociation energy of C_2 . The idea came to me as I was dreaming in a dull moment in a conference (I will not tell which one it was...). Here it is.

It is in fact very simple, if one can quantify the two consecutive bond dissociation energies (BDEs) of acetylene, their difference would be the BDE(4th bond). These values have been determined:^[18] The 1st BDE (for $\text{HCCH} \rightarrow \text{HCC}^\bullet + \cdot\text{H}$) is $130\text{--}134 \text{ kcal mol}^{-1}$, and the 2nd BDE (for $\text{H-CC}^\bullet \rightarrow \text{C}_2 + \cdot\text{H}$) is $110\text{--}117 \text{ kcal mol}^{-1}$. Based on these results the 4th bond in C_2 is $14\text{--}23 \text{ kcal mol}^{-1}$ strong, nicely bracketing our VB results. So the 4th bond can be probed either by good experimental determination or by very accurate computation. I am very excited by the prospects.

Roald: There is, however, another way to look at the problem. In Table 2 are some heats of formation (we know they may be

Table 2: Some heats of formation, in kcal mol^{-1} . Source: NIST Chemistry WebBook.

C	171	C_2	200
CH	142	HCCH	54
CH_2	92	H_2CCH_2	12
CH_3	35	H_3CCH_3	-20

imprecise, and I am especially unsure about what spin state of CH_2 and CH and C they used).

Using these heats of formation, the heats of the following CC bond breakages can be computed (in kcal mol^{-1} units):



The first three entries make relative sense to each other—a π bond is weaker than a σ , and a second π bond is weaker than the first. But what is going on with C_2 ? If the 4th bond in C_2 is as strong as you showed it above to be, are the underlying σ -CC and π -CC bonds in C_2 being weakened relative to acetylene? By >80 kcal mol⁻¹? The distance is just 0.03 Å longer...

Sason: You haven't read our paper carefully.

Roald: I'm getting older; if you explained this, I've plain forgotten. Tell me what's wrong with the above reasoning.

Sason: You are using BDEs, which give you the energy of dissociating a molecule to its ground state fragments. However, as we discuss in Figure 2e in Ref. [12] and in a special subsection (entitled: "Comparing the quadruple bond in C_2 to the triple bond in HCCH"), if one is going to gauge properly the strength of bonds, one has to look at fragments that are *not* in their ground states but in prepared states. Thus, the HC fragment in HCCH is approximately in its $^4\Sigma^-$ state (and hence capable of triple bonding), while the ground state is $^2\Pi$. The $^2\Pi \rightarrow ^4\Sigma^-$ promotion energy is 16.7 kcal mol⁻¹ for each CH fragment. Similarly, the C fragment in C_2 is in its 5S state (and hence capable of quadruple bonding), while the ground state is 3P . The $^3P \rightarrow ^5S$ promotion energy is 96.4 kcal mol⁻¹ for each C fragment. When you dissociate the molecules adiabatically the promotion energies are "released", and since this quantity is very large for C compared with HC, the BDE(C_2) is smaller than the BDE(HCCH). These BDEs do not reflect *the strength of the interaction between the fragments*, which we call the in-situ bond energy (D_{in}), and which is given as the sum of the BDE and the promotion energy (ΔE_{prom}). Simple arithmetic would show that $D_{in}(C_2) > D_{in}(HCCH)$.

The correlation consistent dissociation method described cited above^[18] shows that when you dissociate the molecule in a correlation consistent manner you end with the fragments in the prepared states. In order to derive the BDE you have to subtract from this bond strength the promotion energies of the fragments.

Roald: I understand. The BDE of C_2 (to dissociate it into two ground state C atoms) is 142–150 kcal mol⁻¹. To dissociate the molecule into two C atoms "prepared" (my quotes, not yours) for bonding, your D_{in} , takes $142 + 2(96) = 334$ kcal mol⁻¹. Do I have this right?

Sason: Yes. We actually calculate D_{in} as 303 kcal mol⁻¹, without assuming any valence state of the fragments. In fact, population analyses of our CASSCF and MRCI wave functions by David Danovich show that the valence state of the carbon in C_2 comes close to 5S .

Roald: OK, I would respectfully suggest, in the spirit of the Schwarz and Schmidbaur^[13] paper, that your in-situ bond energy, more than twice the BDE, somehow does not connect to chemical intuition. It's too far away in magnitude from the practical, from the BDE, the energy it takes to break a molecule into two atoms.

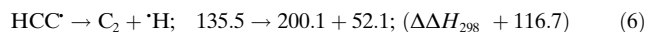
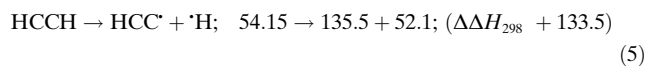
Sason: Yes, but we need that precise definition if we are ever going to make real sense of bonding relationships. We are fortunate that in most cases, the promotion/demotion energies of the fragments, which constitute the bond, are small, as for example in the series, $H_nCCH_n \rightarrow 2H_nC$ ($n=1-3$). In such a case we can make use of the relative BDEs to gauge the

relative bond strengths. But this is not the rule. The great studies of Bill Goddard and Emily Carter^[60] and George Trinquier and Jean Paul Malrieu^[61] showed the impacts of the promotion/demotion energies on the BDEs of C=C bonds.

A beautiful example is tetraazafulvalene, which was isolated by Taton and Chen.^[62] The molecule is "stable" and has a C=C bond length of 1.337 Å, much like any strong C=C bond. However, the measured BDE is just 4 ± 3 kcal mol⁻¹! The BDE is so small because the C=C dissociation leads to two Arduengo carbenes, which have singlet ground states lying 85 kcal mol⁻¹ below the triplet state, which is the one prepared for double bonding. As Chen explains, the kinetic stability arises due to avoided crossing of the prepared triplet states that make the bond, and the ground state which lead to the singlet Arduengo carbenes. He further shows the BDE is a balance between the in-situ bond strength, 172 kcal mol⁻¹, and the sum of the promotion energies, 2×85 kcal mol⁻¹, giving the dismal value BDE = 2 kcal mol⁻¹. Very inefficient investment of energy there...

I'm sure Henry remembers those beautiful 18th century steam engines of the industrial revolution, some running to this day. Despite all the skill of their engineers they never were more efficient than ca. 25%. It took the most careful definition of work and heat, thermodynamics to explain why this was so.

Henry: Might I emphasize that in his derivation of the BDE of the 4th bond, Sason is quoting *experimental* estimates. Of the three species, the thermodynamics of HCC⁺ had been the least certain, but by 2005 the errors for this species too had been narrowed down^[63] to around ± 0.4 kcal mol⁻¹ and so I think it useful to re-quote the current best estimates of the experimental values for ΔH_{298} (kcal mol⁻¹) of HCC⁺ as:



This estimates the value for the enthalpy of the 4th bond as 16.8 kcal mol⁻¹; Sason's error bar of ± 4.5 kcal mol⁻¹ may even be a generous one.

Sason: I am not confused about two-electron bonding. For me covalent bonding is quite clear: if there is electron pairing and if this brings about energy lowering more than a hydrogen bond, then we have a bond. C_2 has a 4th bond that cannot be dismissed as a weakly coupled diradical or any version of a diradical. A bond is a bond, is a bond...

Henry: I have been thinking: how would one explain this 4th bond to say a synthetic organic chemist (several have indeed wandered into my office these last few months and expressed a certain level of skepticism about that bond). It does seem clear that the reason this bond has been hiding, and its existence only recently revealed, is that it is intimately associated with (dynamic) electron correlation. A simple (over simple?) way of thinking of it is that the correlation means that a 4th bond would "avoid" the other three pairs of electrons already forming strong bonds in the internuclear region, and so this 4th electron pair of necessity takes up residency in the extranuclear region. Here it still acts as

a bond, albeit a weakish one. Could it be that the 4th bond in C₂ is the best example to date of one whose origins arise (almost) entirely out of electron correlation effects, and as such it would hardly be surprising if it had properties and an energy rather different from normal bonds.

Sason: Correlation hides the physics/chemistry. It is an electron pair, and a hence a bond.

Henry: A bond is a bond, is a bond...

Roald: Even I am beginning to think there's a bond there. Not that I am going to give up on it behaving like a diradical.

One final peep from me: Even as I spent two formative summers at the then National Bureau of Standards, I never imagined I would make as much use of the NIST Tables as I did in this work. As the BDEs show, the π bond in ethylene is "worth less" than the CC σ bond in ethane. The second π bond, in acetylene, adds about the same. Meanwhile, as one removes hydrogens, these species are moving to higher heats of formation (see Table 2). They are becoming energy rich. Acetylenes are the sweet spot for organic chemists—a class of compounds that are energy-rich yet kinetically persistent. They are made for forming new bonds.

Sason: Just a comment Roald: I just discussed the reasons why this series is so well behaved: small promotion/demotion energies, which make the relative BDEs useful indicators of bonding multiplicity.

It is time to finish our triologue. Shall we stop teasing one another about MO and VB? Both you, Roald, and I know how to walk in between the theories back and forth. We both recognize, and I am confident that Henry shares this, that quantum chemistry has given us two wonderful tools to reason about chemistry, and denying any one of them would impoverish our ability to reason. I am sure we at least reach this consensus...

Roald: Absolutely! There is a difference—I use the passage between MO and VB intuitively. You and Philippe also do, but—here's the difference—your mental promenade through the landscape of understanding is more... professional. That full CI you did on C₂, its transformation to a VB picture, allows you to say things with confidence.

Sason: Thanks Roald. I am disarmed by this compliment...

Concluding Remarks

We have come a long way from the two papers of Shaik, Hiberty, and Wu and their collaborators. What a lot of noise around a simple diatomic! Well, that noise, heated and friendly—is a reflection that our science is alive. C₂ in its ground and many known excited states, hiding inside nearly every organic molecule, and in some very inorganic extended, partially ionic structures—this tiny molecule, thermodynamically metastable as it is, has well-earned the attention we have lavished on it.

And if we disagree in whether it has a quadruple bond or not, well that too tells us a lot about human beings, subspecies chemical theorists. And about the state of chemical theory. Some will say we are unduly complicating life for ourselves, that there is an unambiguous way of defining a bond. Others will say that we will get better at these calculations (amusingly,

what they usually say is "the calculations will get better"), and then we will know the truth.

Even as Roald and Sason argue with each other, their contrasting visions (actually not that different) of the electronic structure of this small molecule manage to touch on just about every aspect of chemistry—spectroscopy, structure, bonding, stability, reactivity. C₂ is a microcosm of our science. And Henry's spirited calculations—the simple ones for his students, the sophisticated ones to get the facts right—point to the way chemists could and will use the tools that human ingenuity in the IT age has placed in our hands.^[64]

C₂ has come alive to us through our debate. Join us, light a candle. As Faraday did. See the excited states of C₂!

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