

Supporting Information (SI)

Eliminating all bonds from the ground state gives rise to ionic bonding in high spin states of heterodiatomics

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S1. COMPUTATIONAL DETAILS

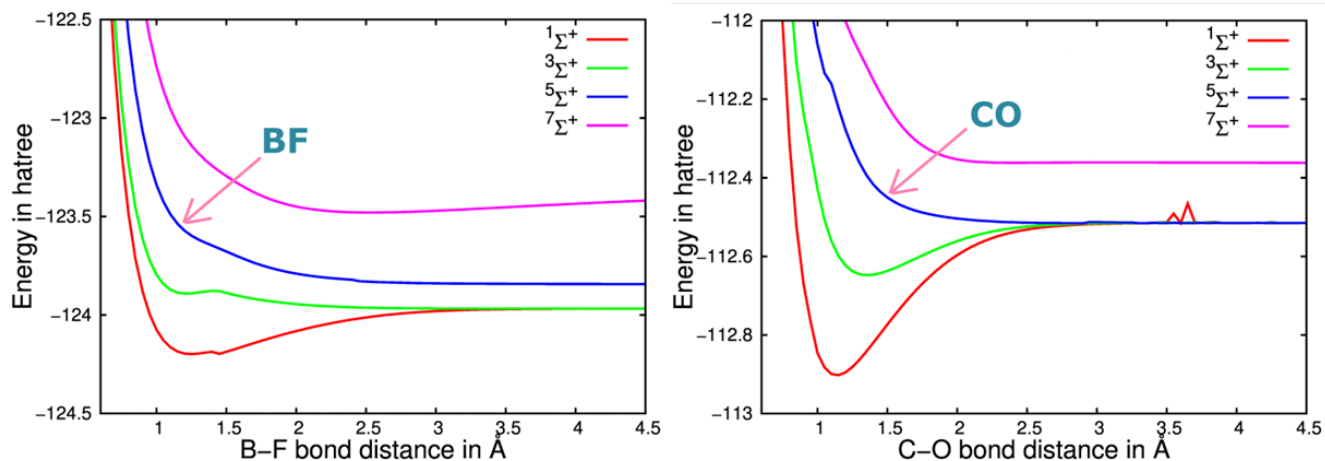
All the Hartree Fock (HF)¹, complete active space self-consistent field (CASSCF)² and multi-reference configuration interaction (MRCI) computations have been done using MOLPRO³ quantum mechanical package. The wavefunctions for the CASSCF computations are considered using full configuration interactions of 'm' electrons in 'n' orbitals and they may be denoted as CAS(m,n). For all the systems mentioned in the manuscript, we have taken full valence CAS i.e. (8,8) for C₂ and its isoelectronics and (10,8) for N₂ and its isoelectronics respectively. We have used cc-pVQZ⁴ basis set for all the aforementioned computations. Additionally, in order to include effects of dynamic correlation, we have performed MRCI computations using the CASSCF orbitals.

The potential energy curves (PECs) are obtained by scanning the CASSCF energy values along the X-Y bond distance (X, Y: the atoms constituting the above-mentioned diatomic systems) at an interval of 0.05 Å starting from 0.5 Å to 7.0 Å. However, to get a magnified view we have given the PECs upto 4.5 Å.

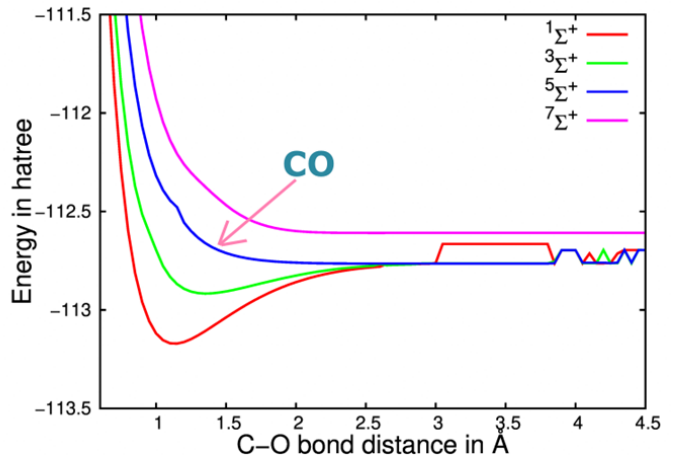
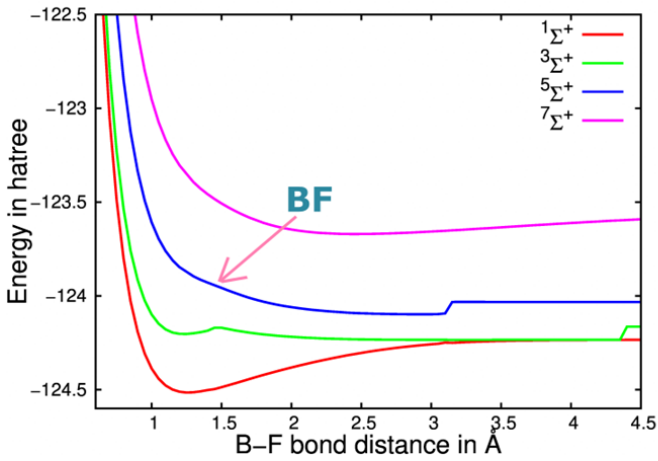
All the PECs obtained from CASSCF and MRCI computations are plotted using GNU PLOT⁵ program. The PECs obtained from the state specific CASSCF computations included a lot of avoided crossings. So, in order to smoothen out the curves, we have taken into account state-averaged PECs for all the spin states (apart from the nonet spin states of C₂, BN, BeO and LiF, since only one configuration state function is possible for those).

S2. POTENTIAL ENERGY CURVES (PECs)

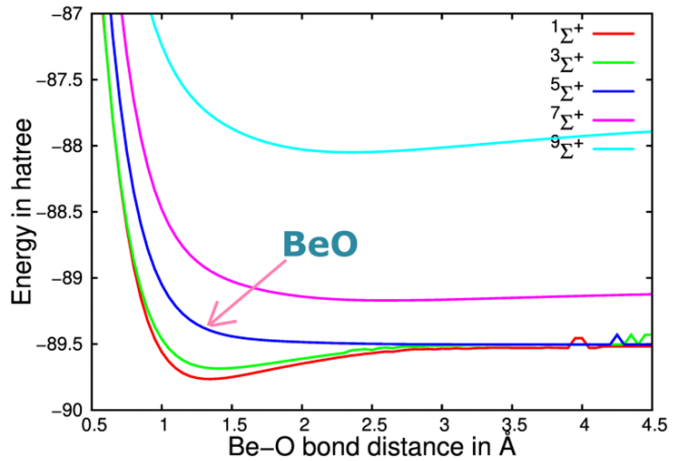
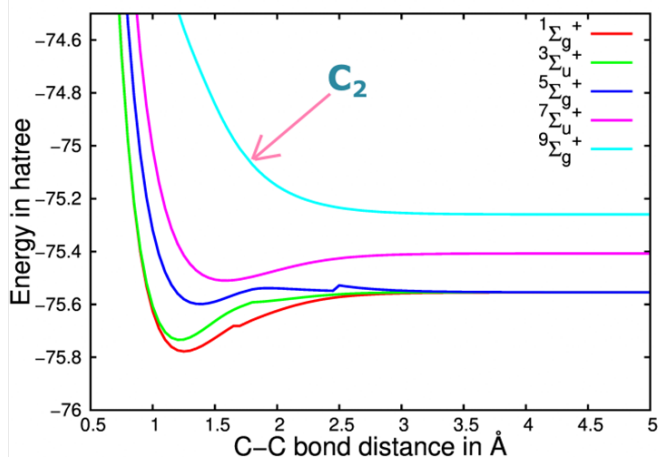
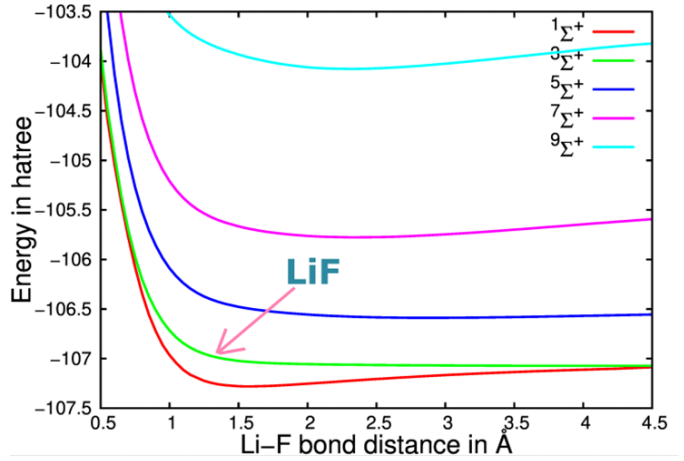
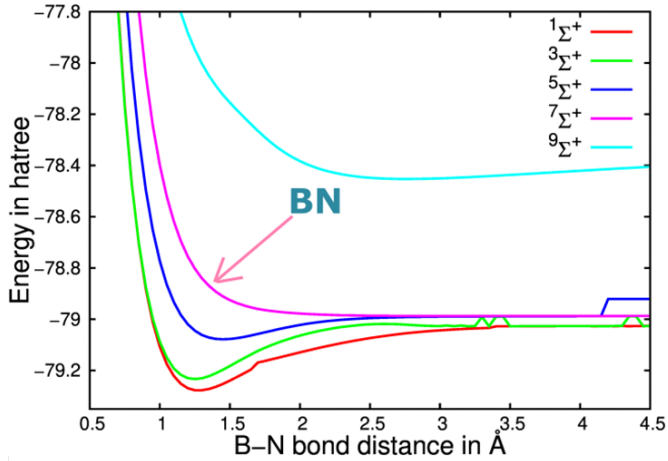
1. CASSCF PECs of the four spin states of (a)BF and (b) CO



2. MRCI PECs of the four spin states of (a) BF and (b) CO

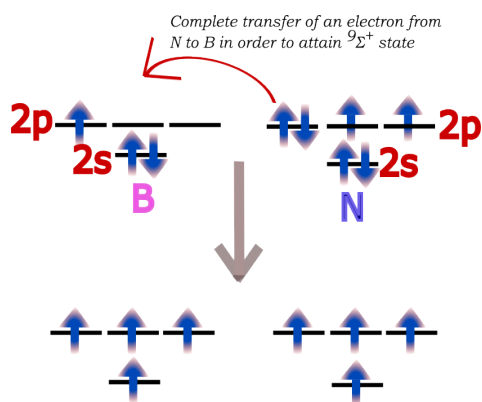


3. MRCI PECs of the four spin states of (a) BN (b) LiF (c) C₂ and (b) BeO



S3. HIGH SPIN IONIC STATES AND THEIR NBO CHARGES

In the main manuscript, we have discussed that as we decimate all the covalent bonds in the high spin states, we attain purely ionic states. For instance, in case of BN complete dissociation occurs in ${}^7\Sigma^+$ state. As we plot the PEC of the ${}^9\Sigma^+$ state, we obtain an ionic picture.⁶ It is obvious because ${}^9\Sigma^+$ is only achievable if an electron is transferred from the nitrogen atom to the boron atom, thus rendering a positive charge on nitrogen and a negative charge on boron. To reinforce this fact, we further computed NBO charges for all the spin states of BN at equilibrium B-N distance of the ionic state (2.75 Å) and at dissociation (7.00 Å). It showed a +1 charge on the nitrogen atom and a -1 charge on the boron atom in the ${}^9\Sigma^+$ state for both the distances. The table depicting the NBO charges for all possible spin states of BN is given below.



B-N distance	2.75 Å	7.00 Å
Spin Multiplicity	(Boron, Nitrogen)	(Boron, Nitrogen)
${}^1\Sigma^+$	+0.198, -0.198	0.000, 0.000
${}^3\Sigma^+$	+0.115, -0.115	0.000, 0.000
${}^5\Sigma^+$	+0.003, -0.003	0.000, 0.000
${}^7\Sigma^+$	+0.003, -0.003	0.000, 0.000
${}^9\Sigma^+$	-0.995, +0.995	-0.999, +0.999

We expected similar results for the isoelectronics BeO and LiF. In BeO as the dissociation occurs at the ${}^5\Sigma^+$, purely ionic states are obtained from ${}^7\Sigma^+$ state onwards and for LiF, the ionic states start from ${}^5\Sigma^+$ state. The tables depicting the NBO charges for these species are given below.

Be-O distance	2.65 Å	7.00 Å
Spin Multiplicity	(Boron, Nitrogen)	(Boron, Nitrogen)
${}^1\Sigma^+$	+0.676, -0.676	0.000, 0.000
${}^3\Sigma^+$	+0.058, -0.058	0.000, 0.000
${}^5\Sigma^+$	+0.019, -0.019	0.000, 0.000
${}^7\Sigma^+$	-0.987, +0.987	-0.999, +0.999
${}^9\Sigma^+$	-1.514, +1.514	-1.000, +1.000

Li-F distance	2.95 Å	7.00 Å
Spin Multiplicity	(Boron, Nitrogen)	(Boron, Nitrogen)
${}^1\Sigma^+$	+0.929, -0.929	+0.938, -0.938
${}^3\Sigma^+$	+0.000, -0.000	0.000, 0.000
${}^5\Sigma^+$	-0.976, +0.976	-0.999, +0.999
${}^7\Sigma^+$	-1.634, +1.634	-1.000, +1.000
${}^9\Sigma^+$	-1.284, +1.284	-1.009, +1.009

S4. GROUND STATE OF BN

Although the CASSCF ground state of BN is ${}^1\Sigma^+$, inclusion of dynamical correlation reports ${}^3\Pi$ to be the ground state. Furthermore, experimental results are consistent with it.⁷ However, both these states are at close proximity to each other. Since in this manuscript we have mostly focused on CASSCF studies of sigma states, we have looked into the ${}^1\Sigma^+$ only. Further, our hypothesis can be modified and used in case of triplet ground states if we rearrange the electrons in the CAS space in order to achieve a singlet state associated with the particular triplet state, which is indeed ${}^1\Sigma^+$ in the case of BN. Detailed discussion on

this has been done in our previous article where we delineated how we can adapt our hypothesis to predict the bond orders of O₂ and B₂, both of which are known to have triplet ground states.⁸

References

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