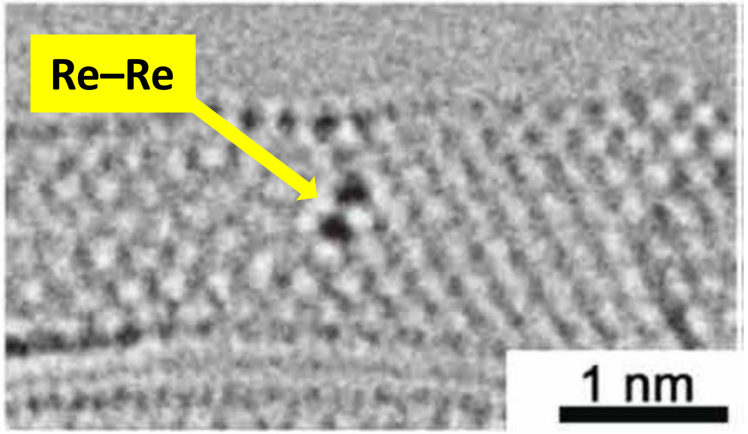
Chemical Bonding

- Effects on Bonding
- Pauling's Rules
- Dative Bonds
- Bond Order
- Multiple Bonds
- Sigma Hole Interactions
- Bond-Stretch Isomers
- Relativistic Effects
- Aurophilicity
- H-Bonding

"Imaging an unsupported metal–metal bond in dirhenium molecules at the atomic scale" by K. Cao, S. T. Skowron, J. Biskupek, C. T. Stoppiello, C. Leist, E. Besley, A. N. Khlobystov and U. Kaiser, 2020, Science Advances. DOI: 10.1126/sciadv.aay5849

Chromatic and spherical aberration-corrected TEM

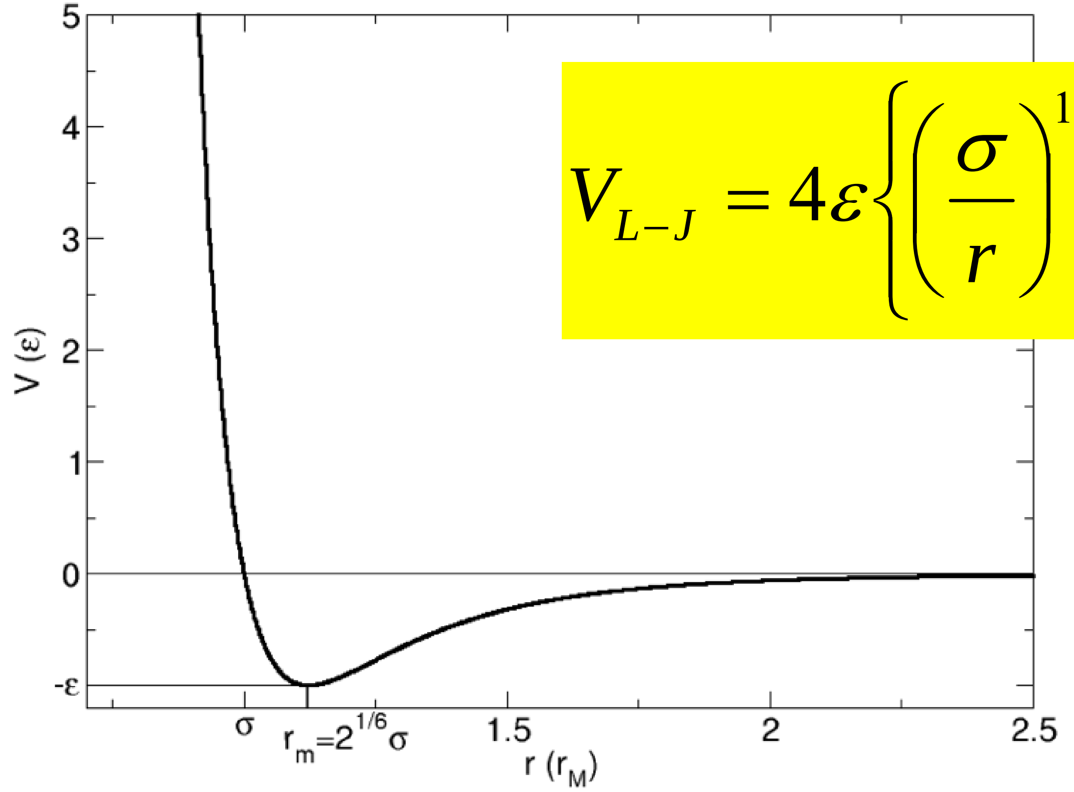


- Re–Re bond length changes in discrete steps correlating with bond order from one to four
- Direct imaging of the Re–Re bond breaking process reveals a new bonding state with the bond order less than one
- A high-amplitude vibrational stretch precedes the bond dissociation

Lennard-Jones Potential

A model for weak **van der Waals bonds** between molecules
Two interacting particles repel each other at very close distance, attract each other at moderate distance, and do not interact at infinite distance

The **repulsive** term (12) - the Pauli repulsion of overlapping electron orbitals
The **attractive** term (6) - attraction at long ranged interactions (dispersion forces)



$$V_{L-J} = 4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\}$$

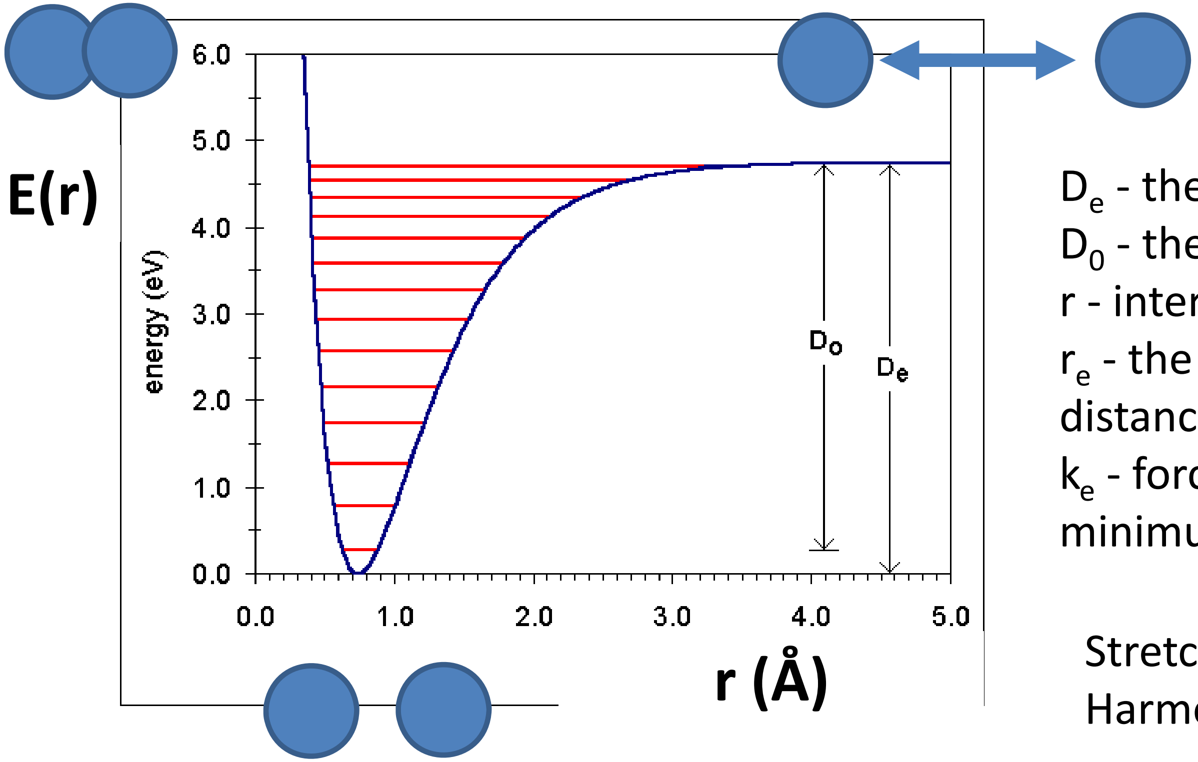
ε = depth of potential well
σ = distance where attractive and repulsive forces are at equilibrium
r_m = distance at the minimum V

Morse Potential

A model for potential energy of **a covalent bond** in a diatomic molecule
Solving the Schrödinger Equation with the Morse Potential can be done analytically

$$E(r) = D_e(1 - e^{\alpha(r - r_e)})^2$$

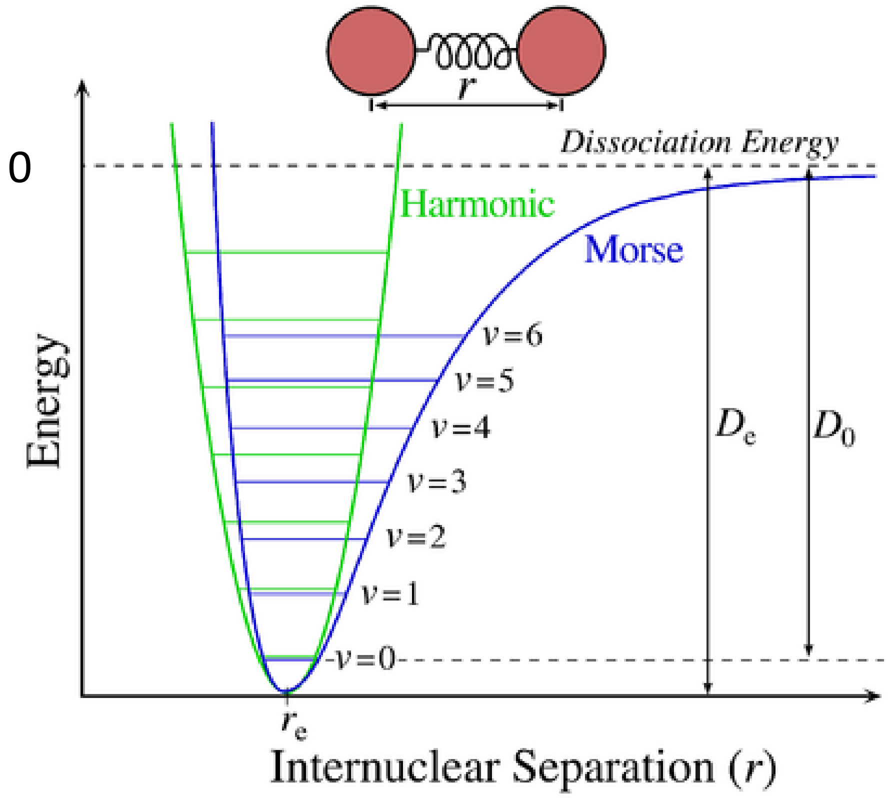
$$\alpha = \sqrt{\frac{k_e}{2D_e}}$$



D_e - the well depth
D_0 - the dissociation energy
r - internuclear distance
r_e - the equilibrium internuclear distance = bond length
k_e - force constant at the well minimum

Stretching vibrations
Harmonic oscillator

Morse Potential



Harmonic oscillator in quantum mechanics
Quantized vibrational energies - levels
$E^n = (\nu + ½)hf$
ν - vibrational quantum number
$\nu = 0$ - the vibrational ground state
Never dissociates

Morse-Potential energy curve
D_0 = bond dissociation energy
The ground-state energy is not 0

$$E^0 = \frac{1}{2}hf$$

Vibrational frequency f

k - force constant
μ - reduced mass

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

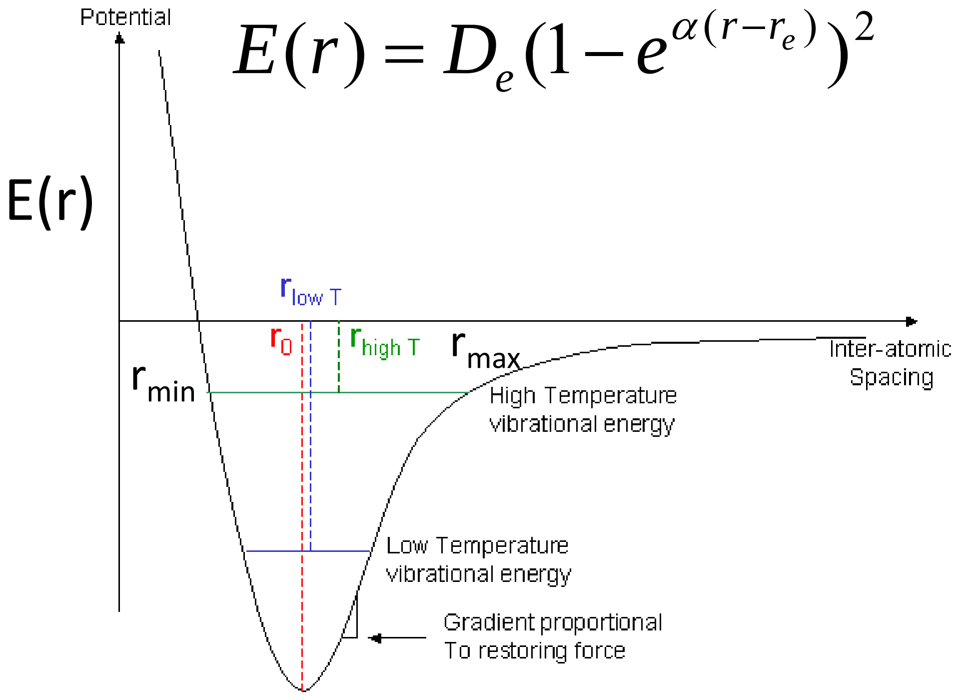
Bond	wavenumber cm^{-1}
C–H	3000
C–D	2200

The C–H bond is a stronger spring (larger k)
The C–D bond has lower zero-point energy E_D^o
Force constant *k* does not change with isotopic H/D substitution

Bond Length and Temperature

Experimental Mo≡Mo bond distance: at room temp. 2.23 Å, at LN2 t. 2.18 Å

$$E(r) = D_e(1 - e^{\alpha(r - r_e)})^2$$



$E^n = (\nu + ½)hf$

Potential energy curve is not parabolic (harmonic) but **unsymmetrical** (anharmonic)

99.9 % of C–H bonds are in the ground vibrational state ($\nu = 0$) at room temp

At high temperature, more high vibronic states are populated

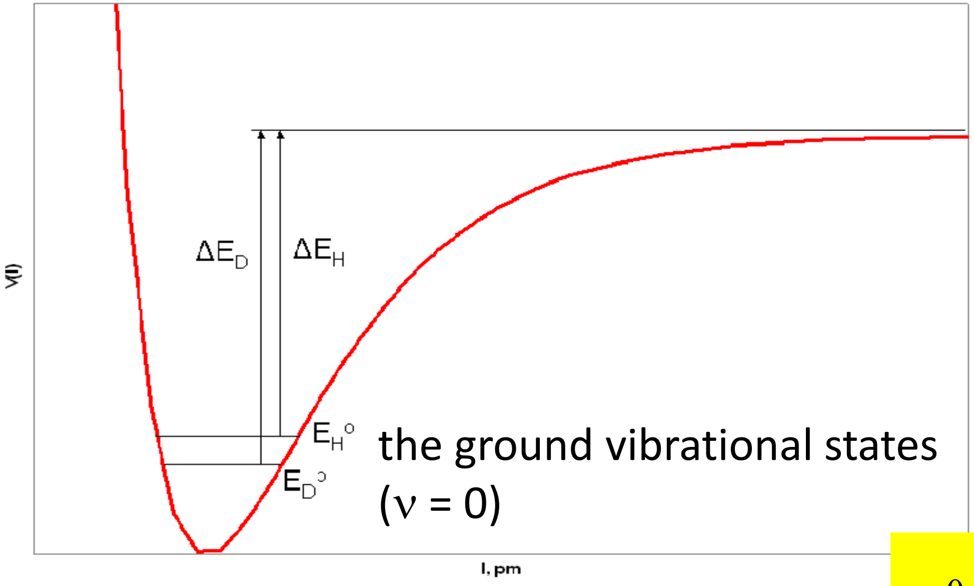
Bond length oscillates at frequency *f* between r_{max} and r_{min}

Average atomic separation = middle points move towards longer r

Longer bonds at higher temperature

Bond Length and Isotopes

Is the C–H bond longer or shorter than the C–D bond?



the ground vibrational states (ν = 0)

A Morse potential curve

The zero point vibrational energy (ZPE) is the lowest possible energy of a system, the ground state energy (ν = 0)

E_D^o and E_H^o (for $\nu = 0$)

the ZPE of R–H and R–D (R is much heavier than H or D) depend upon the reduced mass μ of the molecule

$$E^0 = \frac{1}{2}hf$$

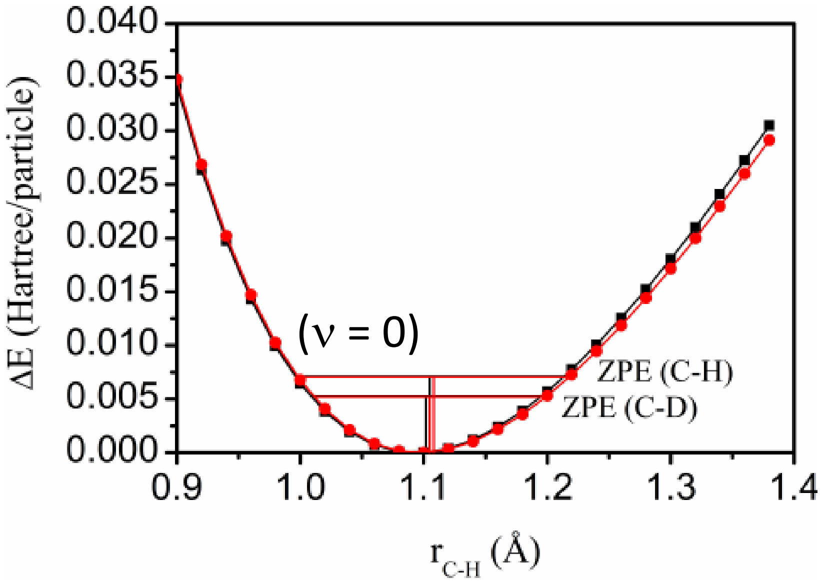
$$f = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

- The **heavier** the atom, the **lower** the frequency of vibration and the **smaller** ZPE
- **Lighter** molecules or atoms have a **greater** frequency of vibration and a **higher** ZPE
- Deuterium is **heavier** than hydrogen and therefore has the **lower** zero point energy

Bond Length and Isotopes

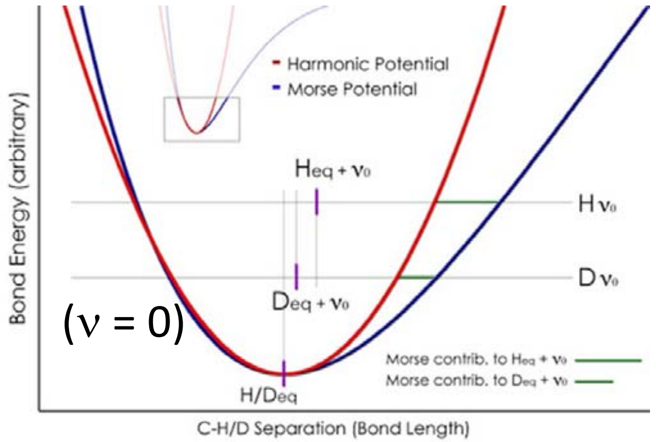
Is the C–H bond longer or shorter than the C–D bond?



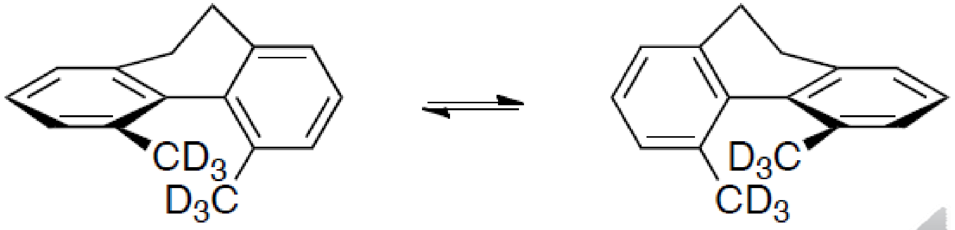
Due to the anharmonicity of the C–H/C–D vibrational potential energy function and the lower ZPE of a C–D bond

The midpoint of C–H level is at a longer distance than C–D

The average C–D bond length is typically ~0.005 Å **shorter** than an equivalent C–H



Secondary Isotope Effect - Steric effect of a CD_3 group **smaller** than CH_3

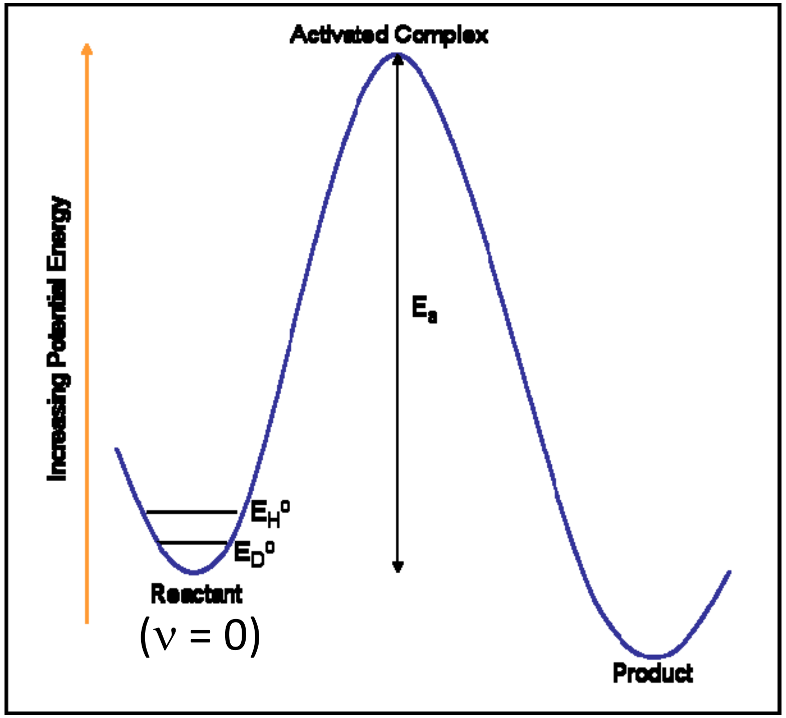


$k_H/k_D = 0.86$

Kinetic Isotope Effects

The **kinetic** isotope effect (KIE) = isotopically substituted molecules exhibit different reaction rates, the change in rate of a reaction due to isotopic substitution
An isotopic substitution **does not influence the electronic** potential energy surface

hydrogen (^{1}H) - deuterium (^{2}H) - tritium (^{3}H)
carbon (^{12}C , ^{13}C), nitrogen (^{14}N, ^{15}N), oxygen (^{16}O, ^{18}O), chlorine (^{35}Cl, ^{37}Cl)

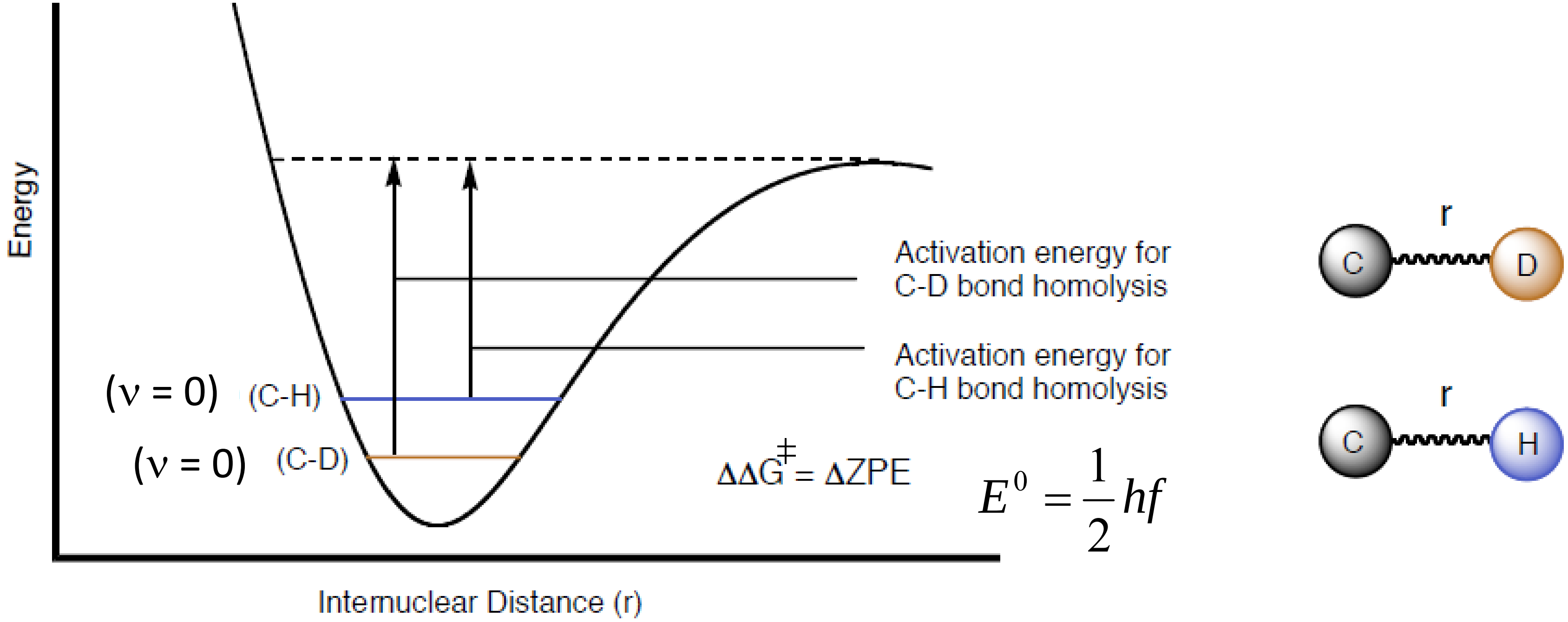


Different bond dissociation energies for R–D and R–H: E_D is greater than E_H

This difference in ZPE due to isotopic replacement results in differing rates of reaction *k* – the rate determining step

The effect is measured in KIE:
The reaction rate for the conversion **of R–D is slower than** the reaction rate for the conversion of **R–H**

Kinetic Isotope Effects



$$\Delta\Delta G^{\ddagger} = \Delta ZPE$$

$$E^{0} = \frac{1}{2}hf$$

Different bond dissociation energies for C–D and C–H:
E_D is greater than E_H - differing rates of reaction *k* – the rate determining step

The kinetic isotope effects:
The reaction rate for the conversion of **C–D** is **slower** than the reaction rate for the conversion of **C–H**

Kinetic Isotope Effects

Isotope replacement does not change the electronic structure of the molecule or the potential energy surfaces of the reactions

The greater the atom mass, the more energy is needed to break bonds
A **heavier** isotope forms a **stronger bond** - less of a tendency to dissociate
The increase in energy needed to break the bond results in a **slower reaction** rate and the observed isotope effect:

The ratio k_H/k_D = 1 to 7

Heavy atom isotope effects = the substitution of carbon, oxygen, nitrogen, sulfur, and bromine, with effects that are much smaller and are usually 1.02 - 1.10
The maximum isotopic rate ratio is proportional to the square root of the inverse ratio of isotopic masses

Secondary kinetic isotope effects = rate changes due to isotopic substitutions at a site other than the bond breaking site in the rate determining step of the reaction, α , β , and γ effects

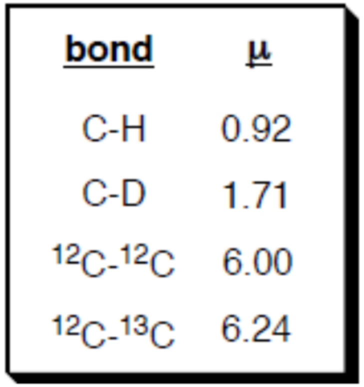
Kinetic Isotope Effects

Harmonic oscilator frequency
Bond stretching frequency - *f*

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$



bond	**μ**
C-H	0.92
C-D	1.71
^{12}C-^{12}C	6.00
^{12}C-^{13}C	6.24

Zero point energy (ν = 0) $E^0 = \frac{1}{2}hf$

Reaction rate

$$k = Ae^{-\frac{E^0}{kT}}$$

Isotope effect

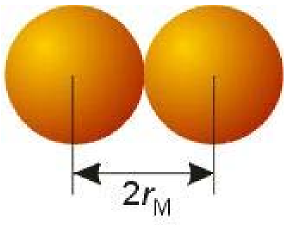
$$\frac{k_H}{k_D} = e^{\frac{h(f_D - f_H)}{2kT}}$$

Pauling's Rules

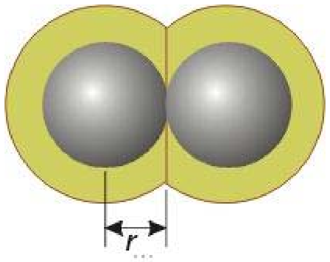
Five principles which could be used to determine the structures of complex ionic/covalent crystals

Pauling's Rule no. 1 Coordination Polyhedra

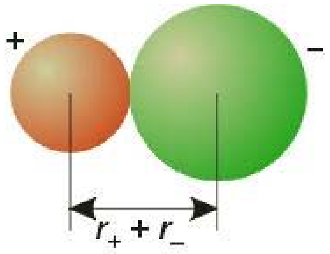
- A coordinated polyhedron of anions is formed about each cation
- Cation-Anion distance is determined by sums of ionic radii
- Cation coordination environment is determined by radius ratio



1 Metallic radius



2 Covalent radius



3 Ionic radius

$r(O^{2-})$ = 140 pm (Linus Pauling)

Bond Length

Pauling

$$R(A-B)=r_A+r_B$$

Schomaker-Stevenson Rule

polar bonds are shorter than the sum of covalent radii

Original c = 9 pm, n = 1
Modified c = 8.5 pm, n = 1.4

$$R(A-B)=r_A+r_B-c\left|\chi_A-\chi_B\right|^n$$

Allred-Rochow electronegativities give the best fit

Ionic Radii

R.D. Shannon and C.T. Prewitt, Acta Cryst. B25, 925-945 (1969)
R.D. Shannon, Acta Cryst. A32, 751-767 (1976)

As the coordination number (CN) increases, the Ionic Radius increases

Sr^{2+}

CN	Radius, Å
6	1.32
8	1.40
9	1.45
10	1.50
12	1.58

As the oxidation state increases, cations get smaller
(6-fold coordination, in Å)

Mn^{2+}	0.810
Mn^{3+}	0.785
Mn^{4+}	0.670
Ti^{2+}	1.000
Ti^{3+}	0.810
Ti^{4+}	0.745

Ionic Radii

The radius increases down a group in the periodic table
The exception - 4d/5d series in the transition metals - the lanthanide contraction

(6-fold coordination, in Å)

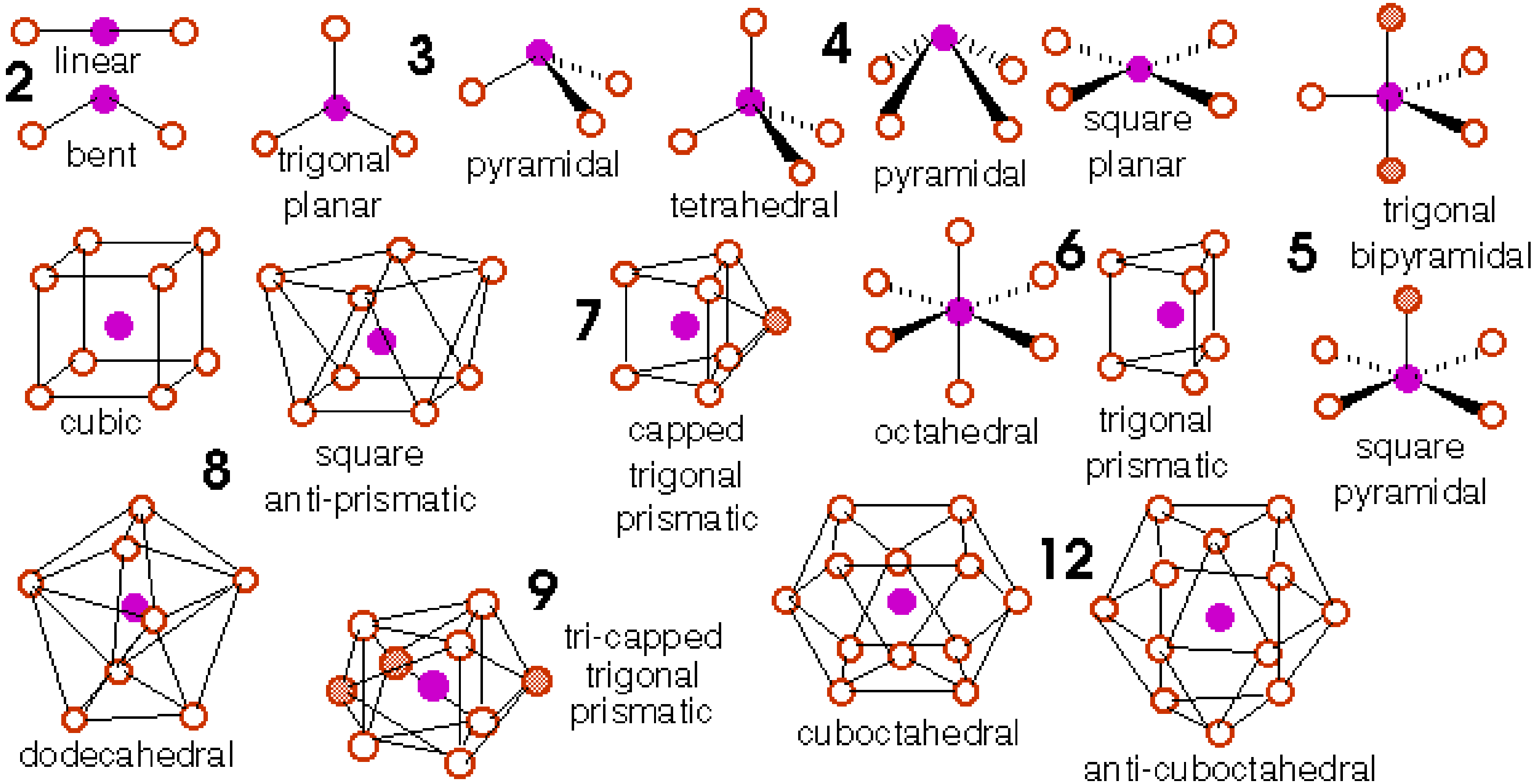
Al^{3+}	0.675
Ga^{3+}	0.760
In^{3+}	0.940
Tl^{3+}	1.025
Ti^{4+}	0.745
Zr^{4+}	0.86
Hf^{4+}	0.85

Left to right across the periodic table the radius decreases

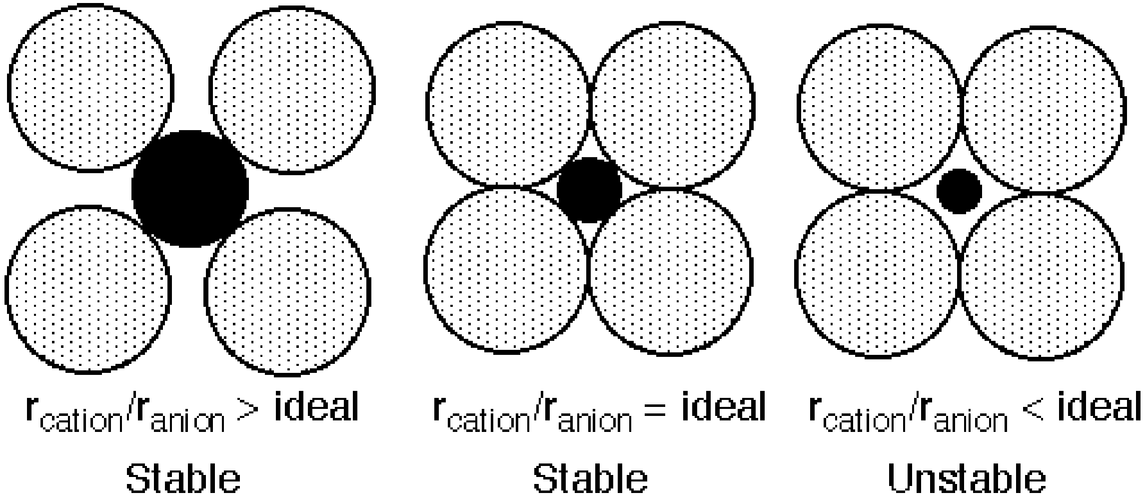
(6 coordinate radii, in Å)

La^{3+}	1.172
Nd^{3+}	1.123
Gd^{3+}	1.078
Lu^{3+}	1.001

Coordination Polyhedra



Cation/Anion Radius Ratio



CN	r/R
12 – hcp/ccp	**1.00 (substitution)**
8 – cubic	**0.732 – 1.00**
6 – octahedral	**0.414 – 0.732**
4 – tetrahedral	**0.225 – 0.414**

optimal radius ratio
for
given CN
ions are in touch

The Same or Not the Same

Three sigma criterion

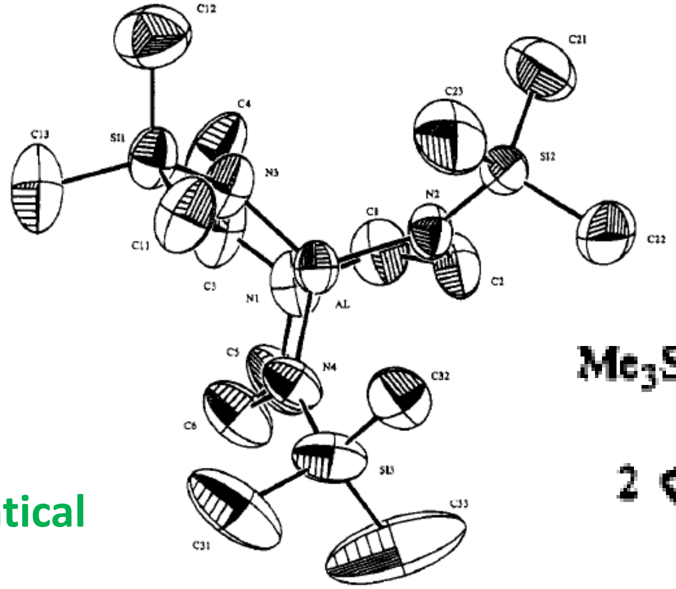
$$\Delta = A \pm B$$

$$\sigma_\Delta = \sqrt{\sigma_A^2 + \sigma_B^2}$$

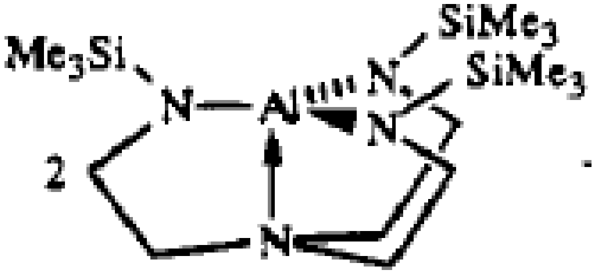
$$\Delta < 3\sigma_\Delta$$ **A, B – are identical**

$$\Delta > 3\sigma_\Delta$$ A, B – are different

σ - standard deviation



Crystallographically imposed C_3 axis??



Al-N(1) 1.983(6)	
Al-N(2) 1.805(5)	Si(2)-N(2) 1.684(5)
Al-N(3) 1.812(6)	Si(1)-N(3) 1.697(6)
Al-N(4) 1.810(6)	Si(3)-N(4) 1.690(6)
Δ = 0.007	Δ = 0.013
σ = 0.008	σ = 0.008
3σ = 0.024	3σ = 0.024

Pauling’s Rules

Pauling’s Rule no. 2 Bond strength and the bond order conservation principle (a rule of local electroneutrality)

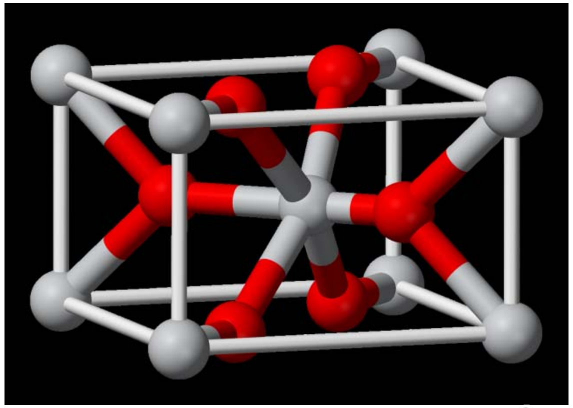
$$v_i = \Sigma s_{ij} = \Sigma \frac{z_i}{CN}$$

The strength of an electrostatic bond: s_{ij} = valence / CN

The bond valence sum of each ion equals its oxidation state

The valence of an ion (V_i, equal to the oxidation state of the ion) is equal to a sum of the valences of its bonds (s_{ij})

In a stable ionic structure the charge on an ion is balanced by the sum of electrostatic bond strengths (s_{ij}) to the ions in its coordination polyhedron



TiO_2 (Rutile) Ti - oxidation state of +4, coordinated to 6 oxygens

$V_{Ti} = +4 = 6\ (s_{ij})$ $\quad s_{ij} = +2/3$

The bond valence of oxygen, coordinated by 3 Ti atoms

$V_o = 3\ (s_{ij}) = 3\ (-2/3) = -2$

Each bond has a valence of s_{ij} with respect to the cation

and $-s_{ij}$ with respect to the anion

Bond Strength

Brown, Shannon, Donnay, Allmann:
Correlation of the valence of a bond s_{ij} with the (experimental) bond distance d_{ij}

$$s_{ij} = \exp \frac{R_{ij} - d_{ij}}{b}$$

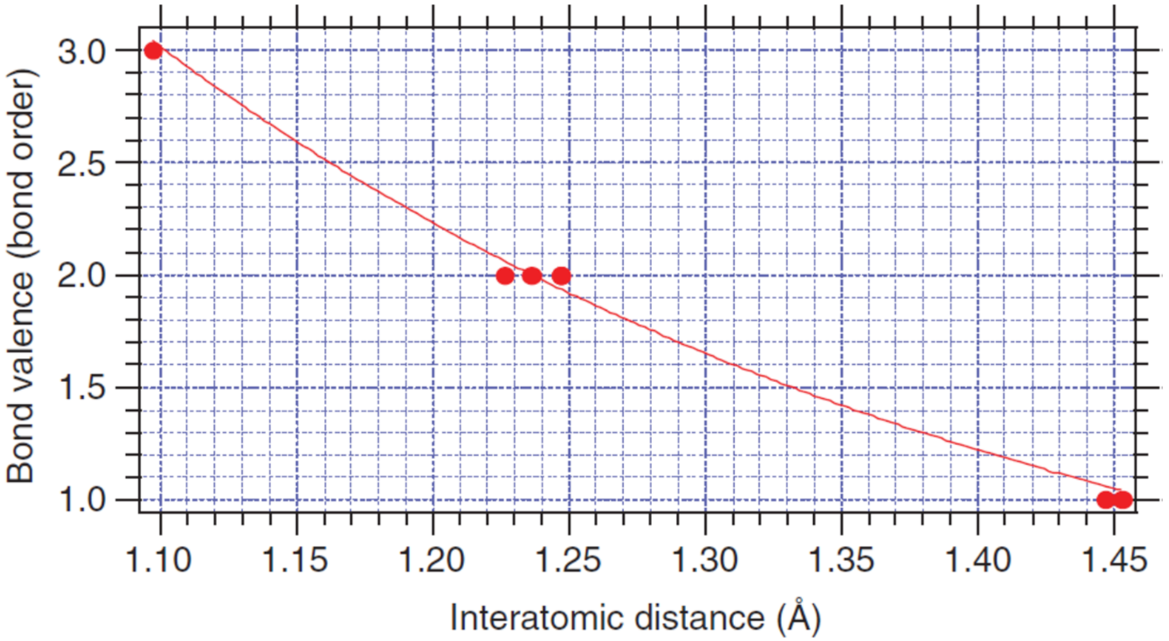
R_{ij} = standard single bond length - determined empirically from (many) structures where bond distances and ideal valences are accurately known

Tables of R_{ij} values for given bonding pairs (i.e., Nb–O, Cr–N, Mg–F, etc.) have been calculated, just as tables of ionic radii are available

A constant *b* = 0.30 - 0.37

$R = d$ $\quad s = e^{0} = 1$
$R < d$ $\quad s = e^{-1} < 1$ a bond longer than R is weaker than 1
$R > d$ $\quad s = e^{1} > 1$ a bond shorter than R is stronger than 1

Bond Strength vs. Bond Length



triple	1.097 Å in N_2
double	1.247 Å in N_2H_2 and dimethyldiazene 1.226 Å of N_2^{2-} in SrN_2 or calculated 1.236 Å in dimethyldiazene
single	1.447 or 1.453 Å in hydrazine N_2H_4

Bond Valence Sum (BVS)

Correlation of the valence of a bond s_{ij} with the (experimental) bond distance d_{ij}

$$s_{ij} = \exp \frac{R_{ij} - d_{ij}}{b}$$

$$v_i = \Sigma s_{ij} = \Sigma \frac{z_i}{CN}$$

Use of **the bond valence sum** concept

A) To check experimentally determined structures for correctness, or bonding instabilities
B) To predict new structures
C) To locate light atoms such as hydrogen or Li ion, which are hard to find experimentally
D) To determine ordering of ions which are hard to differentiate experimentally, such as Al^{3+} and Si^{4+}, or O^{2-} and F^-
E) To check/confirm oxidation states of atoms (Co^{2+} /Co^{3+} , Fe^{2+} / Fe^{3+})

Bond Valence Sum (BVS)

Correlation of the valence of a bond s_{ij} with the (experimental) bond distance d_{ij}

$$s_{ij} = \exp \frac{R_{ij} - d_{ij}}{b}$$

$$v_i = \Sigma s_{ij} = \Sigma \frac{z_i}{CN}$$

$FeTiO_3$ (mineral Ilmenite) possesses the **corundum** structure – an hcp array of oxides with cations filling 2/3 of octahedral holes

Decide which oxidation states are present: Fe(II) Ti(IV) or Fe(III) Ti(III)

Bond Distances (d_{exp}, Å)	Tabulated R_{ij} values	Constants
Fe–O = 3×2.07 and 3×2.20	R_0(Fe–O) = 1.795 Å	b = 0.30
Ti–O = 3×1.88 and 3×2.09	R_0(Ti–O) = 1.815 Å	b = 0.37

Oxygen valence and coordination number O?
Each oxygen is bound to Fe and Ti with both bond distances

Pauling’s Rules

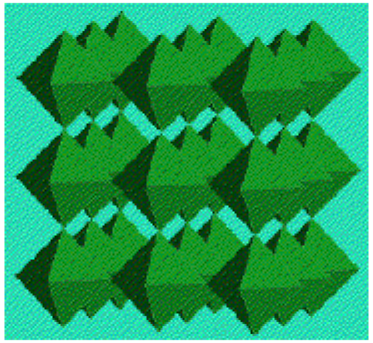
Pauling’s Rule no. 3 Polyhedral Linking

The presence of shared edges, and particularly shared faces **decreases the stability** of a structure

This is particularly true for cations with large valences and small coordination numbers

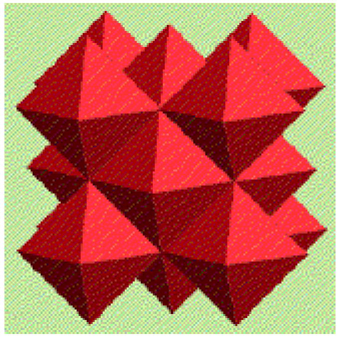
Avoid shared polyhedral edges and/or faces

ReO_3



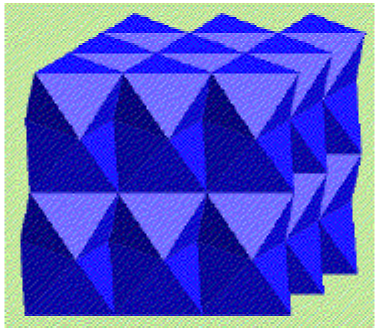
Vertex-Sharing Only

NaCl



Edge-Sharing

NiAs

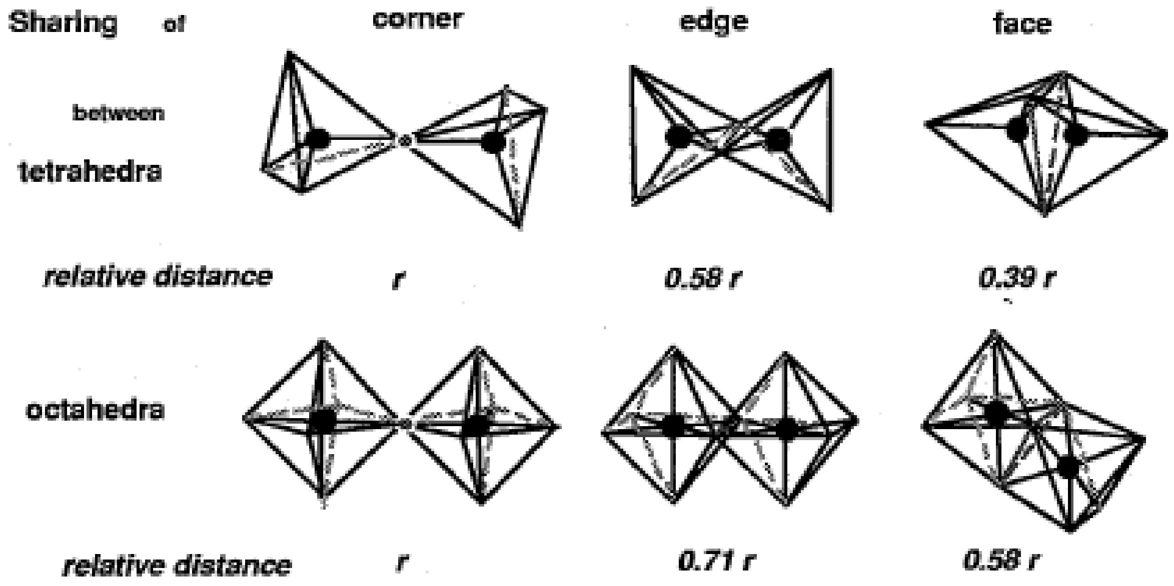


Face-Sharing in Columns

Polyhedral Linking

The Coulombic interactions: maximize the cation-anion interactions (attractive), and minimize the anion-anion and cation-cation interactions (repulsive)

- increasing the coordination number
- decreasing the cation-anion distance



r = Cation-cation distance

Cation-anion distance is constant

The cation-cation (the Coulomb) **repulsion increases** as the

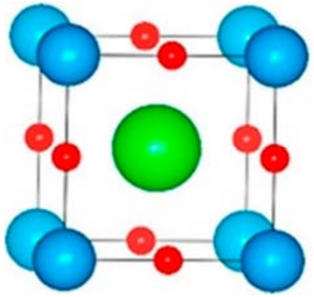
- distance decreases - degree of sharing increases (vertex < edge < face)
- CN decreases (cubic < octahedral < tetrahedral)
- cation oxidation state increases

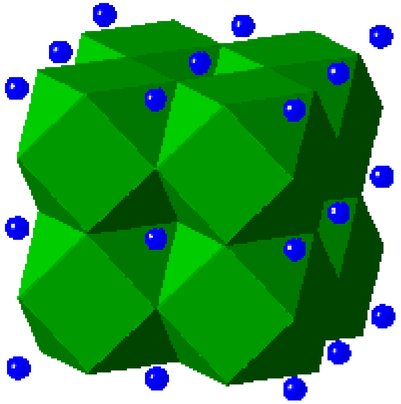
Pauling’s Rules

Pauling’s Rule no. 4 Cation Evasion

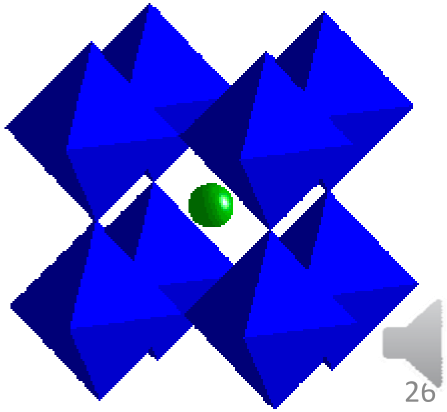
In a crystal containing different cations those with large valence and small coordination number tend not to share polyhedral elements (anions)

Perovskite, $CaTiO_3$





Ca^{II} 12-coordinate **CaO_{12}** cuboctahedra share **FACES**



Ti^{IV} 6-coordinate **TiO_6** octahedra share only **VERTICES**

Pauling’s Rules

Pauling’s Rule no. 5 Environmental Homogeneity (The rule of parsimony)

The number of chemically different coordination environments for a given ion tends to be small

Once the optimal chemical environment for an ion is found, if possible all ions of that type should have **the same environment**

Covalent Radius of Fluorine

1938 Brockway – electron diffraction on F_2(g)
R(F–F) = 145 pm r(F) = 73 pm TOO LONG
Lone pair repulsion, abnormally weak bond
M–F bonds are highly polar

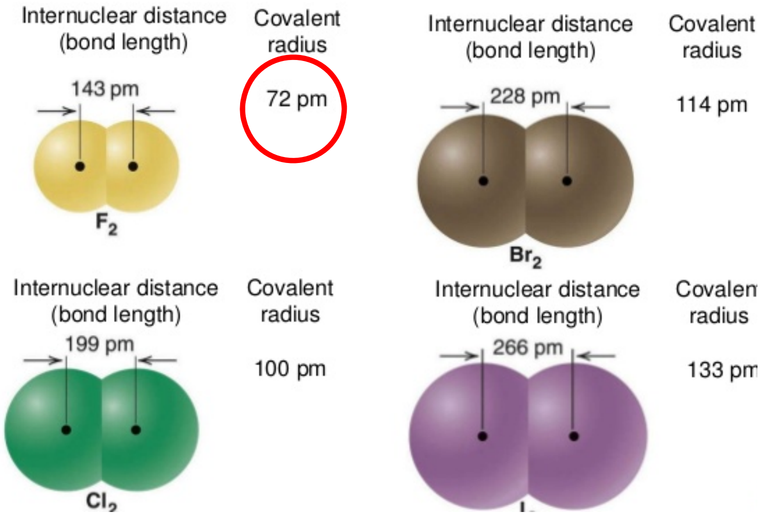
1960 Pauling – backbonding in A–F

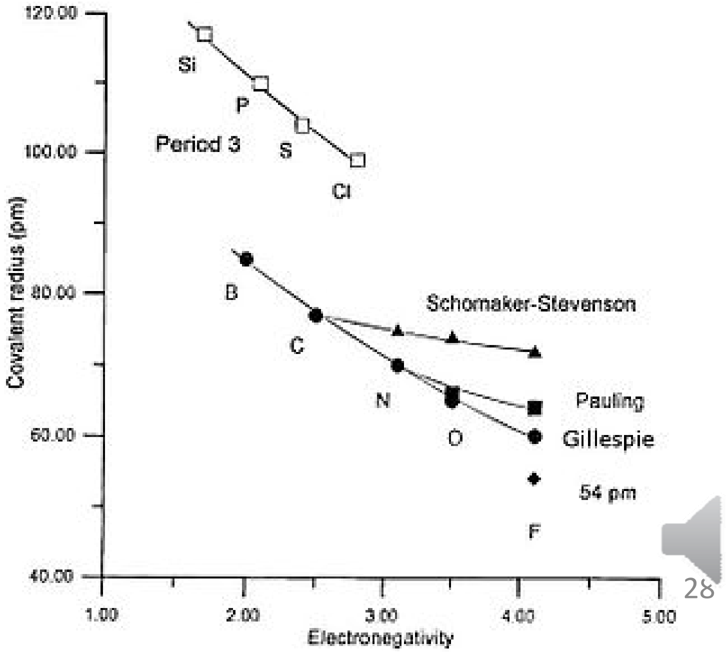
1990 Reed and Schleyer – pi bonding in A–F

1992 Gillespie and Robinson - 54 pm
Longer if a lone pair on EAF_n
Shorter in an incomplete octet BF_3

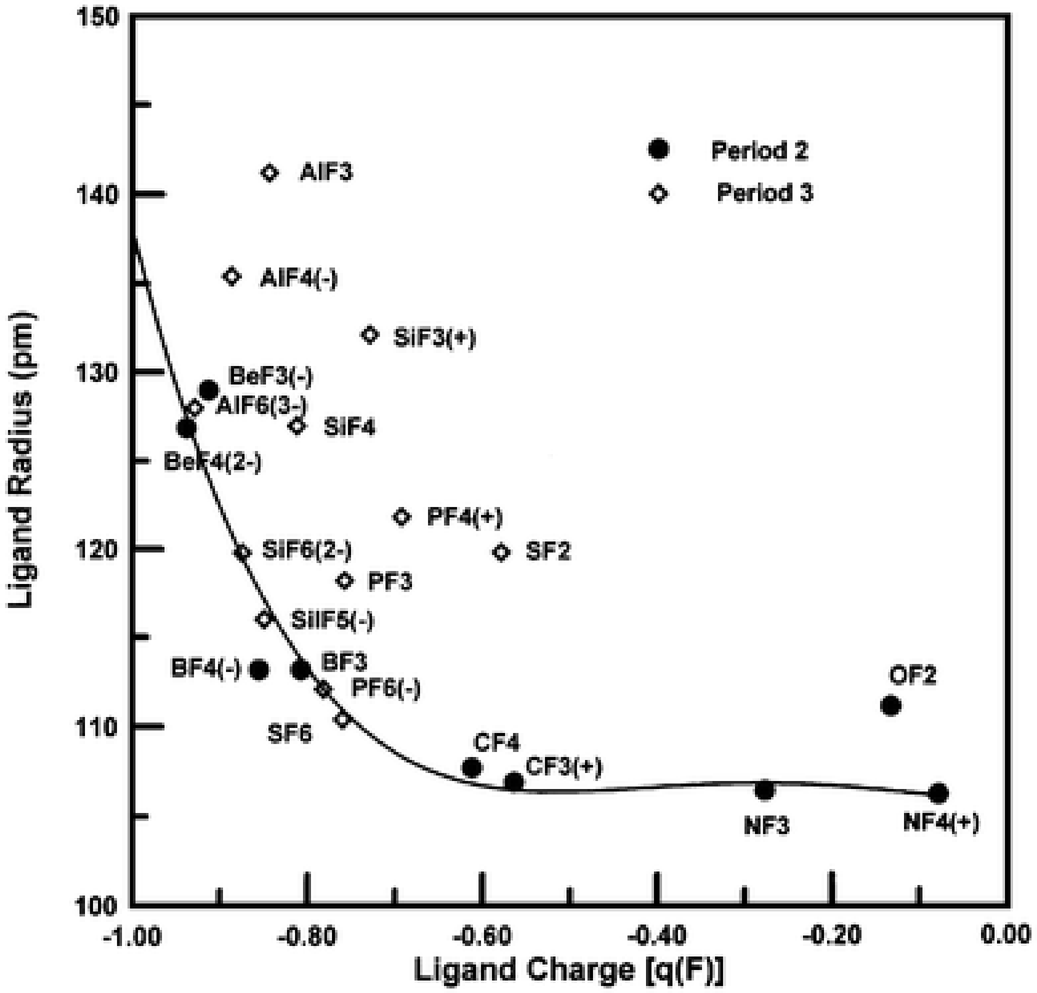
1997 Gillespie - 60 pm, the X–F bond length decreases with a decreasing CN, the smaller the bond angle (<F-A-F) the longer the bond length

2009 Pyykkö - 64 pm in single, 59 pm in double and 53 pm in triple bond character





Ionic Radius of Fluoride



2nd Period

Fluoride radii decrease across the 2nd period with increasing electronegativity of the central atom and therefore with decreasing F ligand charge q(F)

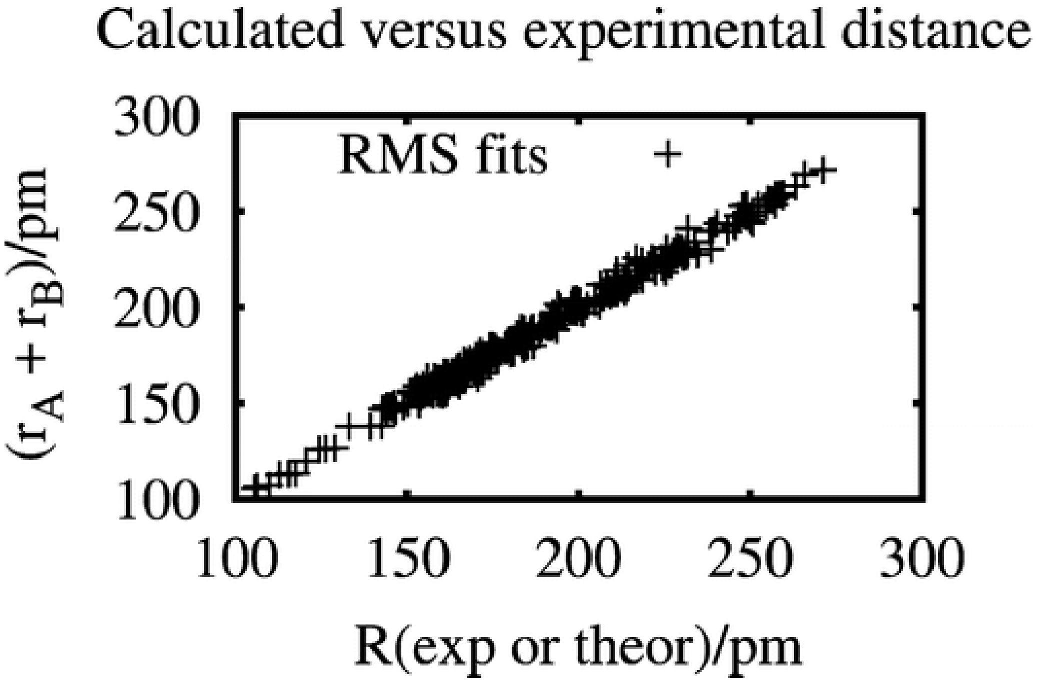
3rd Period 3

The six-coordinated fluorides (SF_6, AlF_6^{3-}) fall on the same smooth curve as for the Period 2 fluorides = close-packed

The 3- and 4-coordinated fluorides of the Period 3 elements (AlF_4^-) do not fall on this curve = not close packed

Additive Covalent Radii

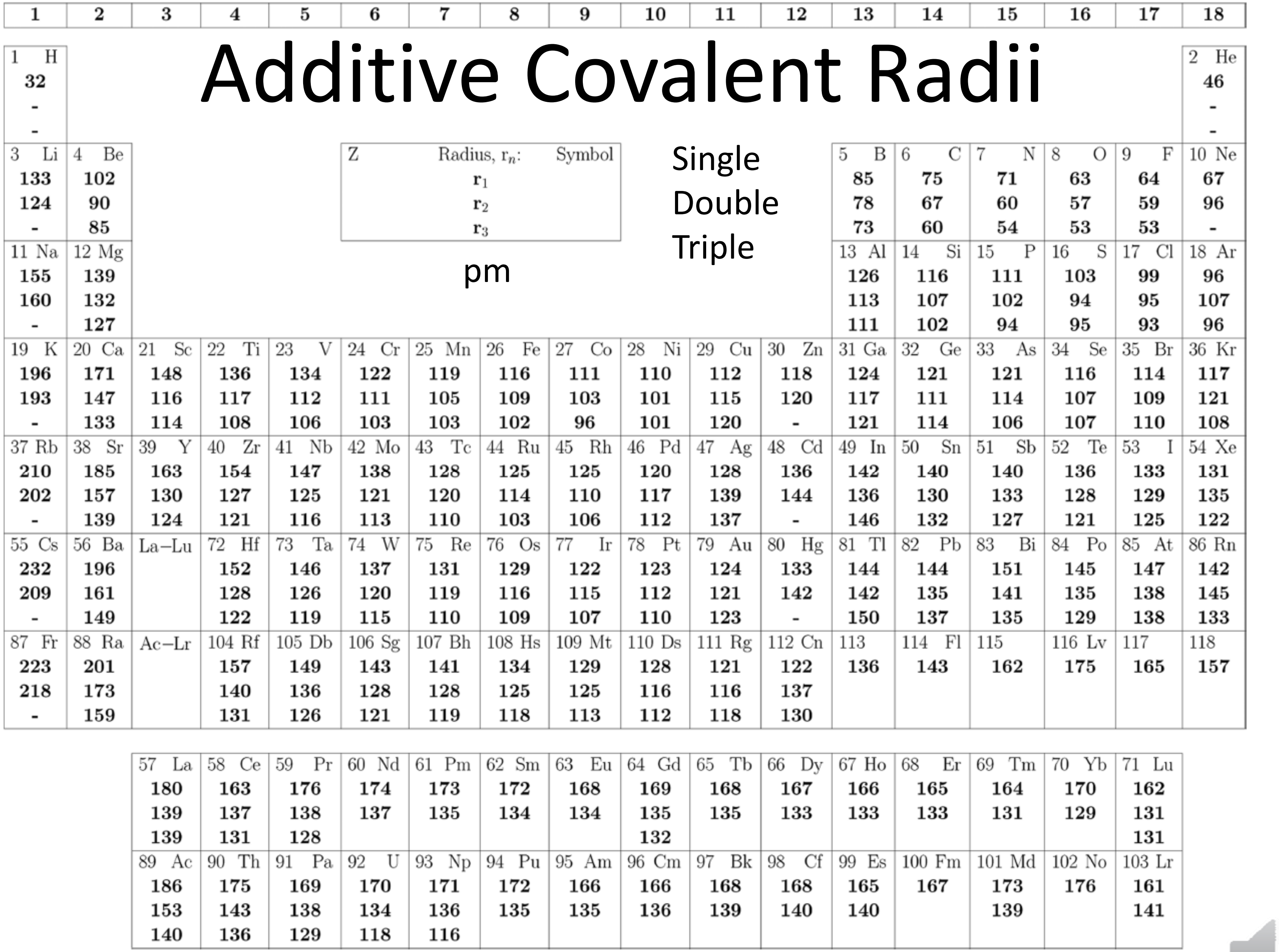
Additive covalent radii = approximate a bond length as the sum of two atomic radii
Predominantly covalent



The A−B bond is not too ionic

Pekka Pyykkö J. Phys. Chem. A, 2015, 119 (11), 2326–2337

Additive Covalent Radii



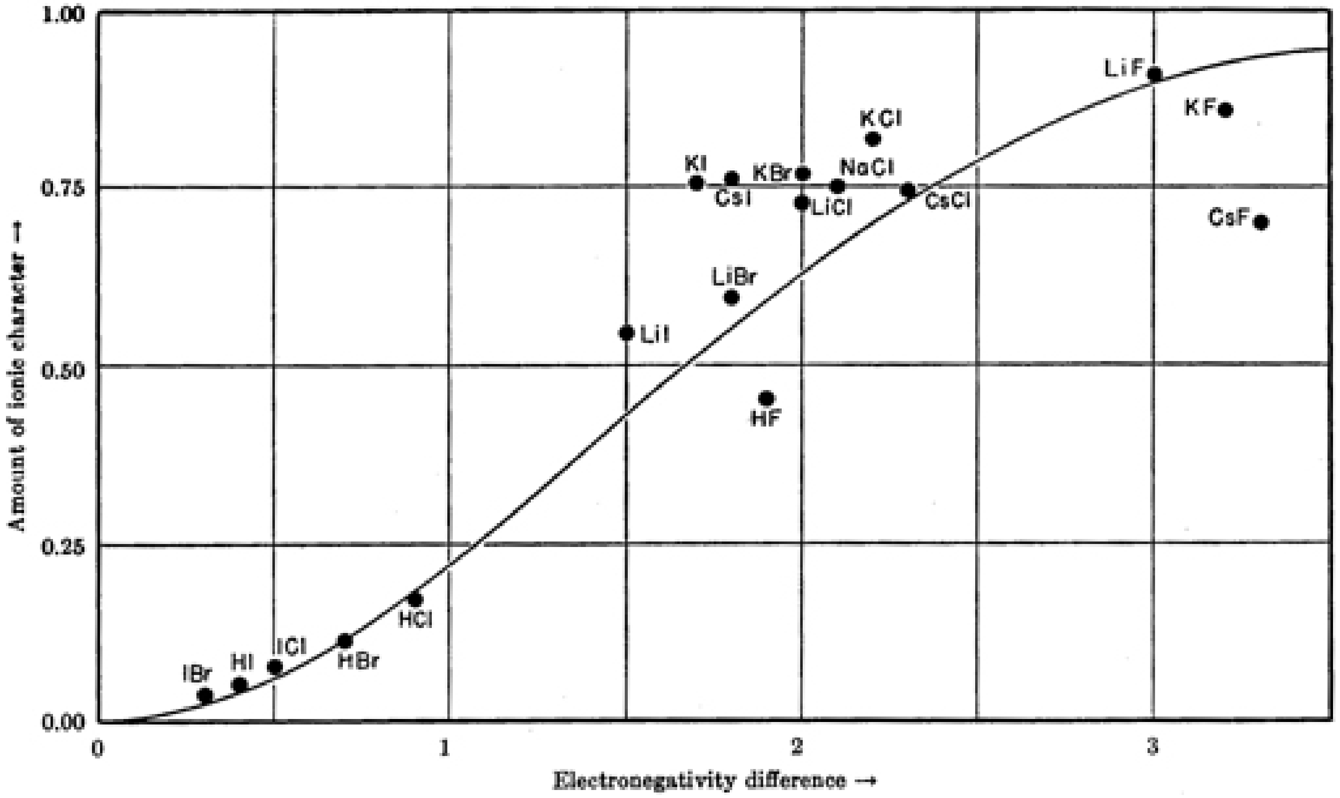
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H **32** **-** **-**																	2 He **46** **-** **-**
3 Li **133** **124** **-**	4 Be **102** **90** **85**				Z Radius, r_n: Symbol $\mathbf{r}_1$ $\mathbf{r}_2$ $\mathbf{r}_3$							5 B **85** **78** **73**	6 C **75** **67** **60**	7 N **71** **60** **54**	8 O **63** **57** **53**	9 F **64** **59** **53**	10 Ne **67** **96** **-**
11 Na **155** **160** **-**	12 Mg **139** **132** **127**											13 Al **126** **113** **111**	14 Si **116** **107** **102**	15 P **111** **102** **94**	16 S **103** **94** **95**	17 Cl **99** **95** **93**	18 Ar **96** **107** **96**
19 K **196** **193** **-**	20 Ca **171** **147** **133**	21 Sc **148** **116** **114**	22 Ti **136** **117** **108**	23 V **134** **112** **106**	24 Cr **122** **111** **103**	25 Mn **119** **105** **103**	26 Fe **116** **109** **102**	27 Co **111** **103** **96**	28 Ni **110** **101** **101**	29 Cu **112** **115** **120**	30 Zn **118** **120** **-**	31 Ga **124** **117** **121**	32 Ge **121** **111** **114**	33 As **121** **114** **106**	34 Se **116** **107** **107**	35 Br **114** **109** **110**	36 Kr **117** **121** **108**
37 Rb **210** **202** **-**	38 Sr **185** **157** **139**	39 Y **163** **130** **124**	40 Zr **154** **127** **121**	41 Nb **147** **125** **116**	42 Mo **138** **121** **113**	43 Tc **128** **120** **110**	44 Ru **125** **114** **103**	45 Rh **125** **110** **106**	46 Pd **120** **117** **112**	47 Ag **128** **139** **137**	48 Cd **136** **144** **-**	49 In **142** **136** **146**	50 Sn **140** **130** **132**	51 Sb **140** **133** **127**	52 Te **136** **128** **121**	53 I **133** **129** **125**	54 Xe **131** **135** **122**
55 Cs **232** **209** **-**	56 Ba **196** **161** **149**	La–Lu	72 Hf **152** **128** **122**	73 Ta **146** **126** **119**	74 W **137** **120** **115**	75 Re **131** **119** **110**	76 Os **129** **116** **109**	77 Ir **122** **115** **107**	78 Pt **123** **112** **110**	79 Au **124** **121** **123**	80 Hg **133** **142** **-**	81 Tl **144** **142** **150**	82 Pb **144** **135** **137**	83 Bi **151** **141** **135**	84 Po **145** **135** **129**	85 At **147** **138** **138**	86 Rn **142** **145** **133**
87 Fr **223** **218** **-**	88 Ra **201** **173** **159**	Ac–Lr	104 Rf **157** **140** **131**	105 Db **149** **136** **126**	106 Sg **143** **128** **121**	107 Bh **141** **128** **119**	108 Hs **134** **125** **118**	109 Mt **129** **125** **113**	110 Ds **128** **116** **112**	111 Rg **121** **116** **118**	112 Cn **122** **137** **130**	113 **136**	114 Fl **143**	115 **162**	116 Lv **175**	117 **165**	118 **157**
		57 La **180** **139** **139**	58 Ce **163** **137** **131**	59 Pr **176** **138** **128**	60 Nd **174** **137**	61 Pm **173** **135**	62 Sm **172** **134**	63 Eu **168** **134**	64 Gd **169** **135** **132**	65 Tb **168** **135**	66 Dy **167** **133**	67 Ho **166** **133**	68 Er **165** **133**	69 Tm **164** **131**	70 Yb **170** **129**	71 Lu **162** **131** **131**	
		89 Ac **186** **153** **140**	90 Th **175** **143** **136**	91 Pa **169** **138** **129**	92 U **170** **134** **118**	93 Np **171** **136** **116**	94 Pu **172** **135**	95 Am **166** **135**	96 Cm **166** **136**	97 Bk **168** **139**	98 Cf **168** **140**	99 Es **165** **140**	100 Fm **167**	101 Md **173** **139**	102 No **176**	103 Lr **161** **141**	

Single
Double
Triple

pm

Pekka Pyykkö J. Phys. Chem. A, 2015, 119 (11), 2326–2337

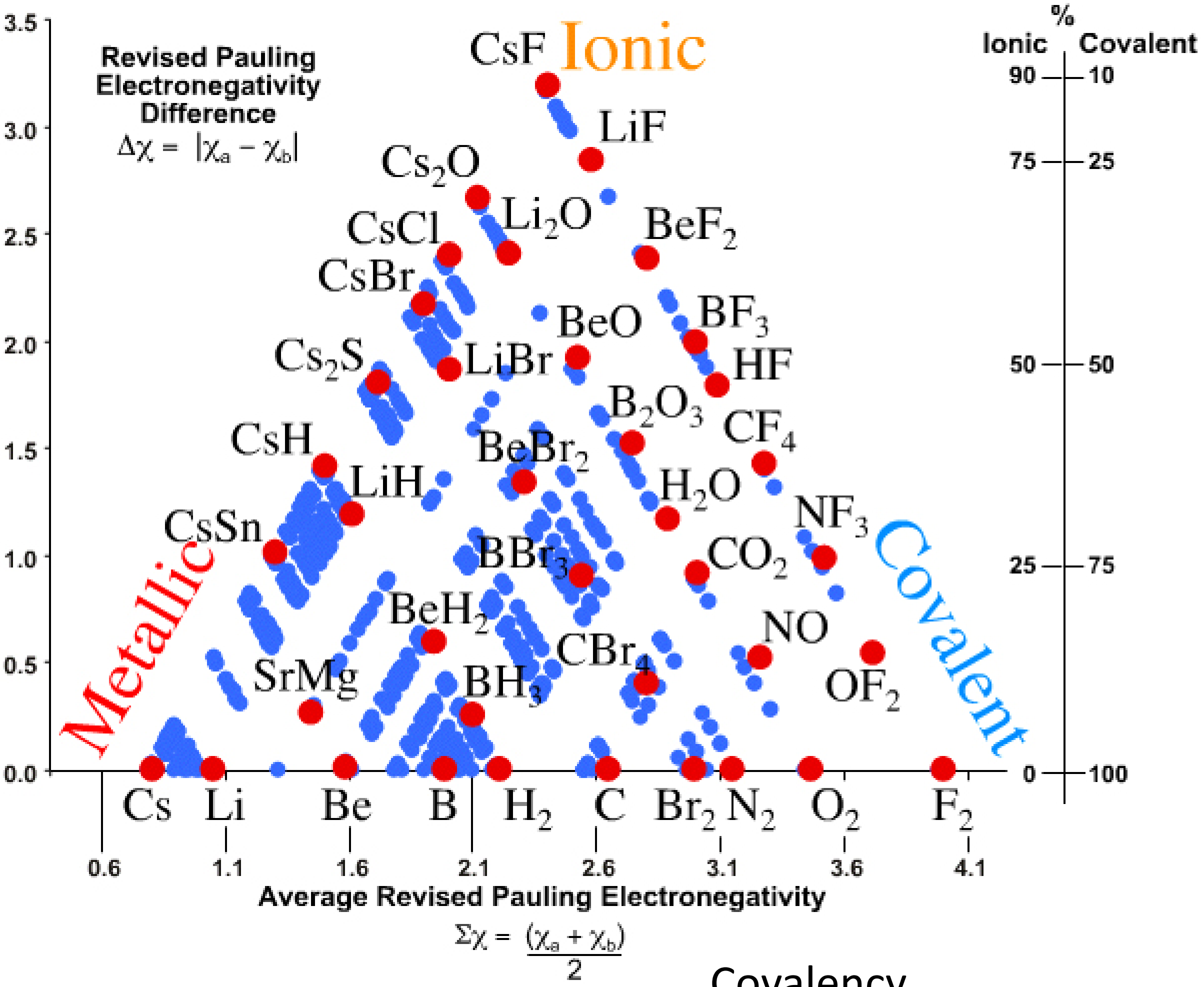
Ionic Character vs. Electronegativity



$$i = 1 - \exp[-0.21(\chi_A - \chi_B)^2]$$

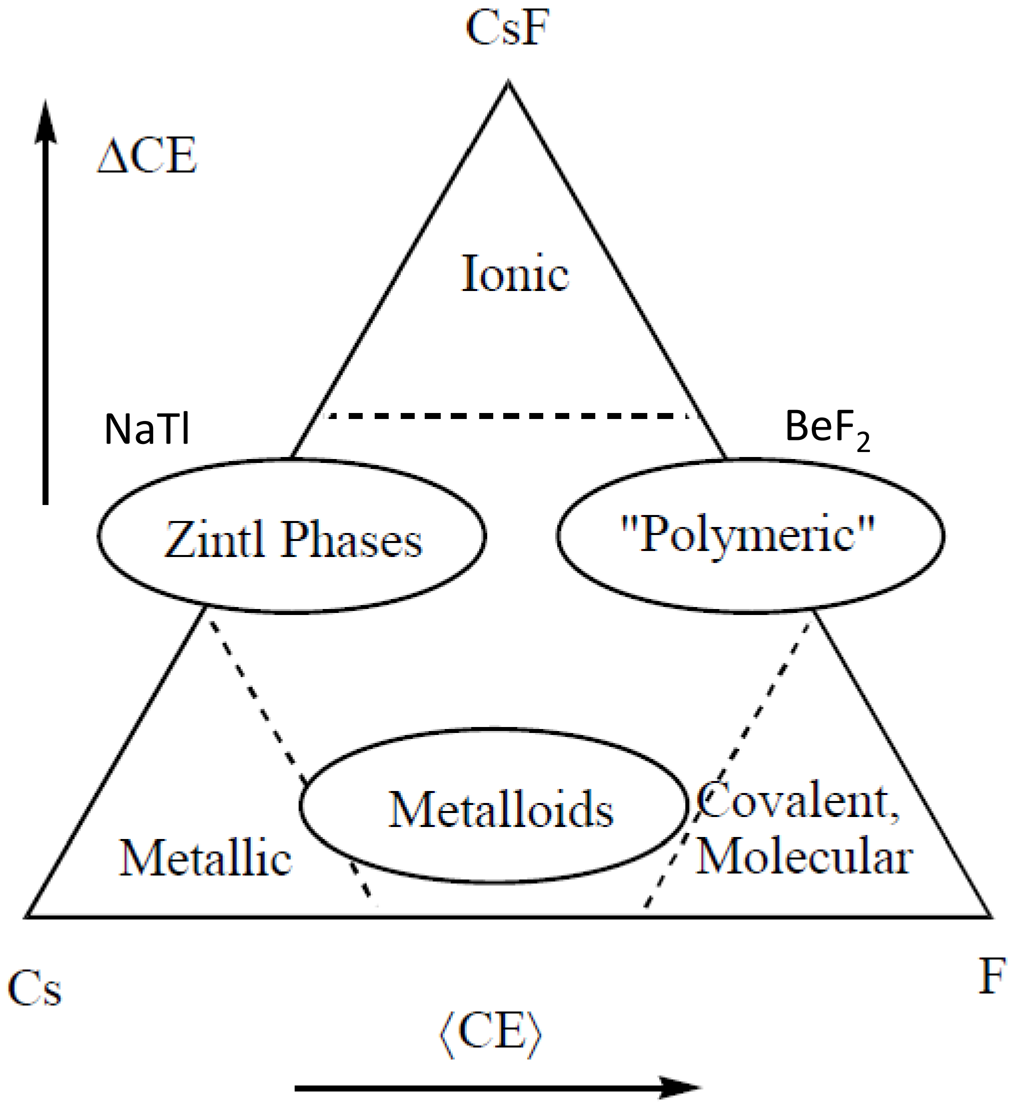
van Arkel-Ketelaar Triangle

Ionicity



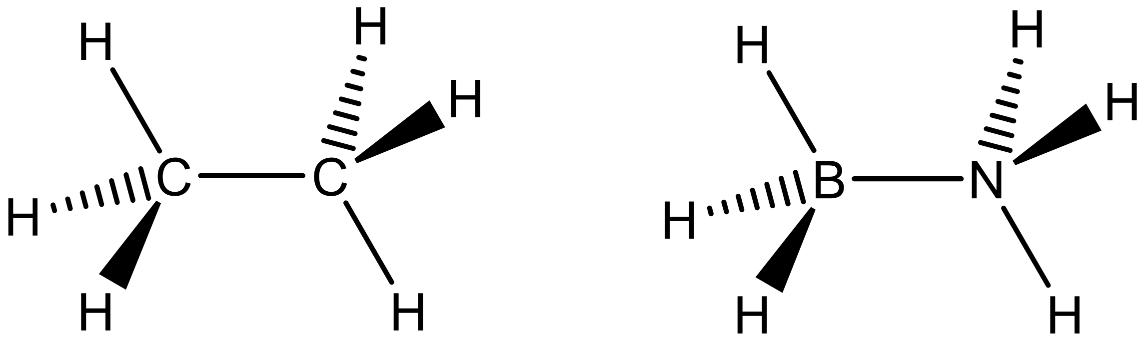
Covalency

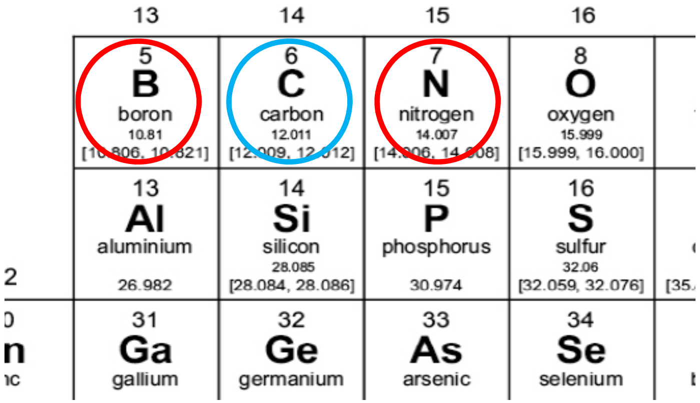
van Arkel-Ketelaar Triangle



Normal vs. Dative Bond

Isoelectronic molecules

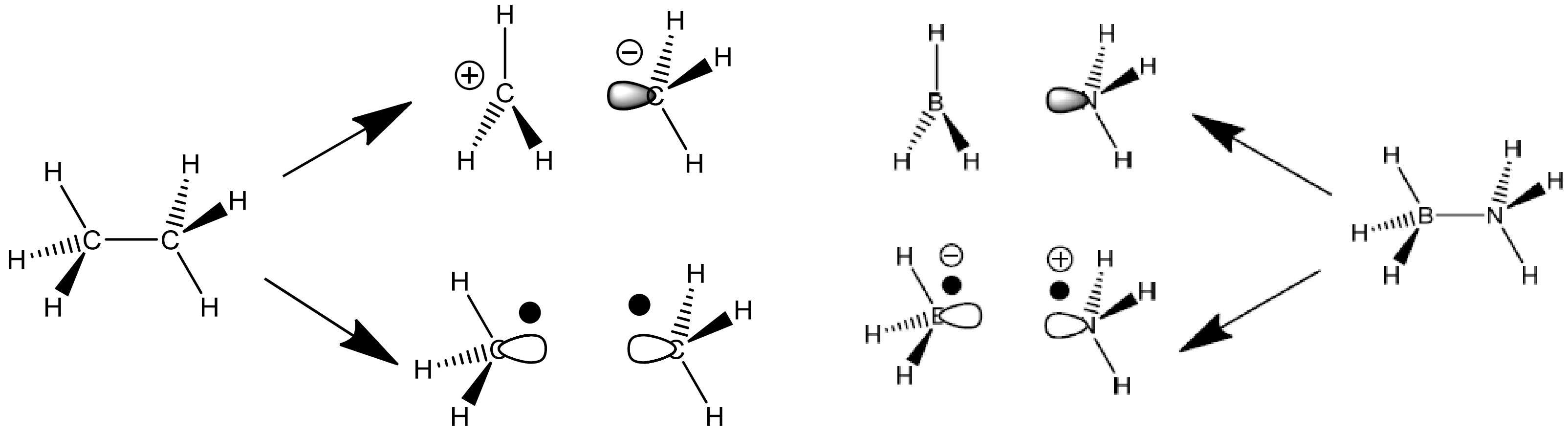




13	14	15	16
5 **B** boron 10.81 [10.806, 10.821]	6 **C** carbon 12.011 [12.009, 12.012]	7 **N** nitrogen 14.007 [14.006, 14.008]	8 **O** oxygen 15.999 [15.999, 16.000]
13 **Al** aluminium 26.982	14 **Si** silicon 28.085 [28.084, 28.086]	15 **P** phosphorus 30.974	16 **S** sulfur 32.06 [32.059, 32.076]
31 **Ga** gallium	32 **Ge** germanium	33 **As** arsenic	34 **Se** selenium

Normal vs. Dative Bond

Heterolytic Bond Cleavage



Charged + Diamagnetic

Neutral + Diamagnetic

Neutral + Radicals

Charged + Radical

Homolytic Bond Cleavage

Badger’s Rule

Empirical relationships linking force constants, bond lengths, bond dissociation energies and bond orders – MANY EXCEPTIONS

1935 Badger’s rule relates vibrational frequencies to bond distances for various atomic pairs

$$r_e = \left(\frac{C_{ij}}{k}\right)^{\frac{1}{3}} + d_{ij}$$

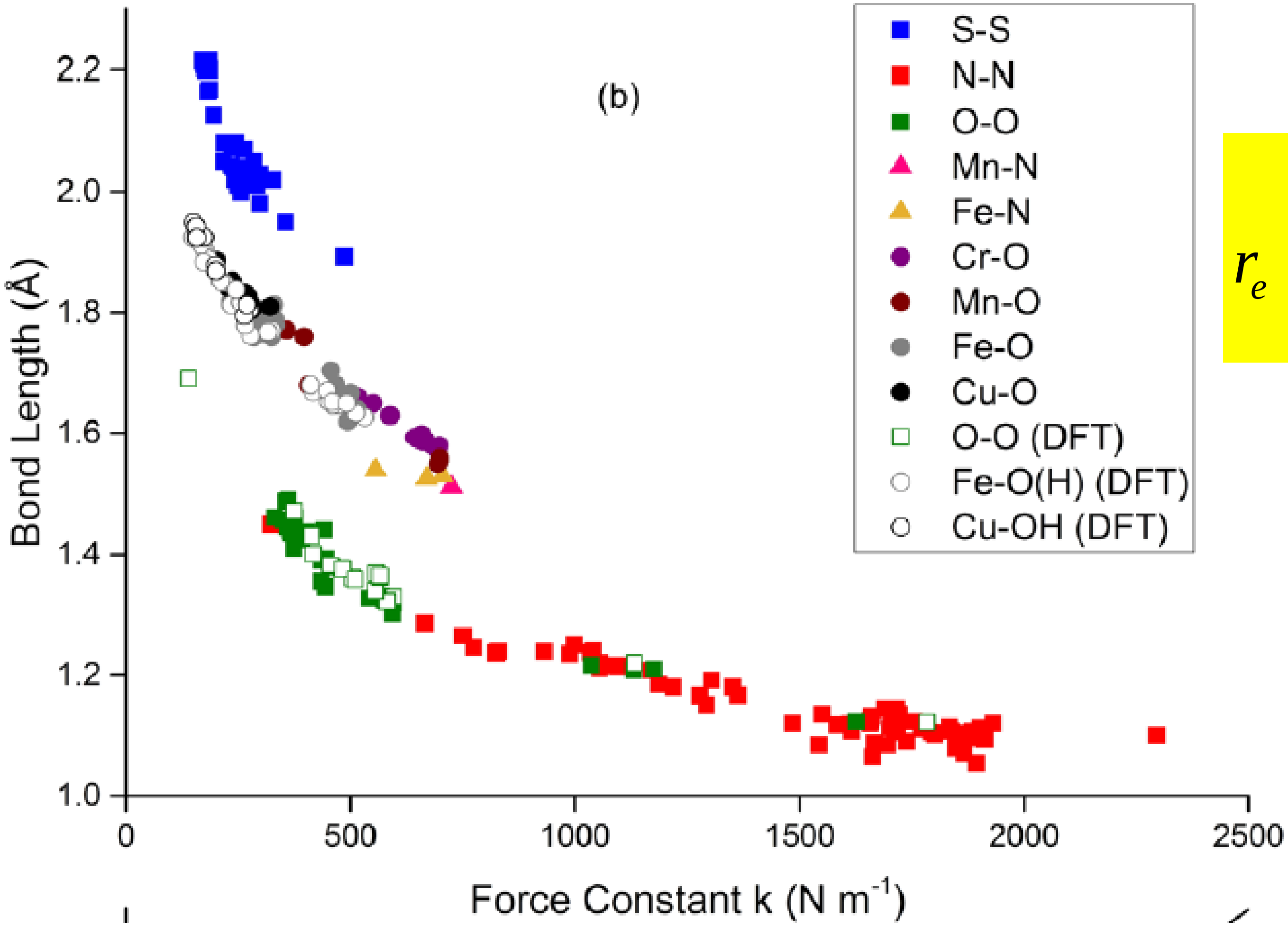
r_e = equilibrium bond distance
k = force constant (can be substituted with v, the stretching frequency)
C_{ij} and d_{ij} = empirically fitted values for a particular atomic pair i-j

Plots of bond distances vs $v^{-2/3}$ or $k^{-1/3}$ for a set of compounds comprising a particular atomic pair are fit to equation to determine C_{ij} and d_{ij}, which then allows a newly measured force constant or vibrational frequency to be used to calculate an unknown bond distance (or vice versa)

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \Rightarrow k = \mu(2\pi\nu)^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

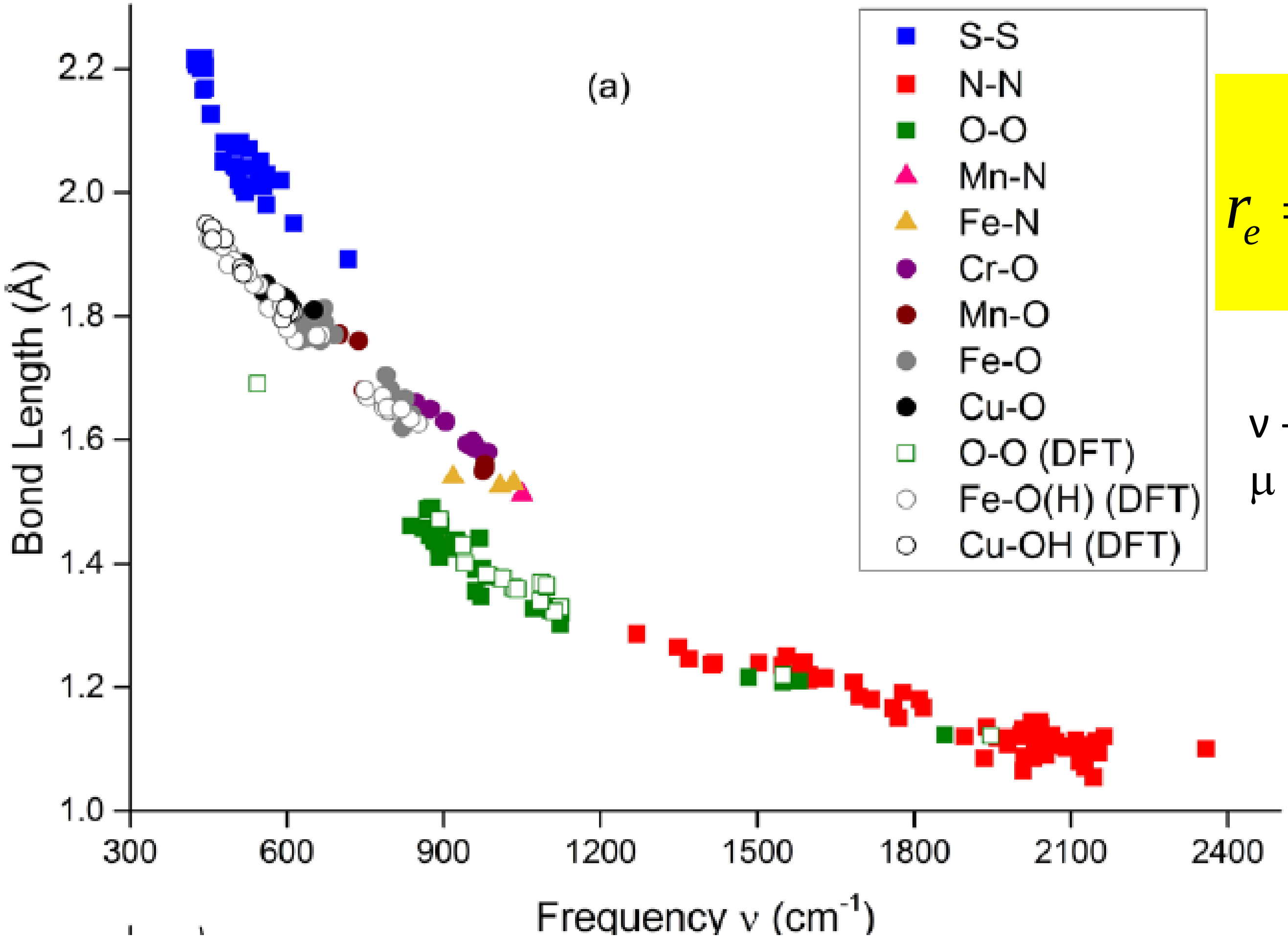
Badger’s Rule



$$r_e = \left(\frac{C_{ij}}{k}\right)^{\frac{1}{3}} + d_{ij}$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Badger’s Rule



$$r_e = \left(\frac{C_{ij}}{\mu(2\pi\nu)^2} \right)^{\frac{1}{3}} + d_{ij}$$

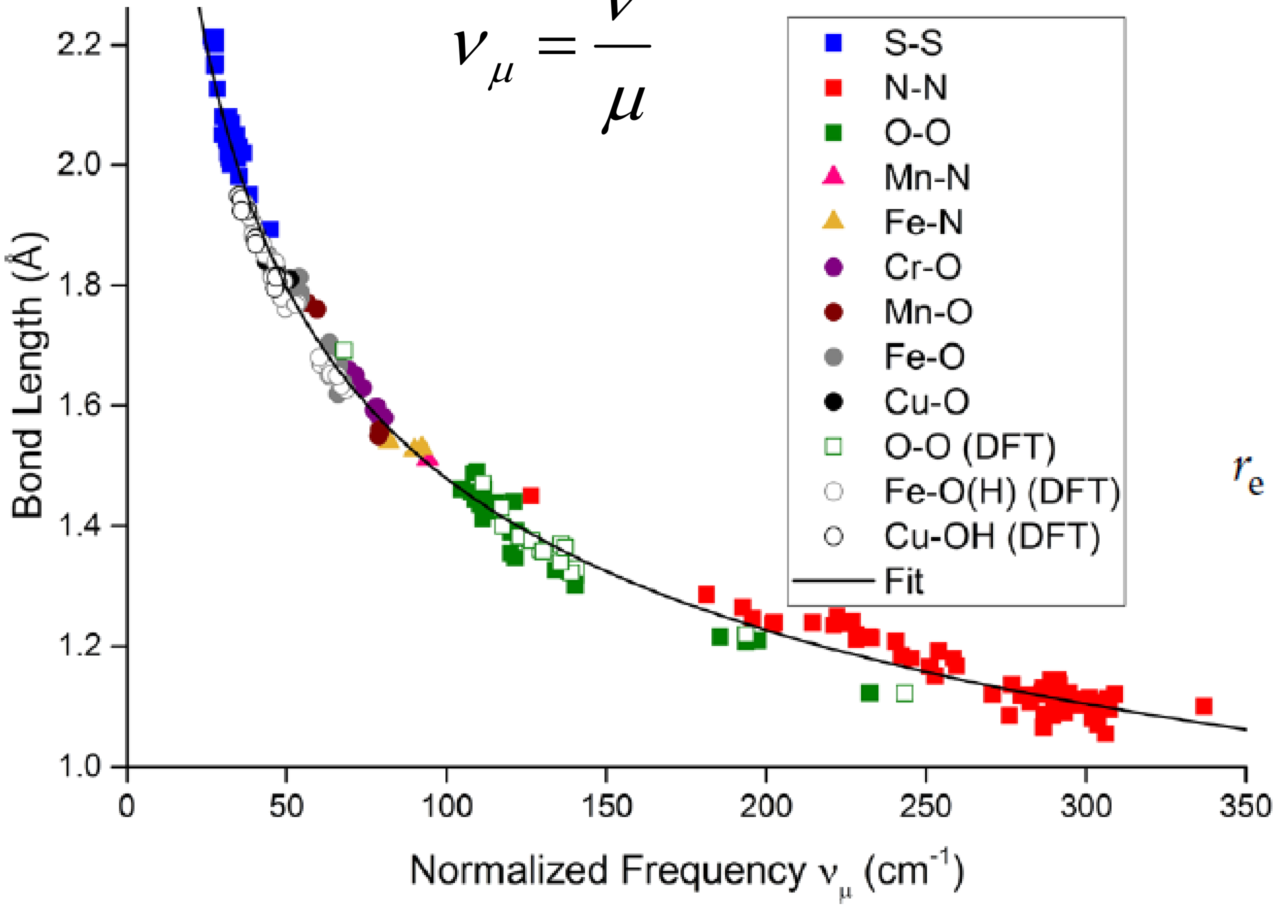
ν - stretching frequency
μ - reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Normalized Badger's Rule

Normalized frequency

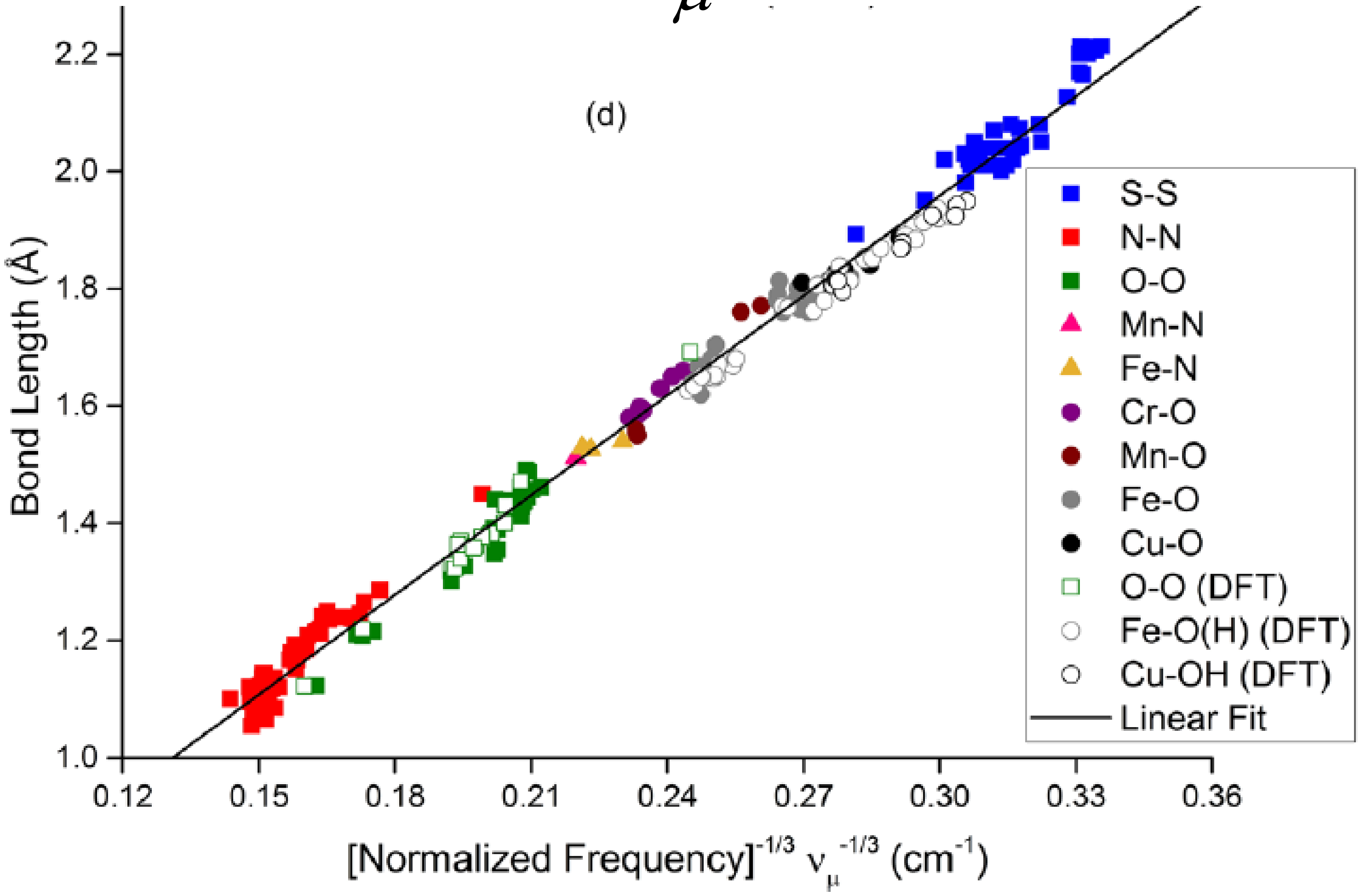
$$\nu_{\mu} = \frac{\nu}{\mu}$$



$$r_{\mathrm{e}} = \left(\frac{181}{\nu_{\mu}}\right)^{1/3} + 0.259$$

Normalized Badger’s Rule

Normalized frequency $\nu_\mu = \dfrac{\nu}{\mu}$



Gordy Relationship

1946 Gordy

$$k = aN\left[\frac{(\chi_A \chi_B)}{r_e^2}\right]^{\frac{3}{4}} + b$$

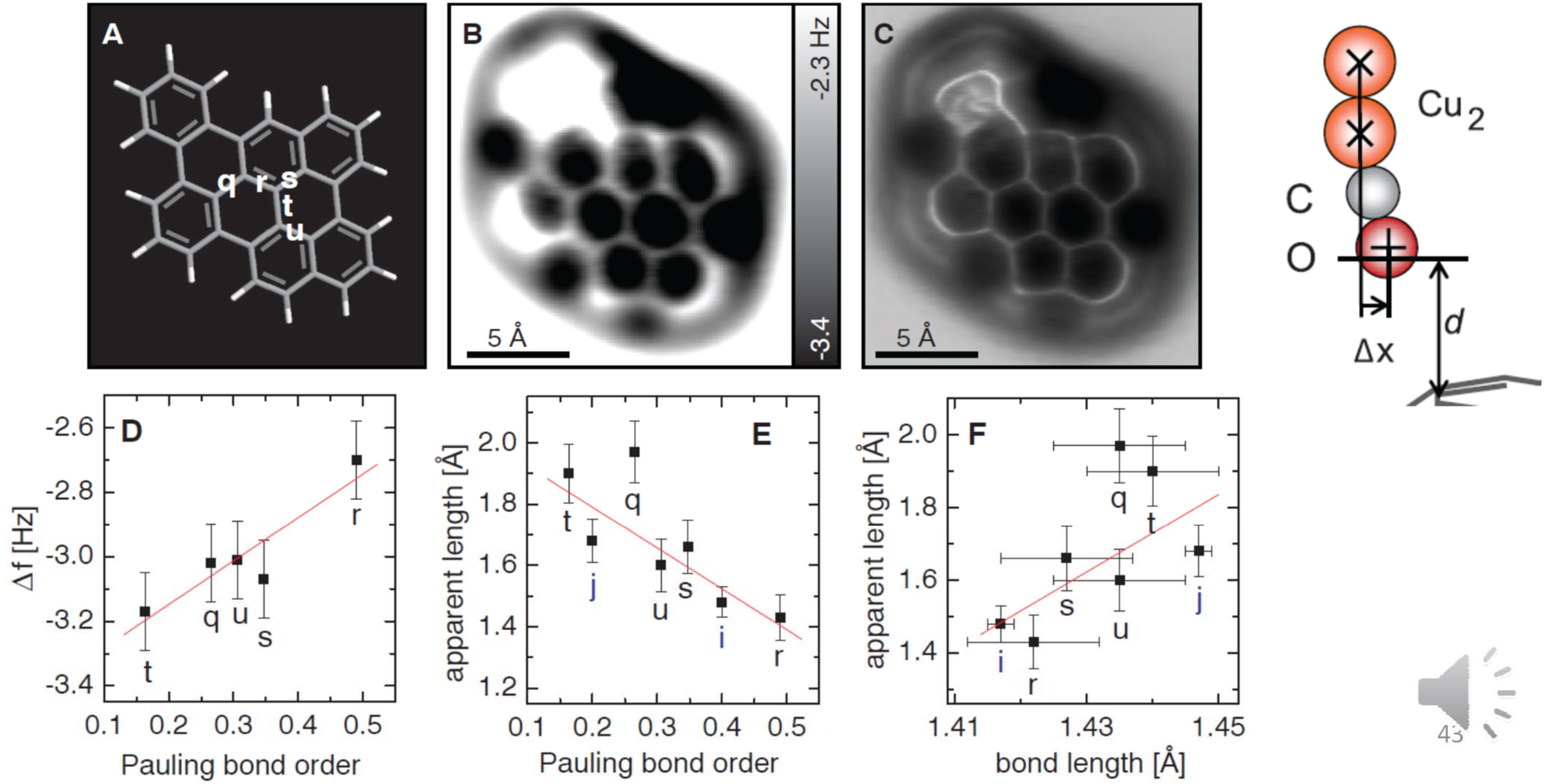
N - fractional bond multiplicity
$\chi_{A,B}$ - electronegativities of bonded atoms
k - force constant of bond stretching
r_e = equilibrium bond distance
a and b - constants, which differ for different families

- Determination of a force constant – spectrum analysis, peak assignment
- Prediction of bond length
- Prediction of bond order
- Determination of electronegativity

Bond Order - an Observable Quantity?

Bond-Order Discrimination by Atomic Force Microscopy
L. Gross, F. Mohn, N. Moll, B. Schuler, A. Criado, E. Guitián, D. Peña, A. Gourdon, G. Meyer, Science 2012, 337 (6100), 1326-1329 DOI: 10.1126/science.1225621

Noncontact atomic force microscopy (AFM) with a CO–functionalized Cu tip



Bond Order

G. N. Lewis 1916
Electron pair sharing between two atoms
Bond order = a measure of the number of electrons shared between two atoms
Resonance structures – fractional bond order

G. Herzberg
Bond order is equal to half the difference between the number of **bonding** electrons and the number of **antibonding** electrons in the (diatomic) molecule
Not a quantum chemical quantity, not calculated from the wave function, semi-integer *formal* bond order
Does not consider the magnitude of overlap and the bond polarity

Parr and Borkman
The delocalized charge density moving freely along the bond axis

k_e - force constant of a bond
r_e - bond length
a - constant

$$N = a\sqrt{\frac{k_e}{r_e}}$$

Bond Order

R. S. Mulliken
A non-integral bonding power of either sign is attributable to every outer electron - the Mulliken population analysis

The effective bond order (EBO)
Each bonding orbital *i* has a natural orbital (NO) occupation number b_i
The corresponding antibonding orbital has the occupation number ab_i
$a = 0$ – full bond, $a = 1$ – no bond

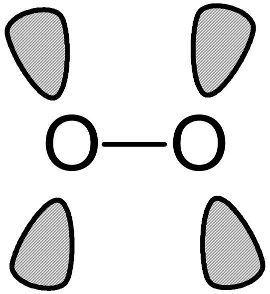
$$\mathrm{EBO} = \sum_i \frac{(b_i - ab_i)}{2}$$

The delocalization index between two any atoms in a system corresponds to the (fractional) number of electron pairs shared or exchanged between these atoms

Multiple Bonds

Dominant form of oxygen is O=O, a colourless paramagnetic gas
Ozone (O_3) is the only other allotrope
Why does not it form O_8 ?

Lone-pair repulsion across the short O–O distance
O is small, and its orbitals highly contracted, and so electrons feel a lot of e-e repulsion

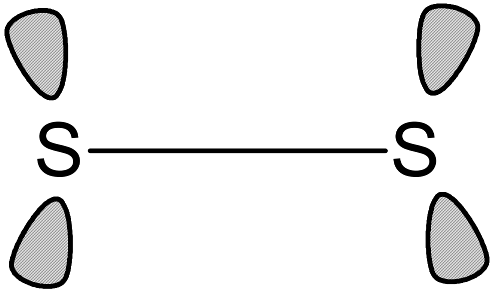


Bond energies

$O_2 \longrightarrow$ -O–O-

Bond Energies: 350   2 × 145

$\Delta H = 350 + (2 \times -145) = +60\ \mathrm{kJ\ mol^{-1}}$



$S_2 \longrightarrow$ -S–S-

Bond Energies: 270   2 × 155

$\Delta H = 270 + (2 \times -155) = -40\ \mathrm{kJ\ mol^{-1}}$

S=S is thermodynamically unstable wrt -S–S- (*catenation*) but stable above 700 °C (Why?)

π-Bonds

Diffuseness of orbitals

2s and 2p orbitals are only shielded from the nucleus by the 1s electrons, therefore they are highly **contracted**, and **π-overlap** is **efficient** for the second period elements

3s and 3p orbitals in the 3rd row and higher elements are more **diffuse**, and so this side-on p-p overlap is **less effective**

Repulsion between core electrons

Second-row elements have only two core electrons (He)

Third-row (Ne) and heavier elements (Ar-Kr-Xe) have a significantly larger number of core electrons that cause **repulsion** between two heavy elements bonded to each other

This prevents the atoms to approach each other closer and form stronger π bonds

Atomic size

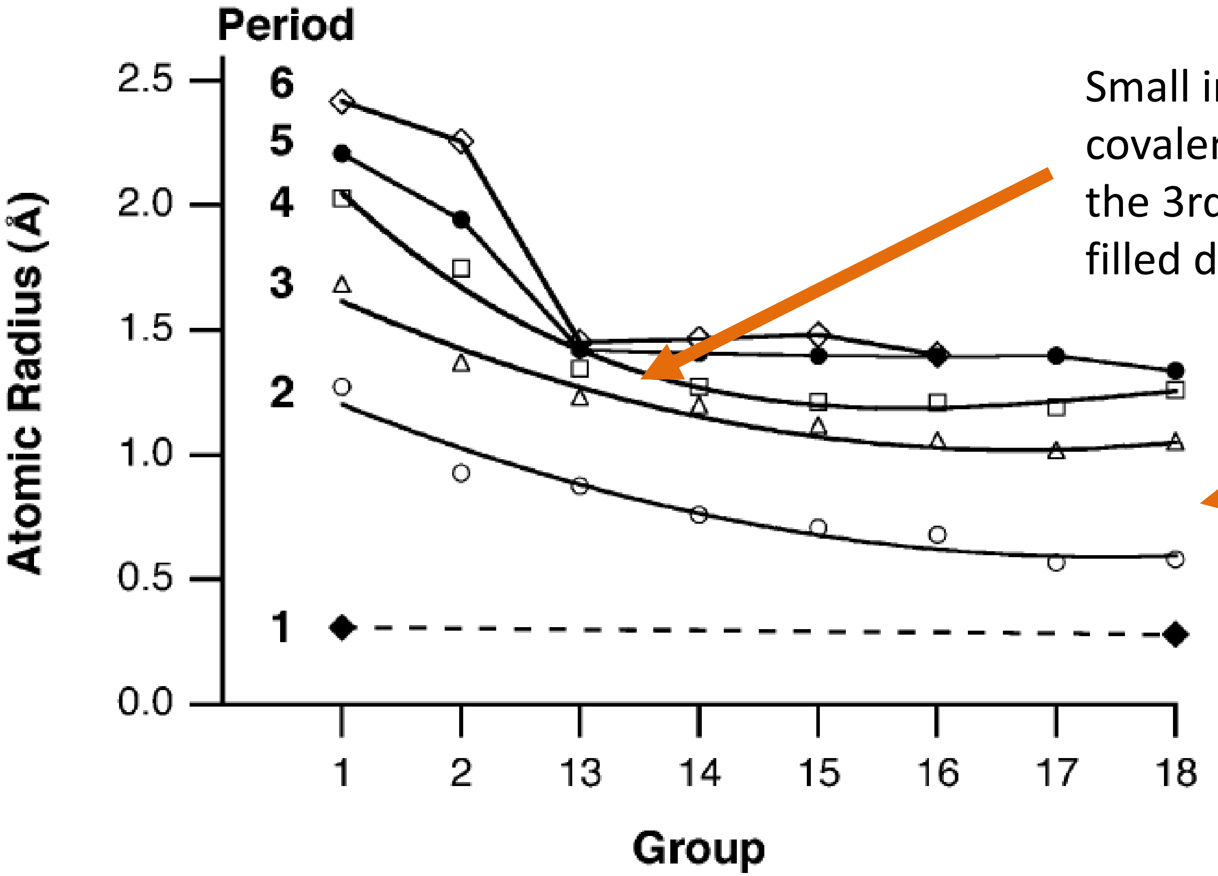
The large jump (50 %) in the covalent radii between the 2nd and 3rd rows of the periodic table (for example, C (0.77 Å), Si (1.17 Å)

Higher coordination numbers observed for the 3rd row

Thermochemistry

π-bond energies in heavy double bonds too small to prevent polymerization

Atomic Radii

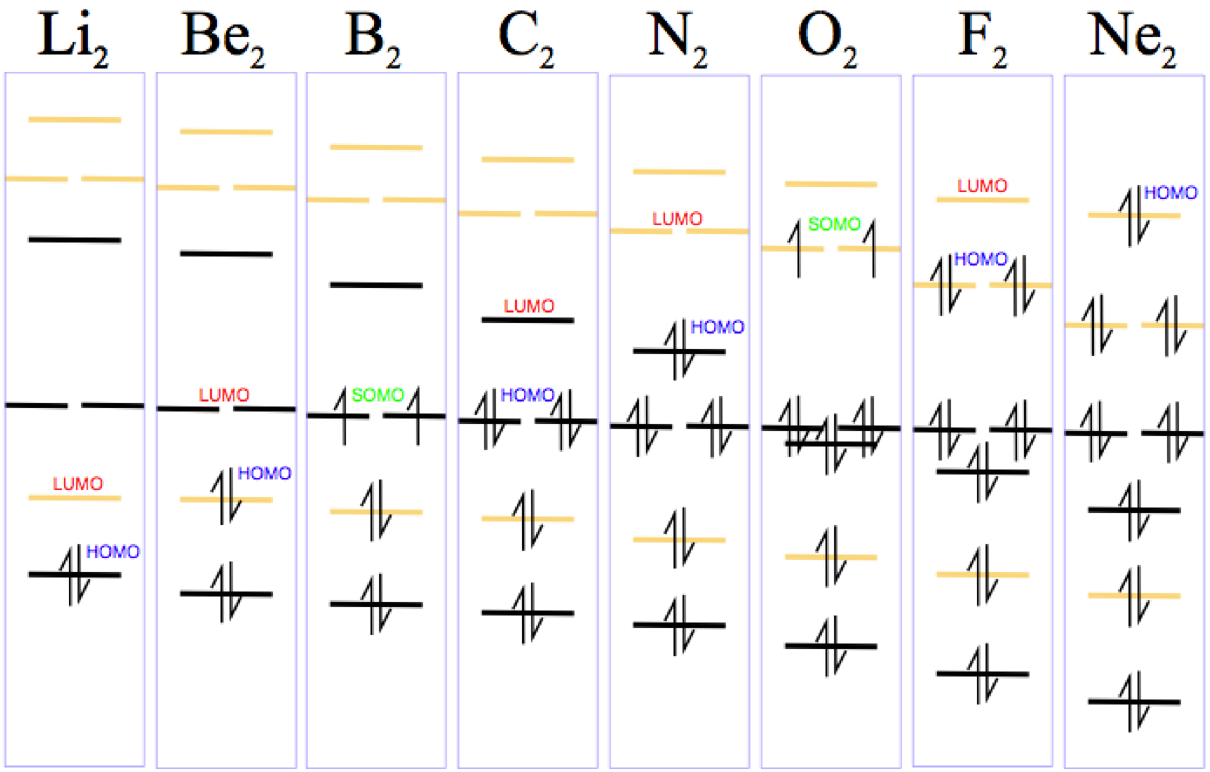


Small increase in the covalent radii between the 3rd and 4th rows - filled d^{10} - poor shielding

~50% increase in the covalent radii between the 2nd and 3rd rows

B. Cordero et al. *Dalton Trans.* **2008**, 2832–2838

Bonding in Diatomic Molecules



bond order = (electrons in bonding MOs – electrons in antibonding MOs) / 2

1	0	1	2	3	2	1	0
Li–Li	Be Be	B–B	C=C	N≡N	O=O	F–F	Ne Ne
known in the gas phase	dimer unknown	known in the gas phase paramagnetic diradical	known in the gas phase at high temp.	stable gas	stable gas paramagnetic diradical. Singlet & triplet states	stable gas	dimer unknown

The Strongest Bond in Chemistry

The strength of a bond depends on

Covalent effects

- The degree of overlap between the interacting atomic orbitals

The elements of the **2nd period** of the periodic table - orbital hybridization,
σ bond formed by sp−sp overlap, two π-bonds of similar strengths
The elements of the **3rd and higher periods** - hybridization is largely absent and π-bonds are much weaker than the corresponding σ-bonds - with increasing atomic number and increasing covalent radius, overlap is reduced and the π-bonds become weaker

Ionic effects

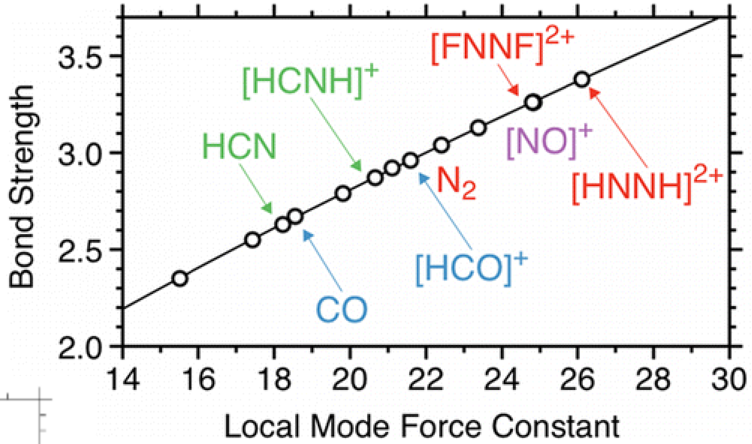
- The bond polarity (electronegativity difference) reflected by the difference in the energies of the atomic orbitals involved in bonding

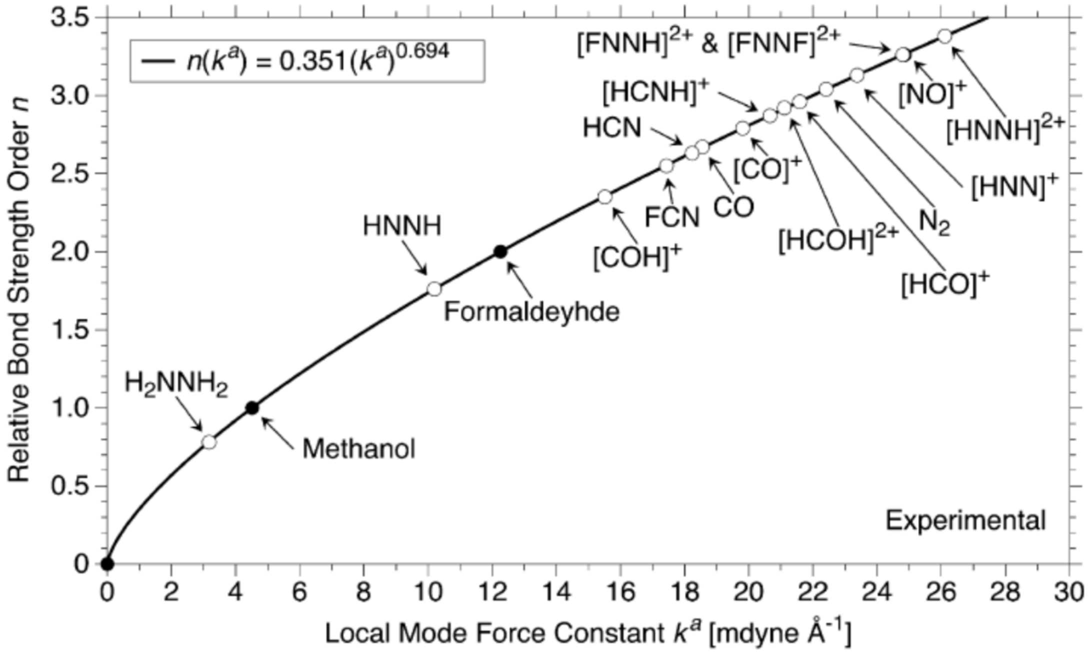
- The effective electronegativity - increased electronegativity means that the energies of the atomic valence orbitals and the bonding orbital(s) are lowered
= a strengthening of the bond

The Strongest Bond in Chemistry

the N≡N bond of the **[H–N≡N–H]$^{2+}$** ($^1\Sigma_g^+$) molecule

Stretching force constant
k (N≡N) = 26.1 mdyn/Å (1 dyn = 10^{-5} N)
Bond length r = 1.080 Å
Relative bond strength order
RBSO = 3.38

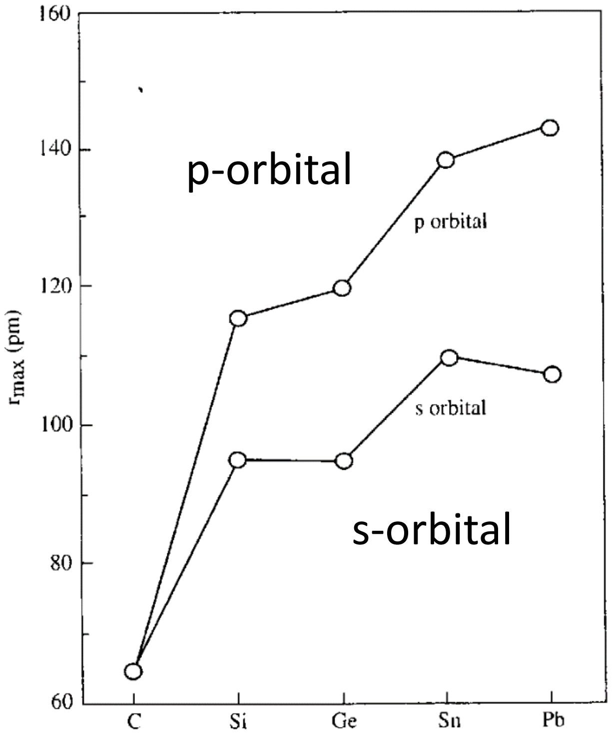




Dinitrogen N$_2$
k = 2293.8 N m^{-1}
Bond length r = 1.1038 Å

D. Cremer et al. *J. Phys. Chem. A* **2013**, *117*, 8981

π-Bonds



Atom n	C 2	Si 3	Ge 4	Sn 5	Pb 6
Orbital energy					
ns	-19.39	-14.84	-15.52	-13.88	-15.41
np	-11.07	-7.57	-7.29	-6.71	-6.48
Ionization energy					
ns	16.60	13.64	14.43	13.49	16.04
np	11.26	8.15	7.90	7.39	7.53
Electron affinity	1.26	1.39	1.23	1.11	0.36
Polarizability	1.76	5.38	6.07	7.7	6.8
Electronegativity					
Mulliken	1.92	1.46	1.40	1.30	1.21
Pauling	2.55	1.90	2.01	1.96	2.33
Allen	2.28	1.76	1.81	1.68	1.91
Atomic radius					
ns	1.58	2.20	2.19	2.48	2.39
np	1.74	2.79	2.88	3.22	3.22

Carbon - 2s and 2p electrons approximately **the same spatial extension** (the core electrons occupy only the 1s orbital)
Heavier Group 14 elements, the *n*p valence electrons (*n* > 2) are **spatially separated** from *n*s due to Pauli repulsion with the (*n*–1)p electrons in the inner shell

Difficult to hybridize *n*s and *n*p orbitals for heavier atoms, tend to preserve the valence *n*s electrons as core-like electrons while carbon shows a preference for an effective hybridization of the s and p - the strong overlap binding ability

π-Bonds

In Group 14 all double-bonded E=E species are unstable!

Exothermic !

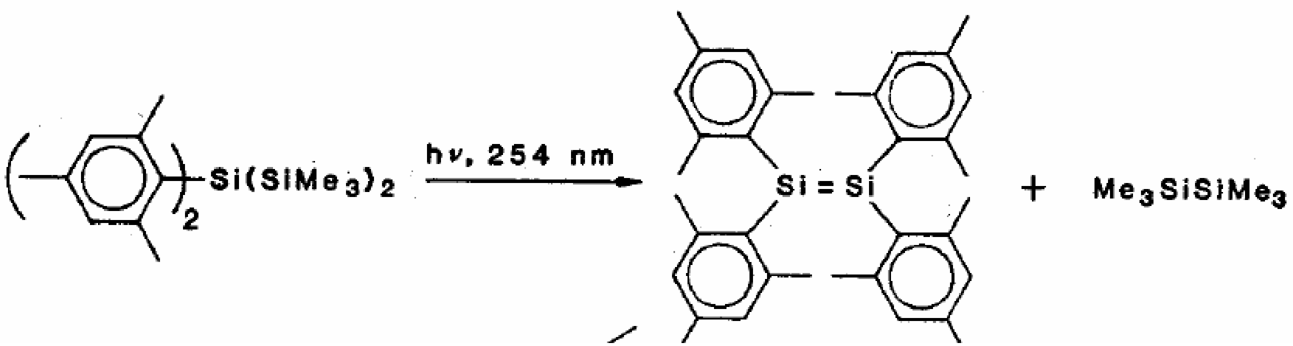
1933 at ICI
R. Gibson, E. Fawcett
High pressure polyethylene

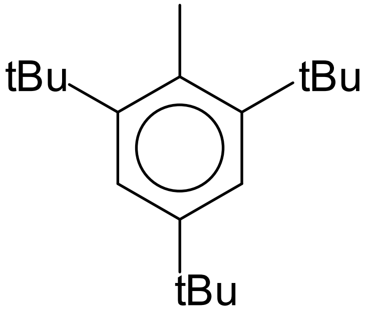
kJ mol^{-1}	E=E	E-E	ΔH
C	602	$-2(356)$	-110
Si	310	$-2(226)$	-142
Ge	270	$-2(188)$	-106
Sn	190	$-2(151)$	-112

C=C **double** bonds are **thermodynamically less stable than** two corresponding **single** bonds but are **kinetically stabilized**
The preparation of polymers involves a catalyst to overcome the kinetic barrier and induce an exothermic reaction

The Si=Si bond are much weaker, the driving force for polymerization is large, hard to prevent polymerization

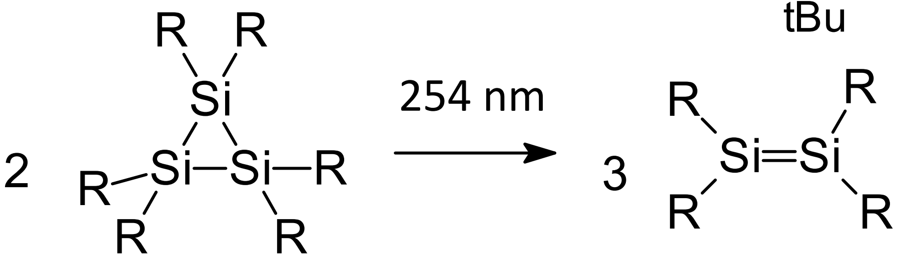
Stabilisation of Si=Si



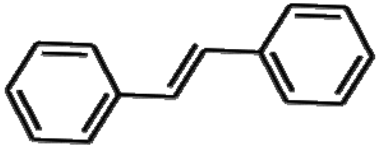


Disilene

Bulky groups can inhibit catenation
Si=Si 216.0 pm
a typical Si–Si 232 pm - 8% shortening
Tetraphenylethene - C=C 12% shortening



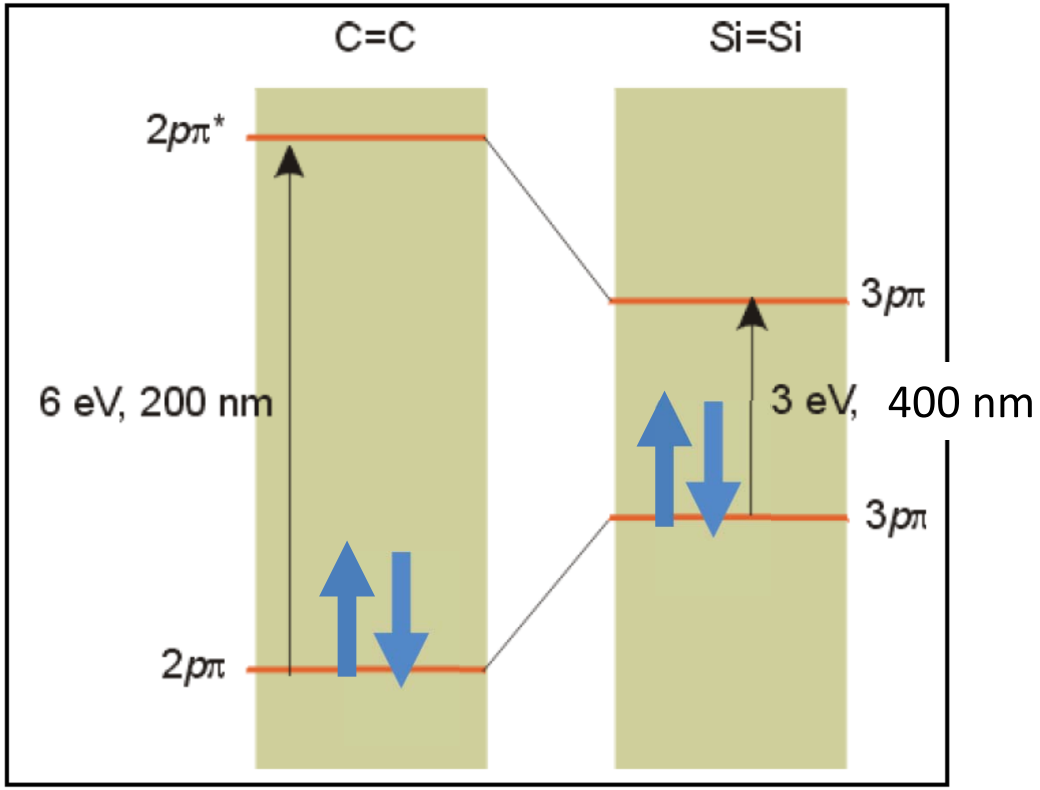
The Z → E isomerization energy of unsymmetrical disilene, (Mes)(tBu)Si=Si(tBu)(Mes)
The barrier to inversion in the disilene is high $E_{act} = 131\ \mathrm{kJ\ mol^{-1}}$
trans-stilbene only 179 kJ $\mathrm{mol^{-1}}$



West, R.; Fink, M.J.; Michl, J. *Science* **1981**, *214*, 1343
Masamune, S. et al. *J. Am. Chem. Soc.* **1982**, *104*, 1150

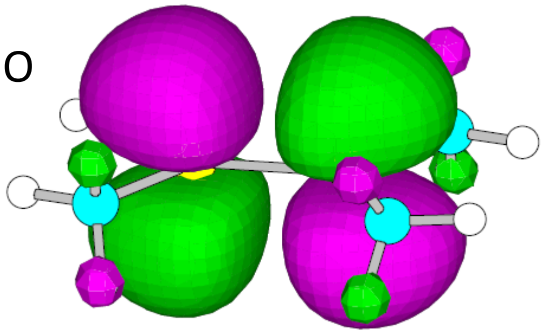
π-Bonds

Differences in reactivity?

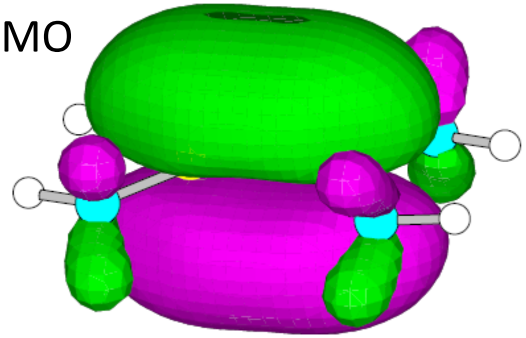


Alkene **Disilene**

LUMO

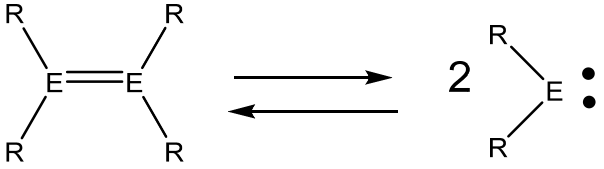


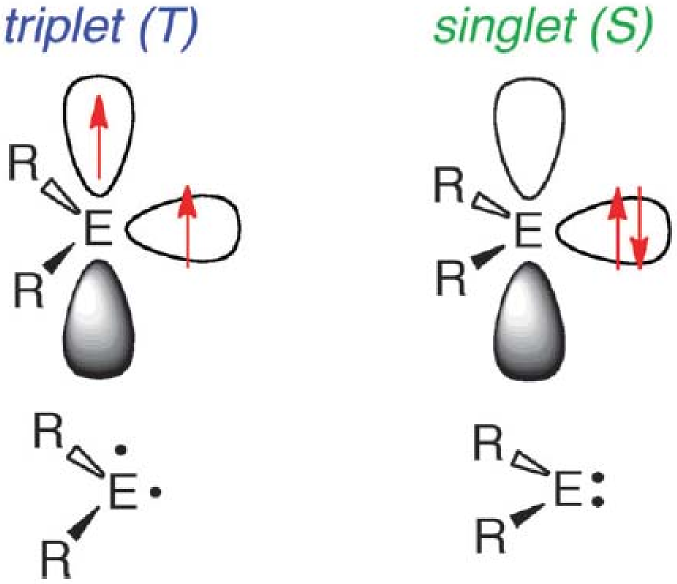
HOMO



Triplet - Singlet

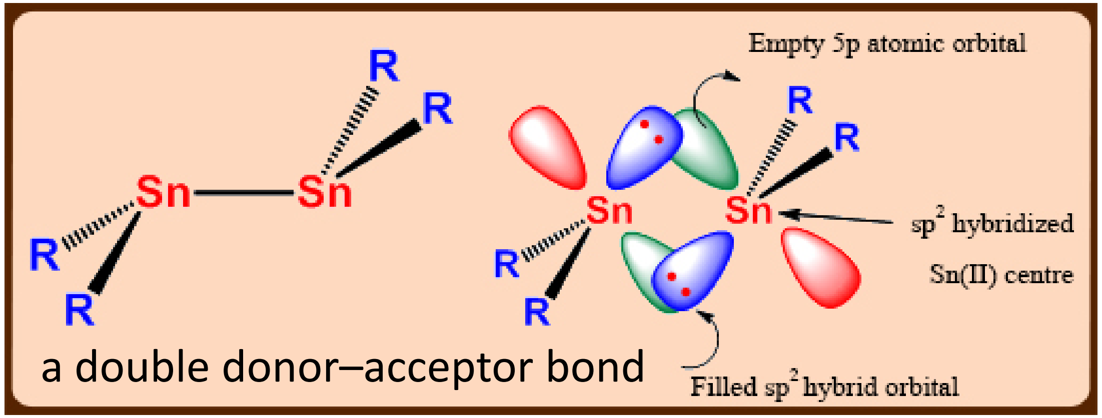
			ΔE_{ST}, kJ mol^{-1}
R_2C:	carbene	triplet	–58.5
R_2Si:	silylene	singlet	69.8
R_2Ge:	germylene	singlet	91.1
R_2Sn:	stanylene	singlet	103.7
R_2Pb:	plumbylene	singlet	145.5



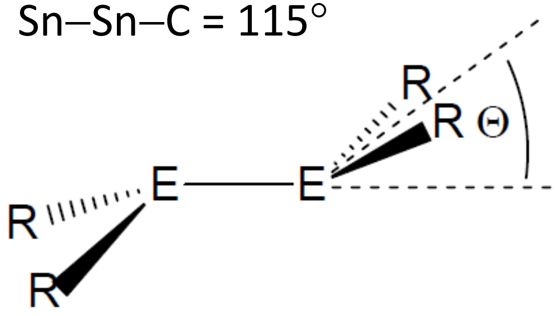


Stabilisation of Sn=Sn

$Sn[N(SiMe_3)_2]_2 + 2\ Li[CH(SiMe_3)_2] \rightarrow Sn[CH(SiMe_3)_2]_2 + 2\ Li[N(SiMe_3)_2]$



Trans-pyramidalization
Sn–Sn–C = 115°



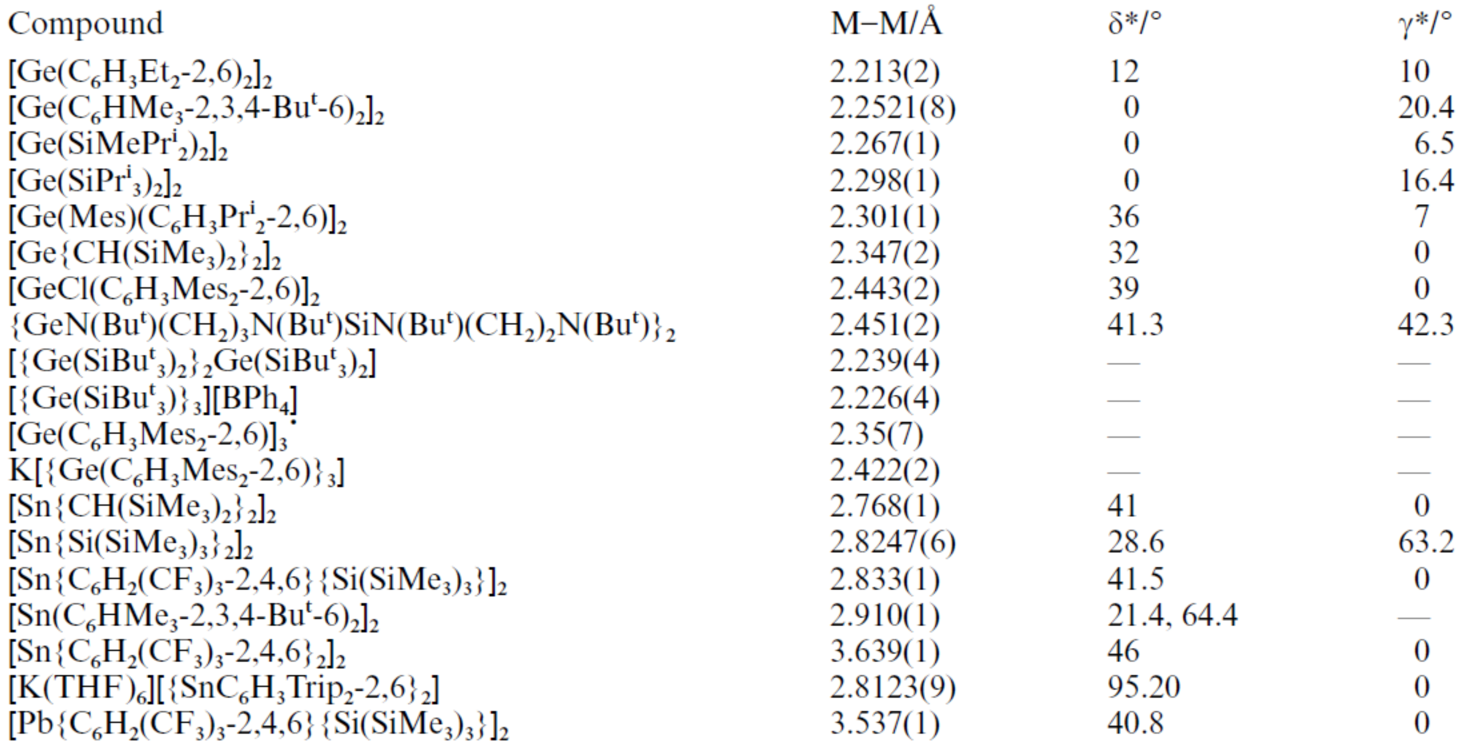
Distannene = the first isolable species with multiple bonding between two heavier main group elements

Sn=Sn distance = 2.768(1) Å - not very short, the compound is dissociated in solution to stannylene R_2Sn:

Sn elemental = 2.80 Å
$Ph_3Sn–SnPh_3$ = 2.770(4) Å

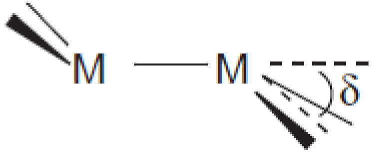
Lappert. M.F. et al. *J. Chem. Soc., Chem. Commun*. **1976**, 261

Double Bond in Heavy Elements

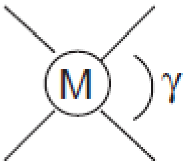


Compound	M–M/Å	δ*/°	γ*/°
$[Ge(C_6H_3Et_2\text{-}2,6)_2]_2$	2.213(2)	12	10
$[Ge(C_6HMe_3\text{-}2,3,4\text{-}Bu^t\text{-}6)_2]_2$	2.2521(8)	0	20.4
$[Ge(SiMePr^i{}_2)_2]_2$	2.267(1)	0	6.5
$[Ge(SiPr^i{}_3)_2]_2$	2.298(1)	0	16.4
$[Ge(Mes)(C_6H_3Pr^i{}_2\text{-}2,6)]_2$	2.301(1)	36	7
$[Ge\{CH(SiMe_3)_2\}_2]_2$	2.347(2)	32	0
$[GeCl(C_6H_3Mes_2\text{-}2,6)]_2$	2.443(2)	39	0
$\{GeN(Bu^t)(CH_2)_3N(Bu^t)SiN(Bu^t)(CH_2)_2N(Bu^t)\}_2$	2.451(2)	41.3	42.3
$[\{Ge(SiBu^t{}_3)_2\}_2Ge(SiBu^t{}_3)_2]$	2.239(4)	—	—
$[\{Ge(SiBu^t{}_3)\}_3][BPh_4]$	2.226(4)	—	—
$[Ge(C_6H_3Mes_2\text{-}2,6)]_3{}^{\cdot}$	2.35(7)	—	—
$K[\{Ge(C_6H_3Mes_2\text{-}2,6)\}_3]$	2.422(2)	—	—
$[Sn\{CH(SiMe_3)_2\}_2]_2$	2.768(1)	41	0
$[Sn\{Si(SiMe_3)_3\}_2]_2$	2.8247(6)	28.6	63.2
$[Sn\{C_6H_2(CF_3)_3\text{-}2,4,6\}\{Si(SiMe_3)_3\}]_2$	2.833(1)	41.5	0
$[Sn(C_6HMe_3\text{-}2,3,4\text{-}Bu^t\text{-}6)_2]_2$	2.910(1)	21.4, 64.4	—
$[Sn\{C_6H_2(CF_3)_3\text{-}2,4,6\}_2]_2$	3.639(1)	46	0
$[K(THF)_6][\{SnC_6H_3Trip_2\text{-}2,6\}_2]$	2.8123(9)	95.20	0
$[Pb\{C_6H_2(CF_3)_3\text{-}2,4,6\}\{Si(SiMe_3)_3\}]_2$	3.537(1)	40.8	0

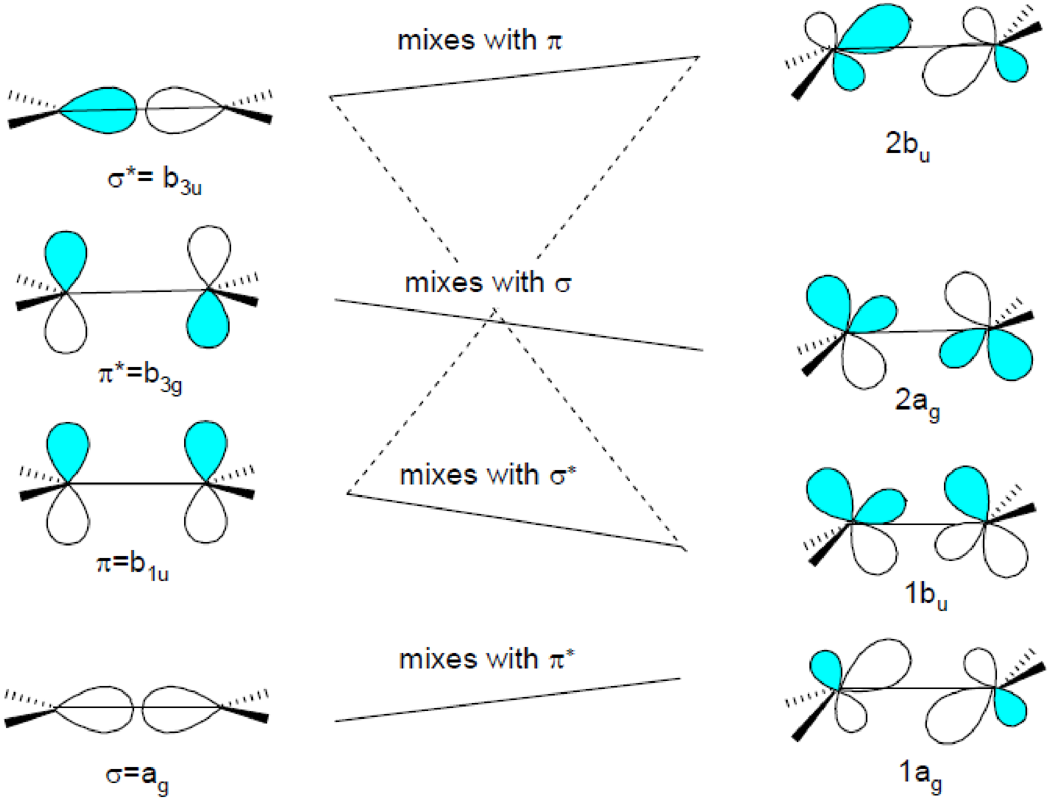
Trans-pyramidalization
out-of-plane angle, δ

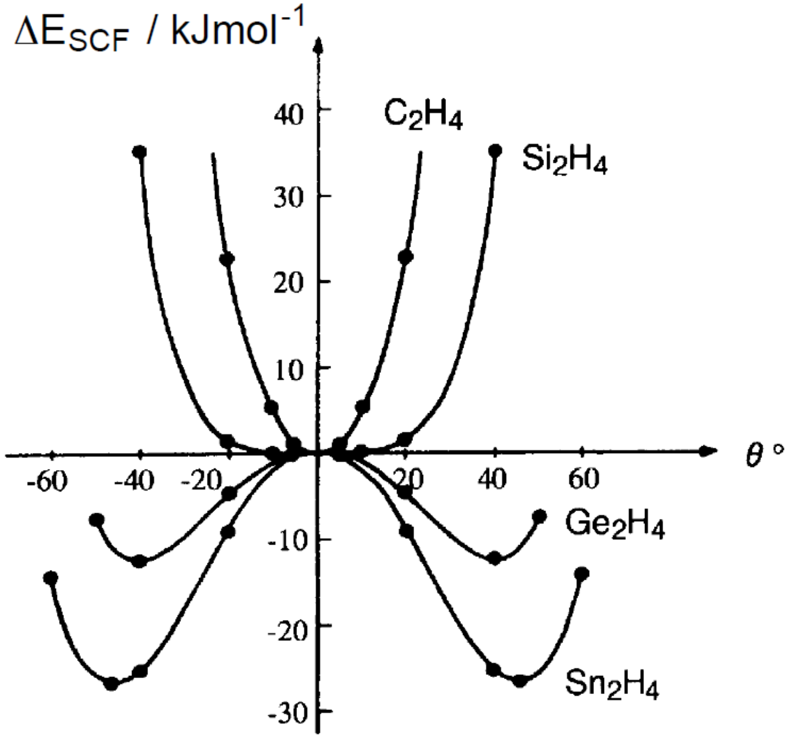


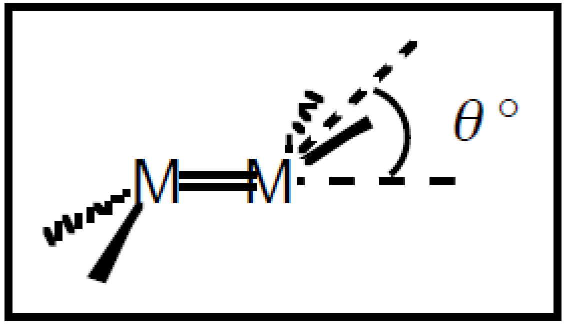
Twist angle, γ



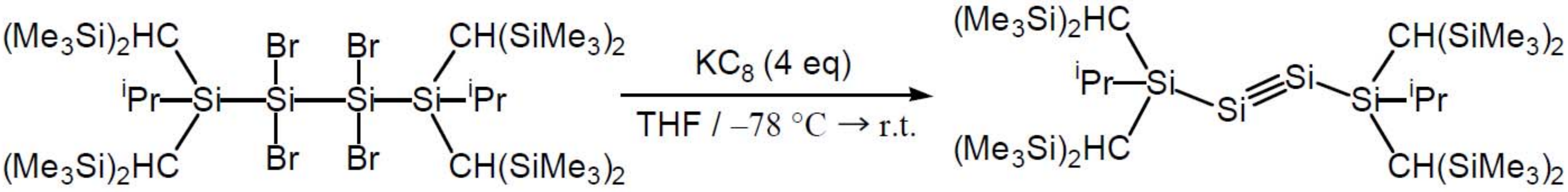
Double Bond in Heavy Elements



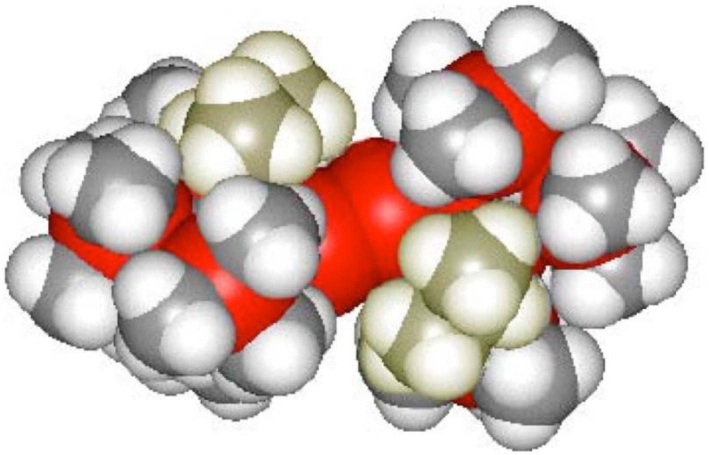




Triple Bond - Disilyne



Disilyne



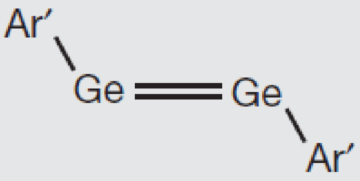
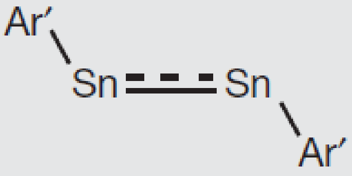
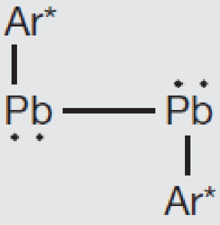
$\mathrm{Si{\equiv}Si}$ 206.22(9) pm
Half the magnitude of the bond shortening of alkynes $\mathrm{C{\equiv}C}$ /alkenes $\mathrm{C{=}C}$

$\mathrm{Si{=}Si}$ 216.0 pm
$\mathrm{Si{-}Si}$ 232 pm

The substituents at the $\mathrm{Si{\equiv}Si}$ group are trans-bent a bond angle of 137.44(4)°

Sekiguchi, A.; Kinjo, R.; Ichinohe, M. *Science* **2004**, *305,* 1775

Heavier Gr14 Alkyne Analogues

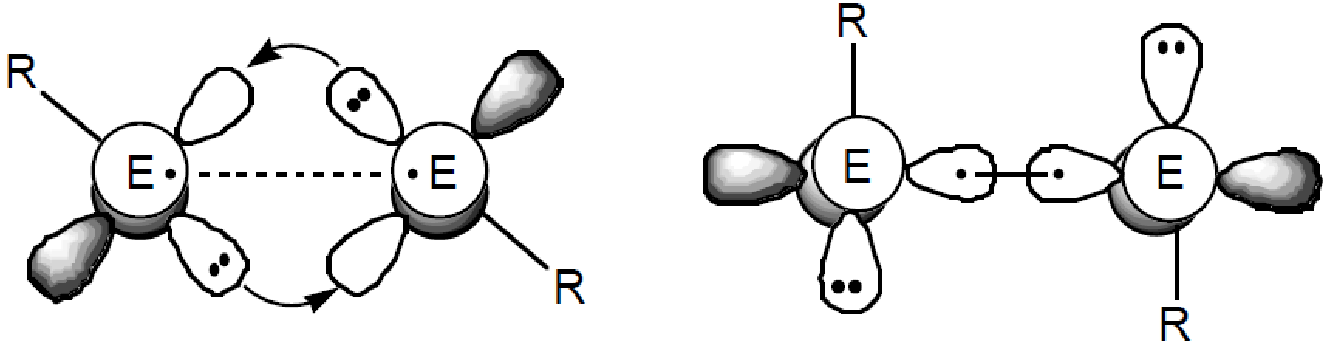
	Compound	M≡M (Å)	M≡M–C bending angle (degrees)	Shortening* (%)
		2.0622(9) (ref. 21)	137.44(4)	11.87
Digermyne		2.285(6) (ref. 22)†	128.67(8)	6.35
Distannyne		2.6675(4) (ref. 23) †	125.1(2)	5.07
Diplumbyne		3.1811 (ref. 24)‡	94.26(4)	−9.69

* Shortening with respect to a single bond.

† Ar′ = C_6H_3-2,6(C_6H_3-2,6-*i*-Pr_2)$_2$.

‡ Ar* = C_6H_3-2,6(C_6H_2-2,4,6-*i*-Pr_3)$_2$.

Heavier Gr14 Alkyne Analogues



The 6s^2 valence electrons are stabilized by **relativistic effects** - they participate less in bonding

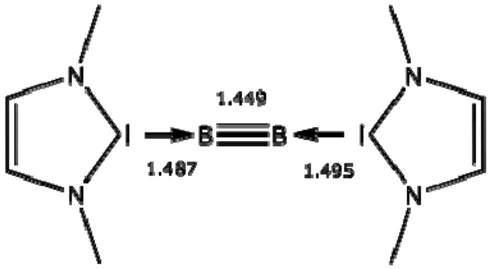
In an atom of a heavy element**, the velocities of its electrons** are close to the speed of light if they approach the nucleus, Einstein's theory of relativity indicates that the electrons at such high velocities have higher masses, **increasing** their electromagnetic **attraction** with the positive nucleus and leading to the **contraction** of the inner atomic orbitals in comparison to non-relativistic analogs

The Pb-Pb single bond formed by head-to-head overlap of 6p orbitals, which have a larger radius than 6s and hence form longer bonds

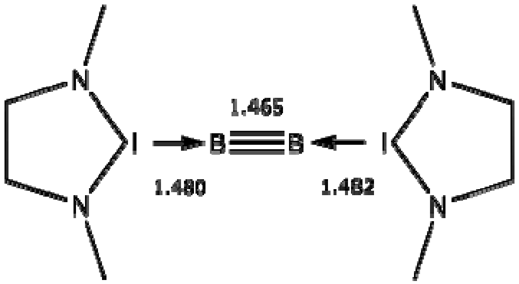
Triple $E\equiv E$ Bond in Gr13

Diboryne

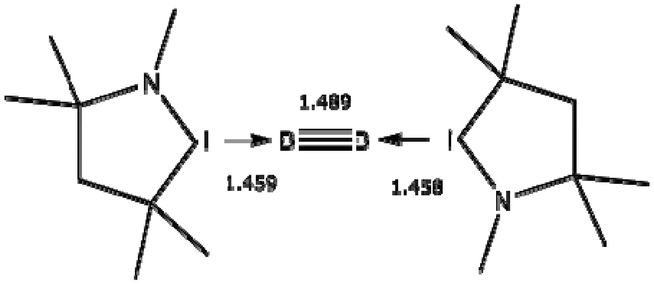
R_2C: carbene stabilized B_2



Braunschweig et al., *Science* **2012,** *336*, 1420



Braunschweig et al., *Angew. Chem. Int. Ed*. **2014**, *53*, 9082

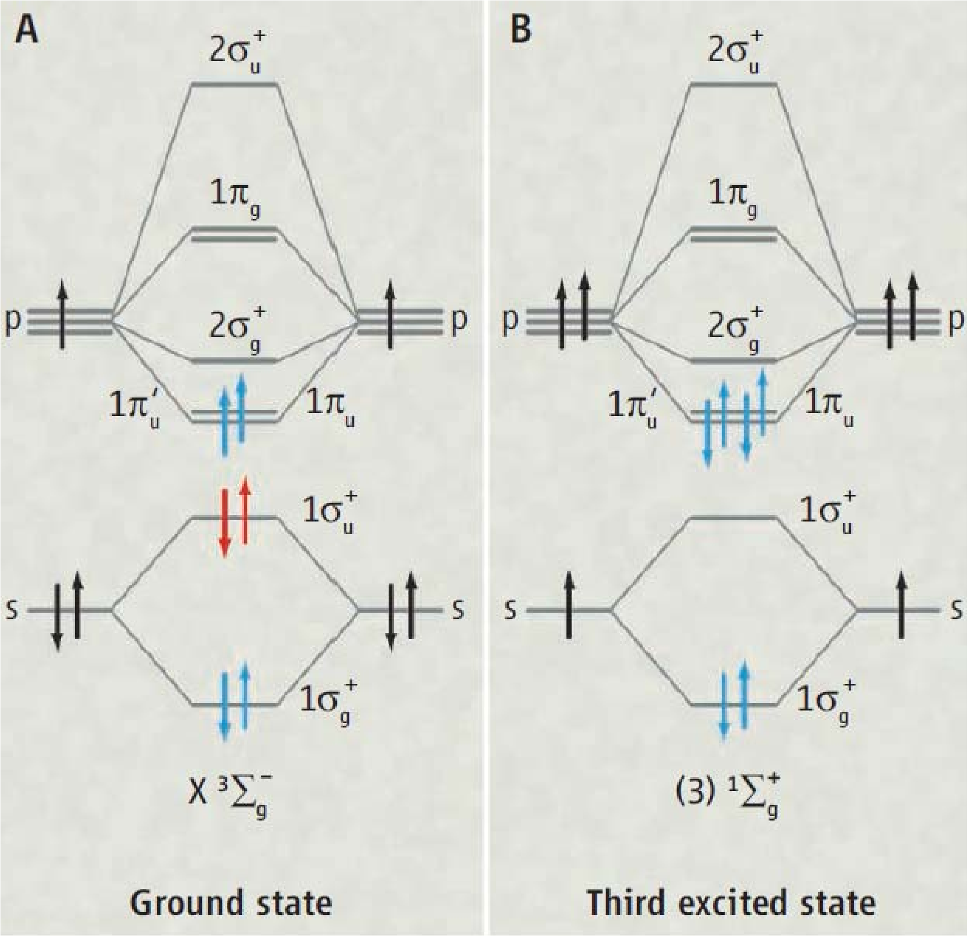


Braunschweig et al., *Angew. Chem. Int. Ed*. **2015**, 54, 13801
cyclic (alkyl)(amino)carbenes = CAAC

C=B=B=C an electron deficient (4-π-electron) cumulene

Braunschweig, Dewhurst, Organometallics **2014**, *33*, 6271

Triple E≡E Bond in Gr13



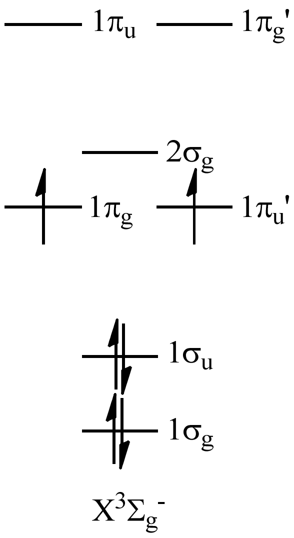
Molecule B_2

(NHC)→B≡B←(NHC)

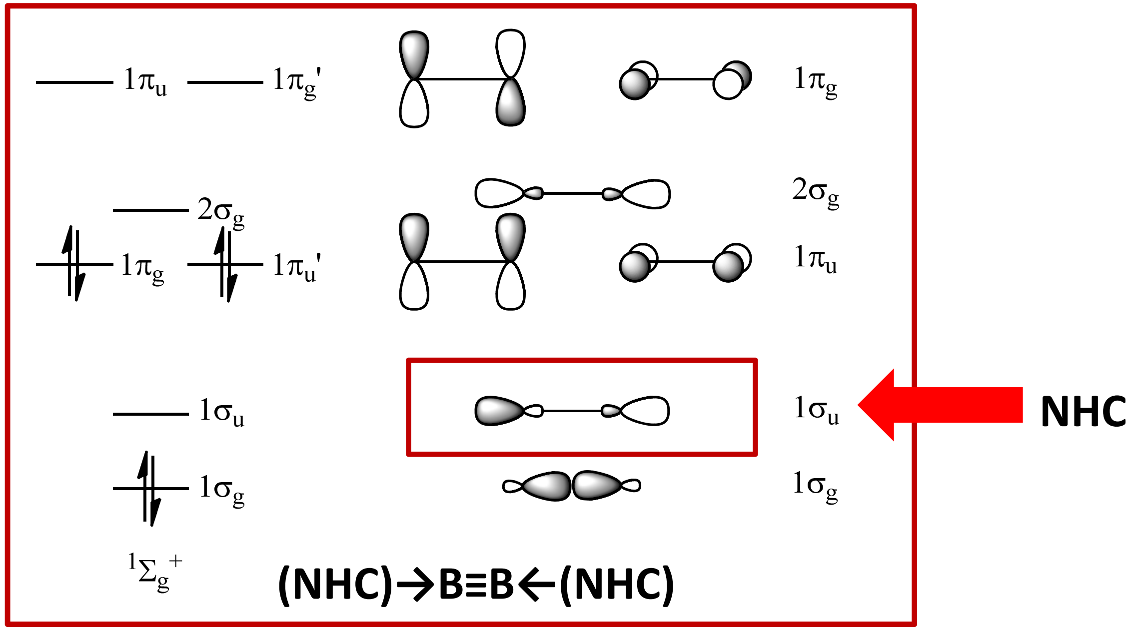
B_2 molecule
The ground state has two doubly occupied bonding orbitals (blue) but one doubly occupied antibonding orbital (red) - a bond order = 1
a single bond B–B

(NHC)→B≡B←(NHC)
the excited state has three doubly occupied bonding orbitals and hence **a triple bond B≡B**

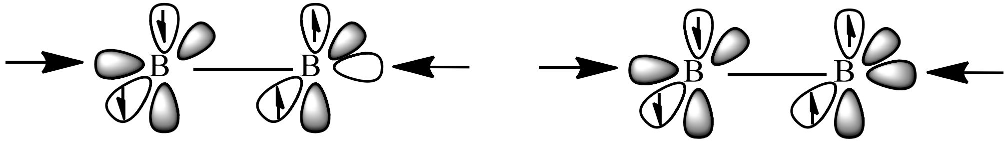
Triple E≡E Bond in Gr13



Molecule B_2



(NHC)→B≡B←(NHC)

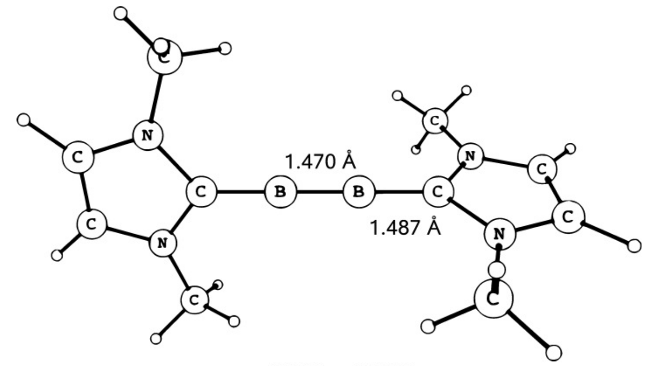


$B_2[X^3\Sigma_g^-] \longrightarrow B_2[(3)^1\Sigma_g^+]$ = 106.6 kcal/mol

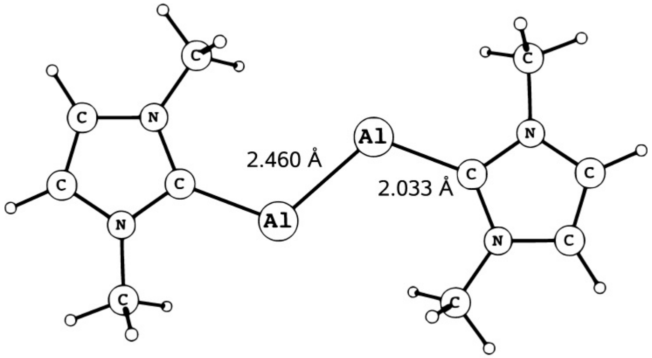
$B_2(NHC)_2 \longrightarrow B_2[X^3\Sigma_g^-] + 2\ NHC$ = 187.7 kcal/mol

Triple M≡M Bond in Gr13

Quantum chemical calculations DFT
NHC = N-Heterocyclic Carbenes

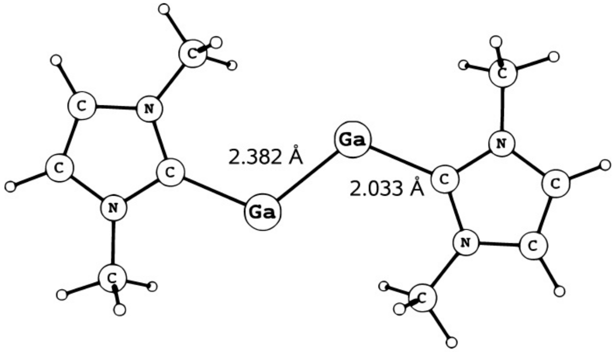


a(CBB) = 180.0°

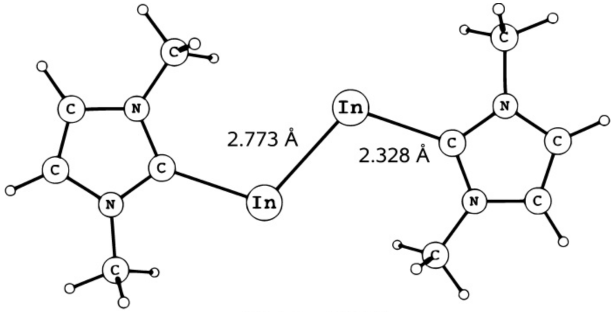


a(CAlAl) = 117.8°
d(CAlAlC) = 180°

anti-periplanar
trans-bending
E=E double bond



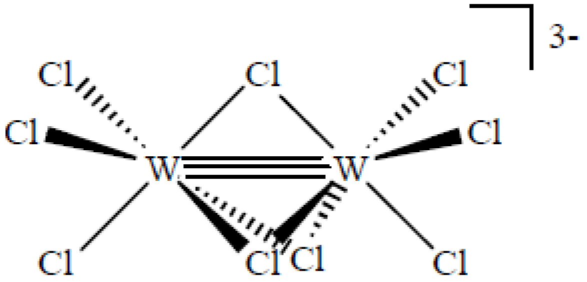
a(CGaGa) = 117.5°
d(CGaGaC) = 180°



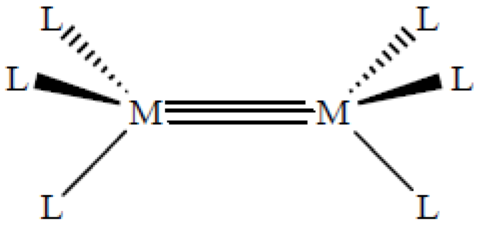
a(CInIn) = 113.0°
d(CInInC) = 180°

N. Holzmann, A. Stasch, C. Jones, G. Frenking, *Chem. Eur. J.* **2011**, *17*, 13517

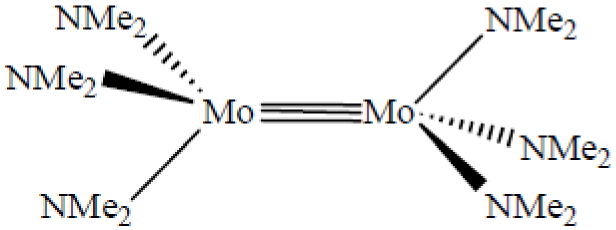
Triple M≡M Bond



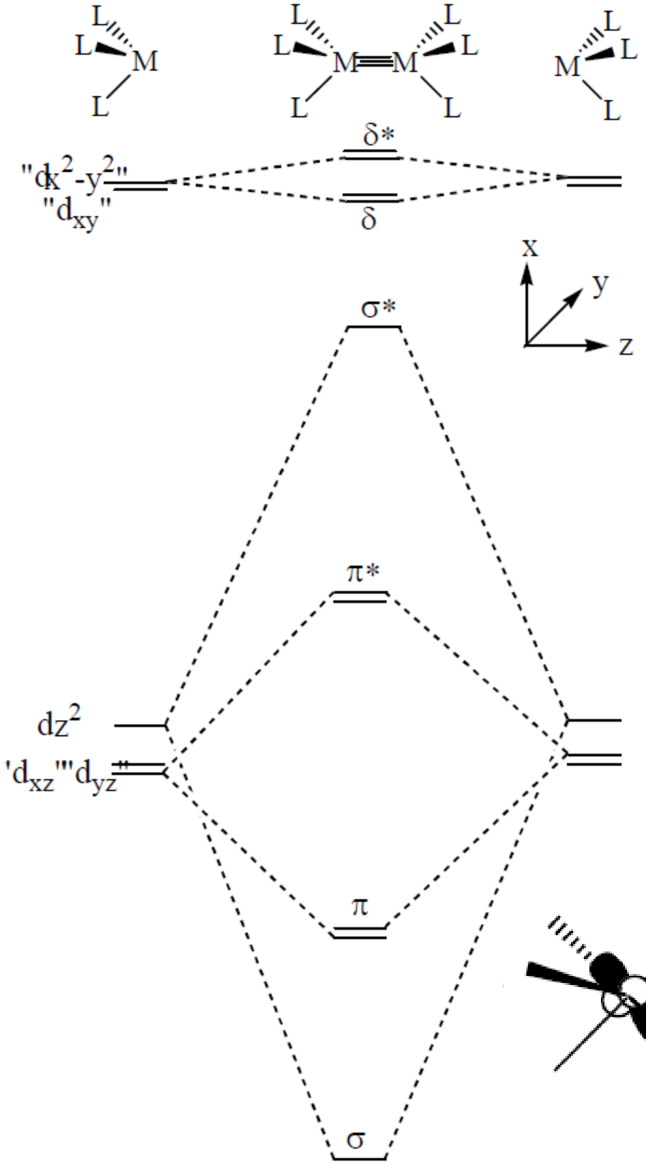
Bridged

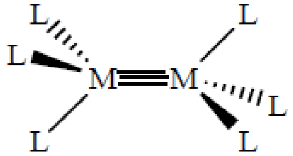


Non-bridged (eclipsed)

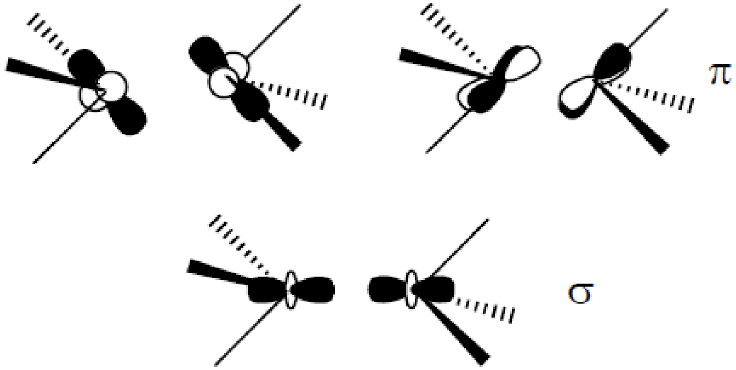


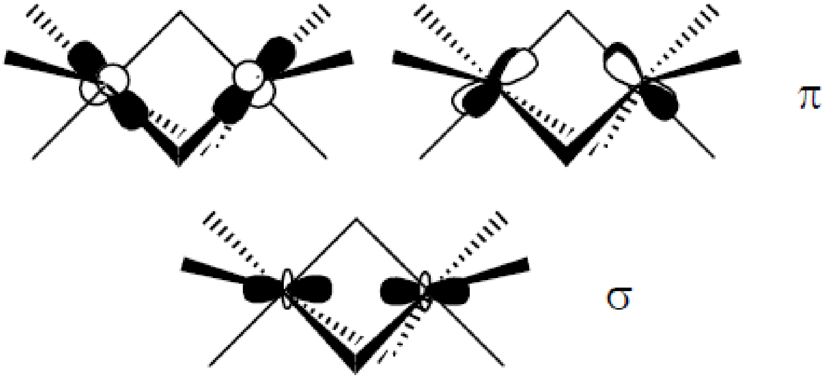
Non-bridged (staggered)



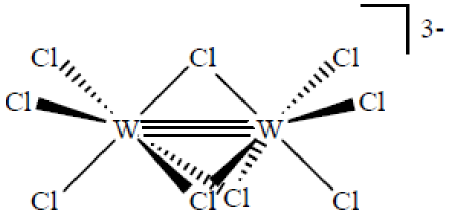


Non-bridged (staggered)





Triple M≡M Bond



Bridged

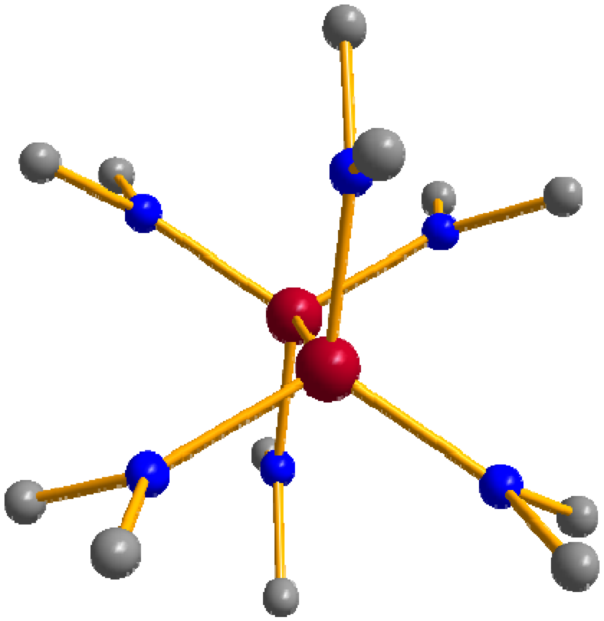
	Configuration	rM-M / pm	Magnetism
$Cr_2Cl_9^{3-}$	$\sigma^2(\delta/\pi)^4$	310	Paramagnetic
$Mo_2Cl_9^{3-}$	$\sigma^2(\delta/\pi)^4$	253-288	Variable
$W_2Cl_9^{3-}$	$\sigma^2(\delta/\pi)^4$	242-250	Diamagnetic

$Cr_2Cl_9^{3-}$ two $CrCl_3$ fragments held together by 3 bridging Cl, no d-orbital overlap, no direct Cr-Cr bond, paramagnetic with **6 unpaired** electrons

$Mo_2Cl_9^{3-}$ the Mo-Mo distance depends on the cation present in the crystal structure, variable bonding and magnetism

$W_2Cl_9^{3-}$ good overlap and a **triple W-W** bond with no unpaired electrons

Triple M≡M Bond

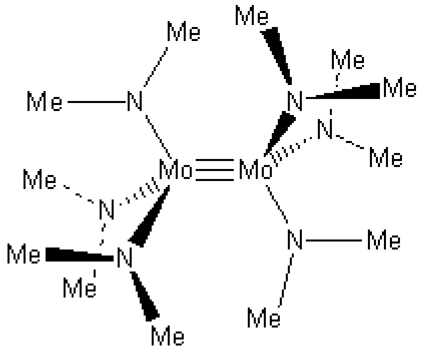


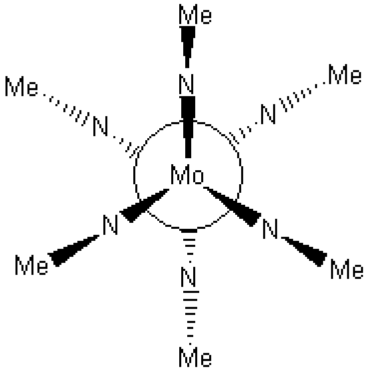
$Mo_2(NMe_2)_6$
a $\sigma^2\pi^4$ triple bond
a short Mo–Mo bond length of 2.214(2) Å

M.H. Chisholm, F.A. Cotton, B.A. Frenz, W.W. Reichert, L.W. Shive, B.R. Stults, *J. Am. Chem. Soc.* **1976**, *98*, 4469

$W_2(NMe_2)_6$
a W–W bond length of 2.294(1) Å

M.H. Chisholm, F.A. Cotton, M. Extine, B.R. Stults, *J. Am. Chem. Soc.* **1976**, *98*, 4477

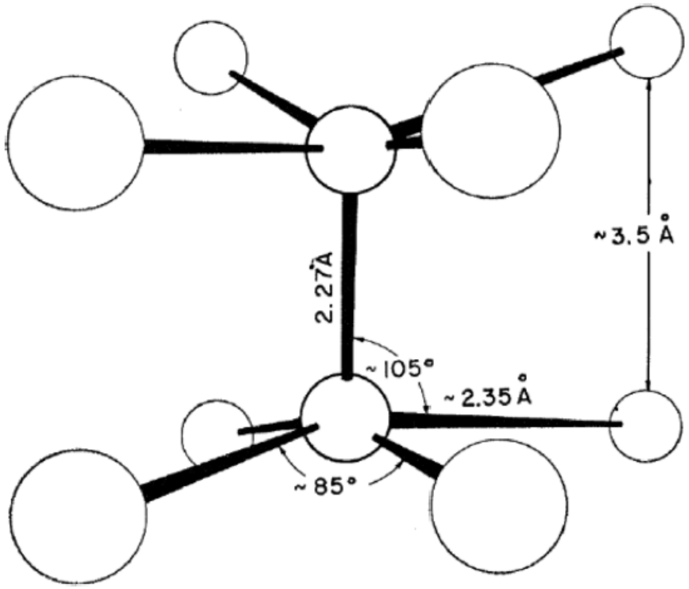


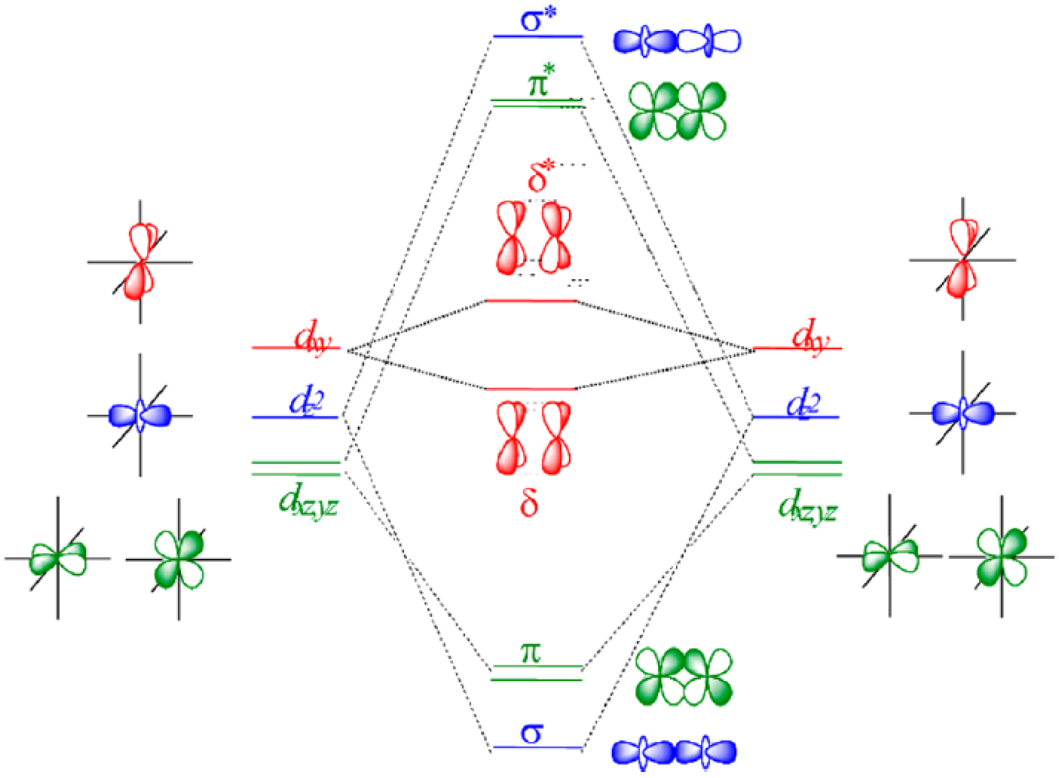


Quadruple Bond

1964 F. A. Cotton – **the first bond order higher than 3**

$[Re_2Cl_8]^{2-}$





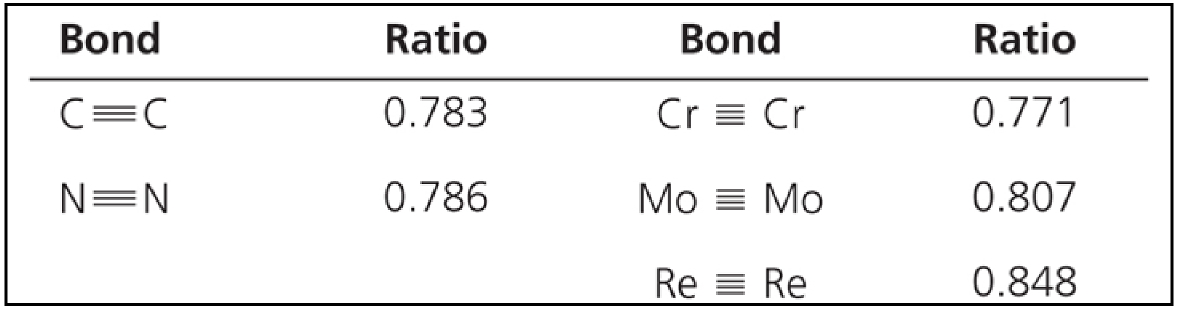
Eclipsed

δ–δ^* transition 14700 cm^{-1} (1.82 eV)

EBO = 3.2

the sum of the partial bond orders 0.92 (σ), 1.74 (π) and 0.54 (δ)

Formal Shortness Ratio (FSR)



Bond	Ratio	Bond	Ratio
$C\equiv C$	0.783	$Cr\equiv Cr$	0.771
$N\equiv N$	0.786	$Mo\equiv Mo$	0.807
		$Re\equiv Re$	0.848

F. A. Cotton - A short bond?

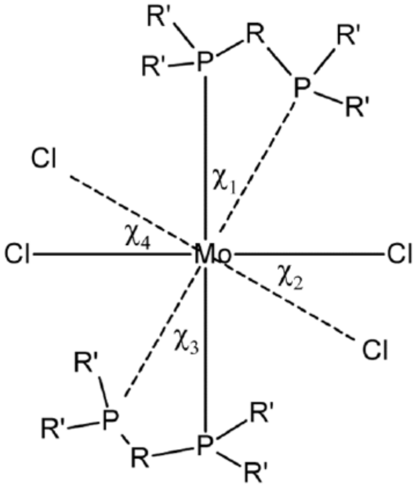
The FSR is a dimensionless number given by the ratio of the atom–atom **distance, *d***, of a bond and **the sum of the radii** of the two atoms involved, $r_A + r_B$:

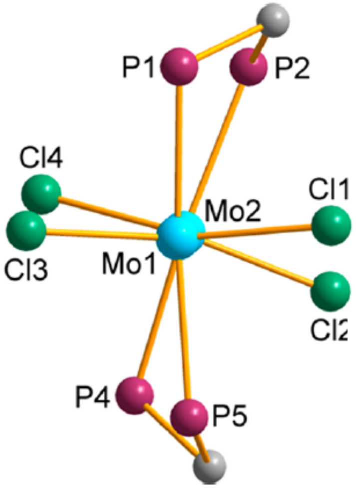
$$FSR = d/(r_A + r_B)$$

The advantage of this formalism is its interelement applicability
The FSR is a useful tool for comparing formal multiple bonding and short metal–metal distances

Quadruple Bond

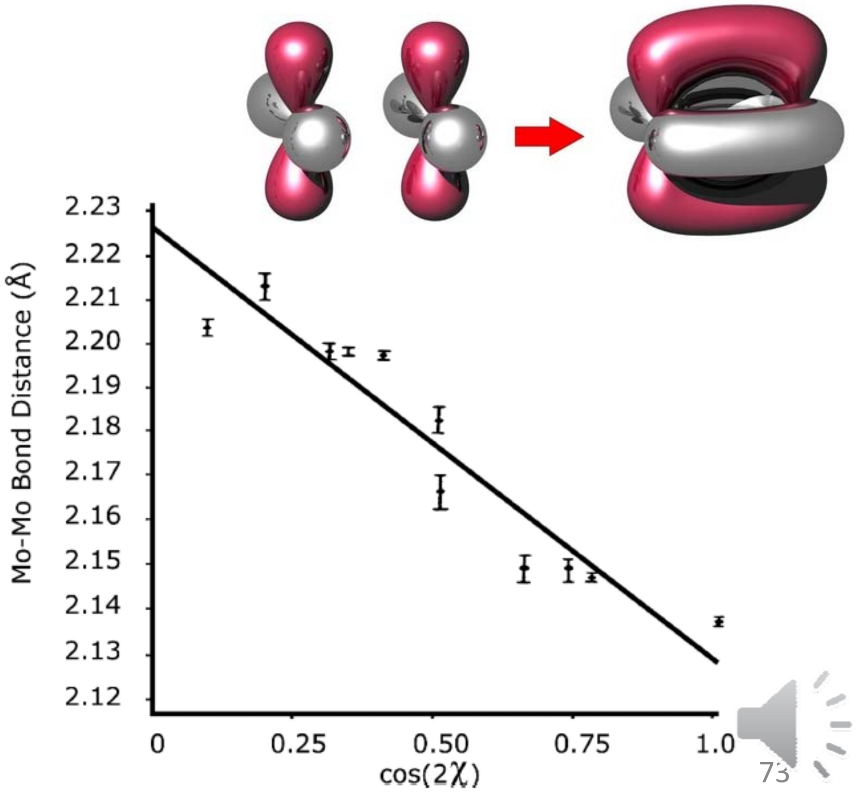
The Mo−Mo distances changes as torsional strain is introduced by bridging diphosphines with concomitant diminution of the d_{xy}−d_{xy} overlap, i.e., the δ bond





$Mo_2X_4(PR_3)_4$ and Mo_2X_4(diphosphine)$_2$

X = Cl and Br



Internal twist χ

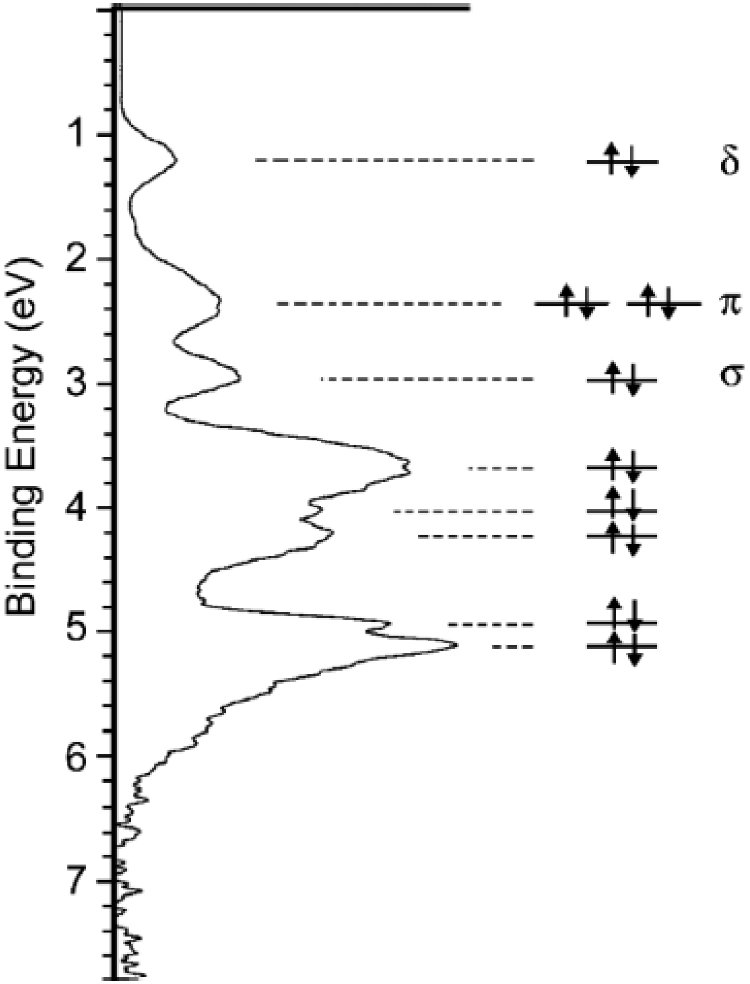
rotation about the metal−metal bond

average of 4 torsion angles

χ = 0° - an eclipsed configuration (b.o. = 4)

χ = 45° - a staggered configuration (b.o. = 3)

Quadruple Bond in PES



PES spectrum of the $[Re_2Cl_8]^{2-}$ anion

1 eV = 1.6×10^{-19} J

Oxidation $Mo_2(TiPB)_4$ to $[Mo_2(TiPB)_4]^+$

$Mo_2^{4+} \rightarrow Mo_2^{5+}$
one unpaired electron (EPR)

Mo−Mo distance 0.06 Å longer
electron removed from a bonding δ orbital

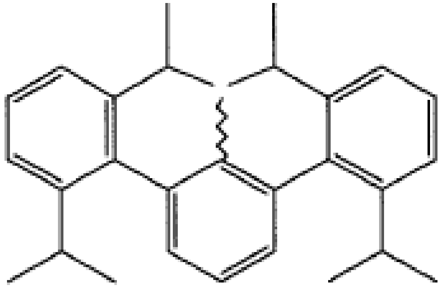
b.o. = 3.5

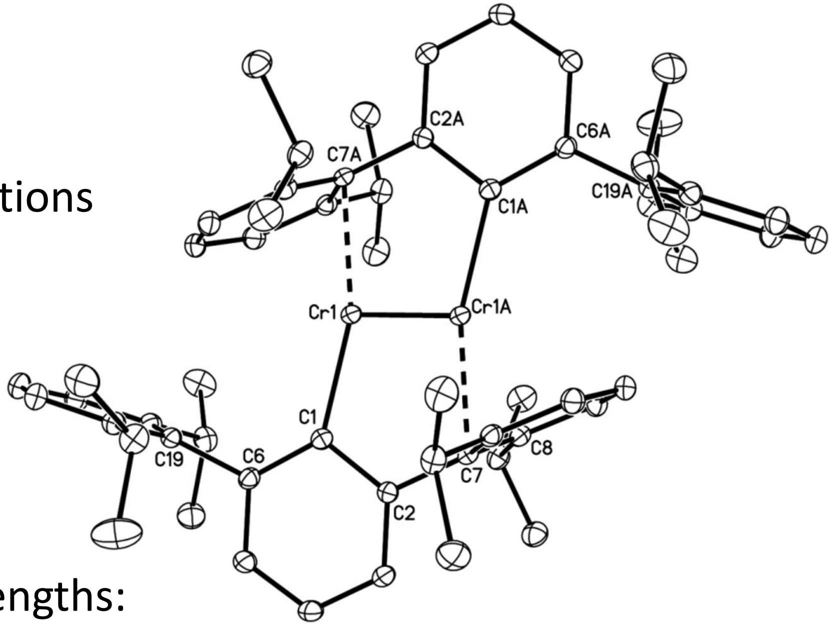
Quintuple Cr-Cr Bonding

Strategies for stabilization of multiple bonds

- Maximum of valence electrons at metal
- Minimum number of attached ligands
- Bulky ligands to prevent intermolecular reactions

Monovalent m-terfenyl ligands





Bond lengths:
Cr-Cr = 1.8351 Å
Cr(1)-C(1A) = 2.131 Å
Cr(1)-C(7A) = 2.2943 Å
Bond angle: Cr(1A)-Cr(1)-C(1) = 102.78°

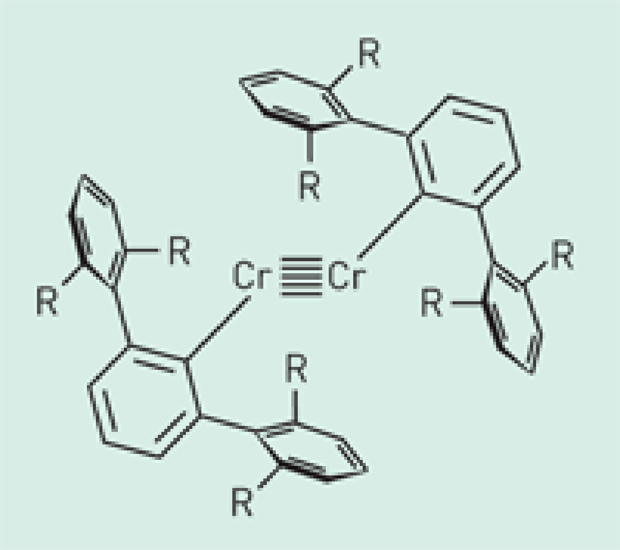
T. Nguyen, A. D. Sutton, M. Brynda, J.C. Fettinger, G. J. Long, P. P. Power, *Synthesis of stable compound with fivefold bonding between two chromium(I) centers*, *Science* **2005**, *310*, 844. Doi 10.1126/science.1116789

Quintuple Cr-Cr Bonding

$CrCl_2(THF)_2 + LiAr' \rightarrow \frac{1}{2}\,[Cr(\mu\text{-}Cl)Ar']_2 + LiCl$

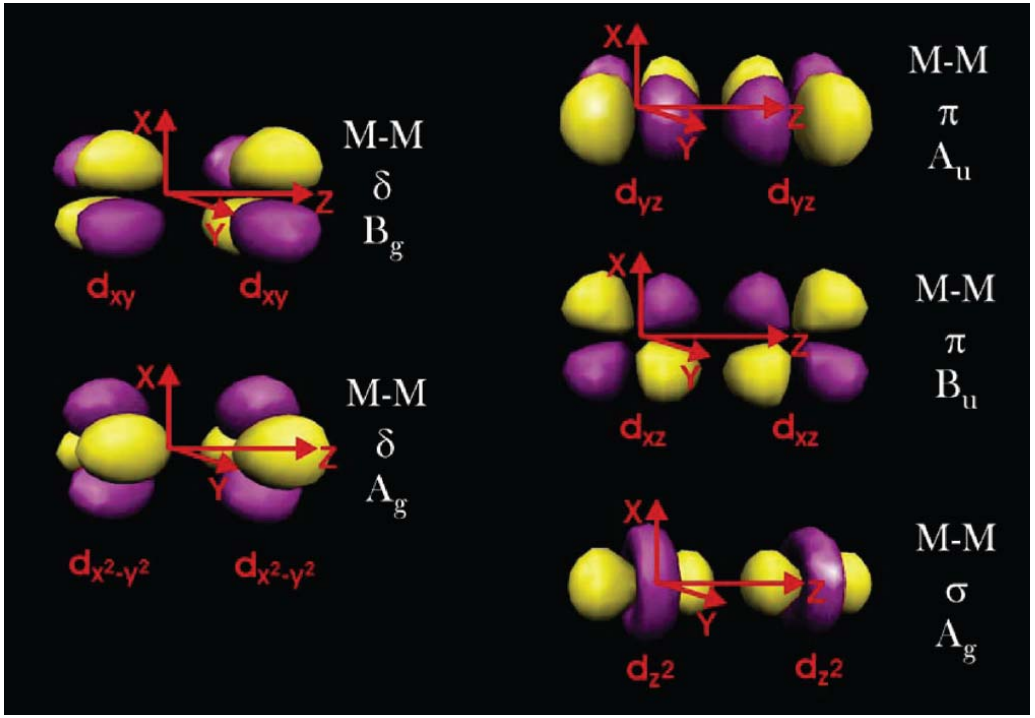
in THF, $Ar' = C_6H_3\text{-}2,6(C_6H_3\text{-}2,6\text{-}iPr_2)_2$

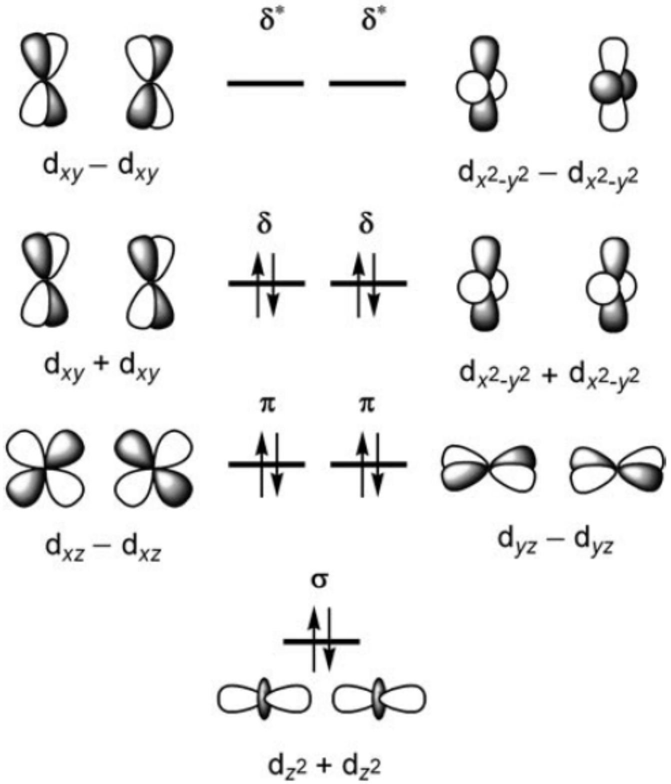
$[Cr(\mu\text{-}Cl)Ar']_2 + 2\,KC_8 \rightarrow [Cr_2(C_6H_3\text{-}2,6\text{-}(C_6H_3\text{-}2,6\text{-}iPr_2)_2)_2]$
$+ KCl$



Quintuple Cr-Cr Bonding

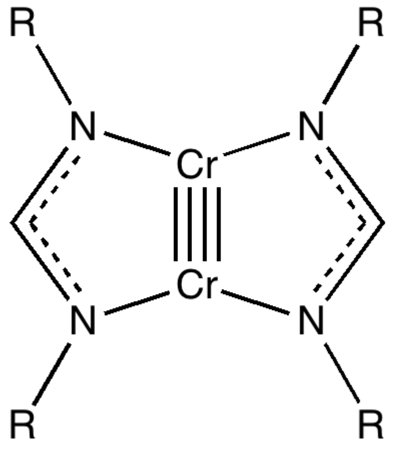
Cr-Cr bonding = $\sigma + 2\pi + 2\delta$

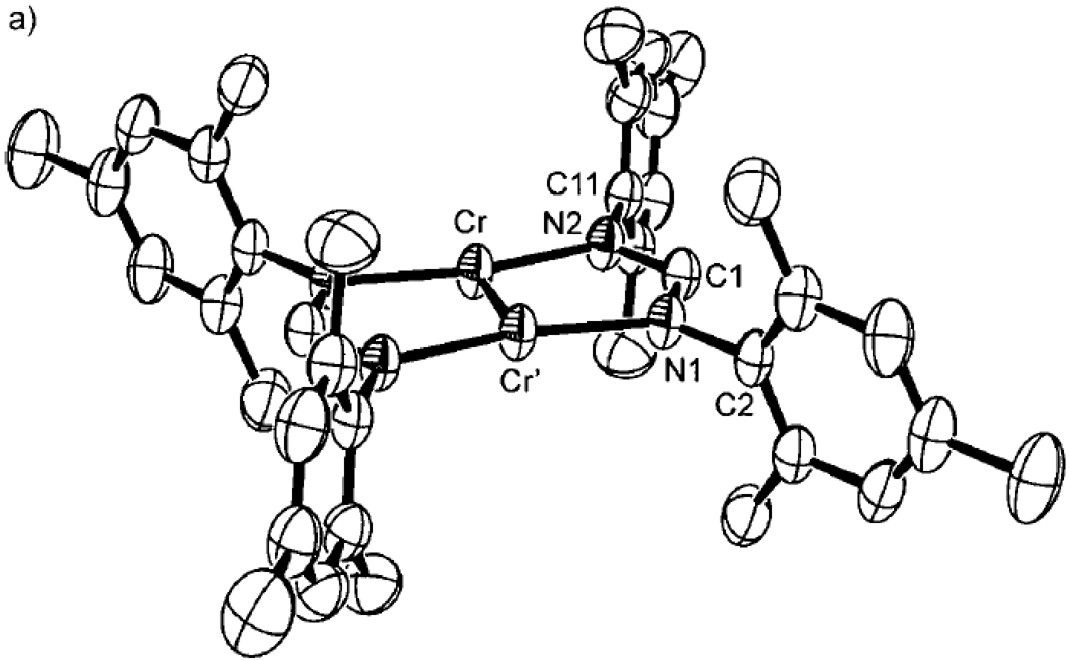




Quintuple bond = **five electron pairs** play a role in holding the metal atoms together
It does not imply that the bond order is five or that the bonding is very strong since the ground state of the molecule mixes with higher energy configurations with less bondin character, this gives lower, usually non-integer, bond orders

Quintuple Cr-Cr Bonding

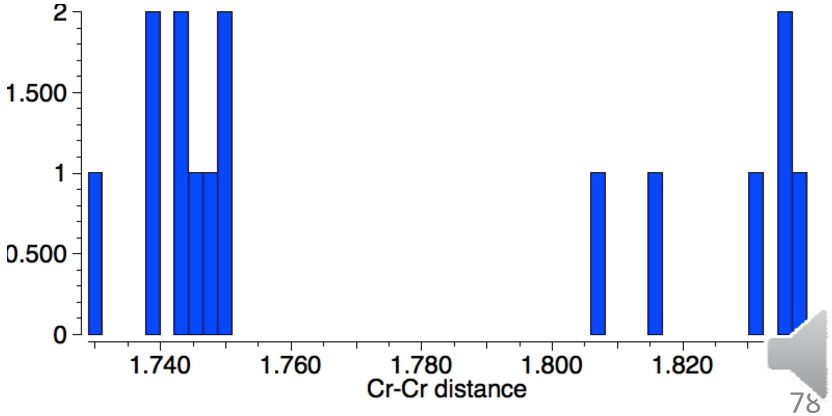




Amidinate ligand

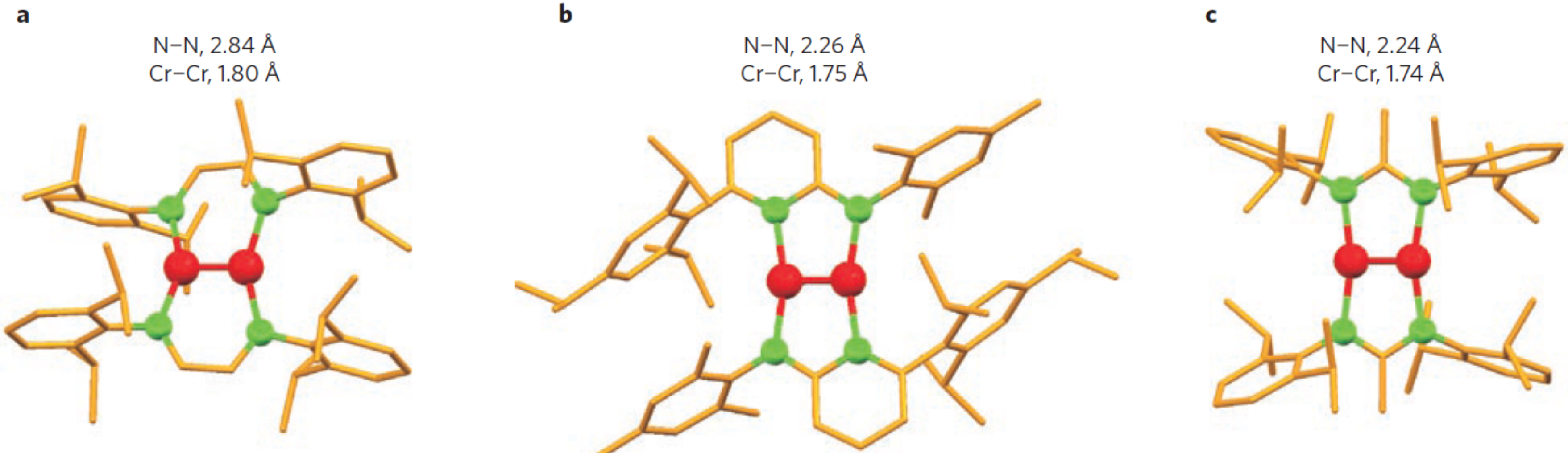
Cr-Cr
R = Mes **1.7404(8) Å**
R = Xylyl **1.7397(9) Å**

Cottons “formal shortness ratio” (FSR)
FSR = 0.733
the FSR of dinitrogen is 0.786



Quintuple Cr-Cr Bonding

The Hein–Cotton concept
three-atom bridging ligands to establish short metal–metal distances



2

Diazadiene

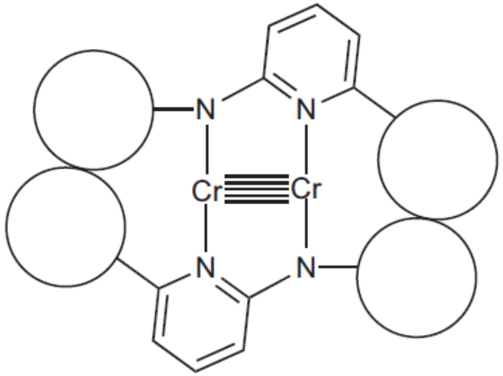
3

4

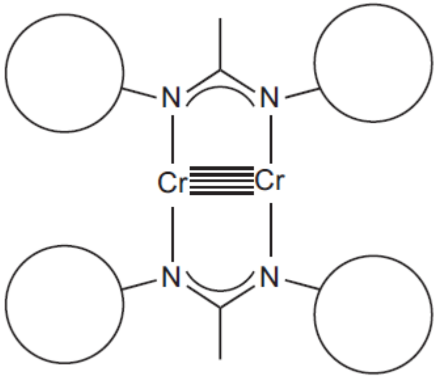
Amidinate

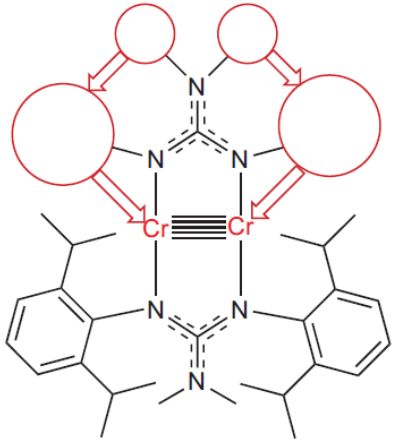
Importance of the ligand in establishing short metal–metal bonds:
The N–N distances correlate with the Cr–Cr bond lengths

The Shortest M–M Bond

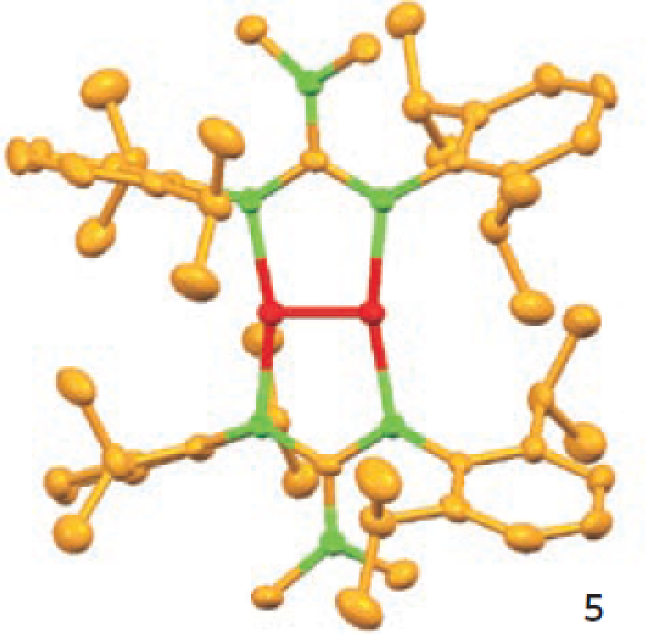


a





Cr-Cr, 1.7293(12) Å



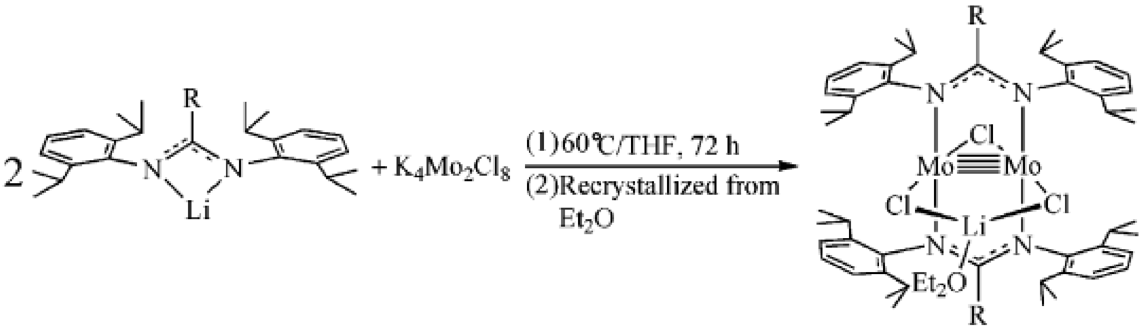
5

2009 Kempe

Steric pressure
a bulky substituent at the bridging carbon
a further reduced M-M distance

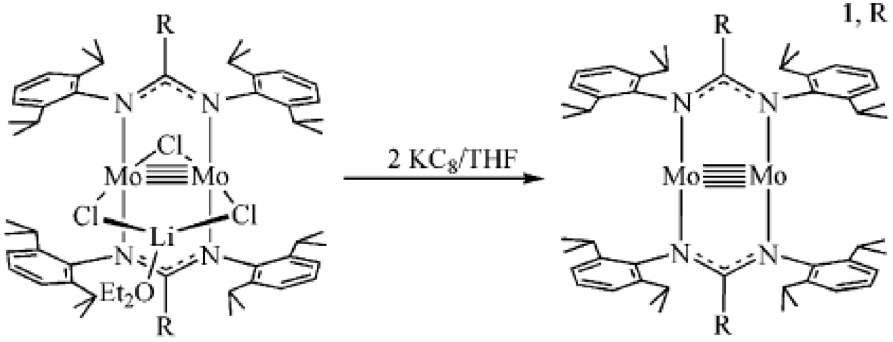
Guanidinates π system is delocalized and planar

Quintuple Mo-Mo Bond



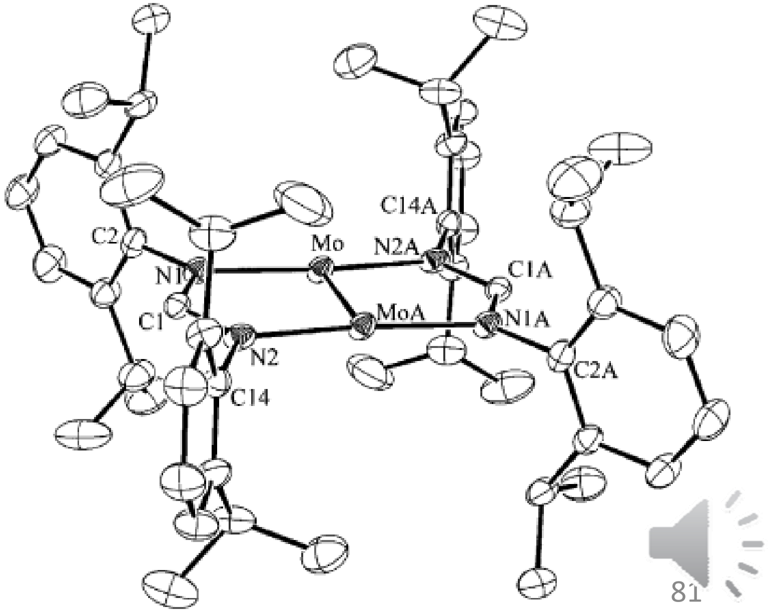
1, R = H; 2, R = Ph

2009 Tsai
the first Mo–Mo
quintuple bond



3, R = H; 4, R = Ph

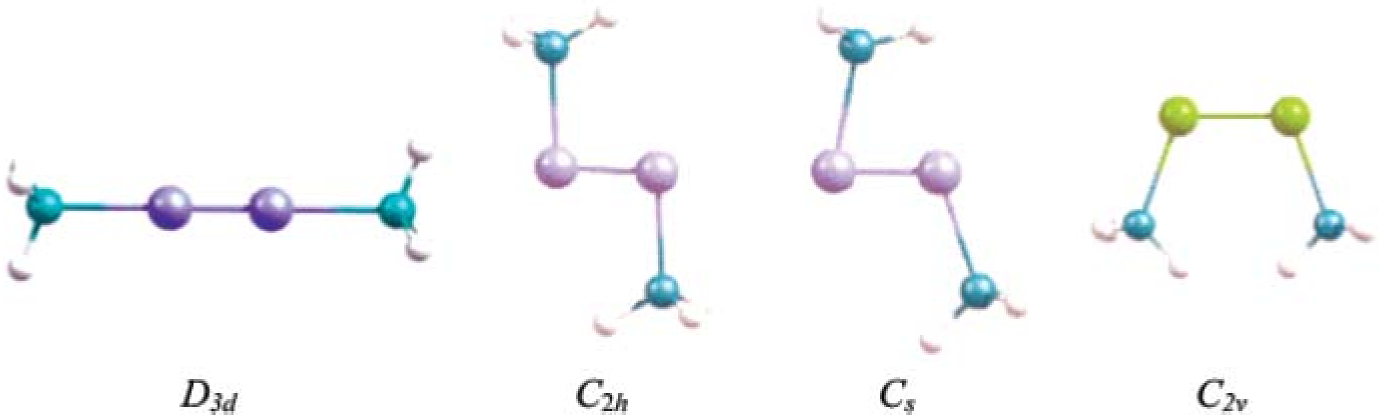
diamagnetic



Mo-Mo quintuple bond lengths
3 - 2.0187(9) Å
4 - 2.0157(4) Å

The shortest Mo-Mo quadruple bond
2.037(3) Å

Bonding in R-MM-R



R. Hoffmann - the potential energy surfaces of RMMR
R = H, F, Cl, Br, CN, and CH_3; M = Cr, Mo, and W

The potential energy surface is complex with several local minima
The linear geometry is always a minimum, but almost never the global minimum
A preference for either a **trans-bent** conformation or one of **the R groups bridging**
The potential energy surface is relatively flat
The lowest energy conformation - the best compromise between maximization of the MM bonding and minimization of orbital interactions that are MR antibonding
The MM quintuple bond persists

Sextuple Bonding in Gr6 M_2 Dimers

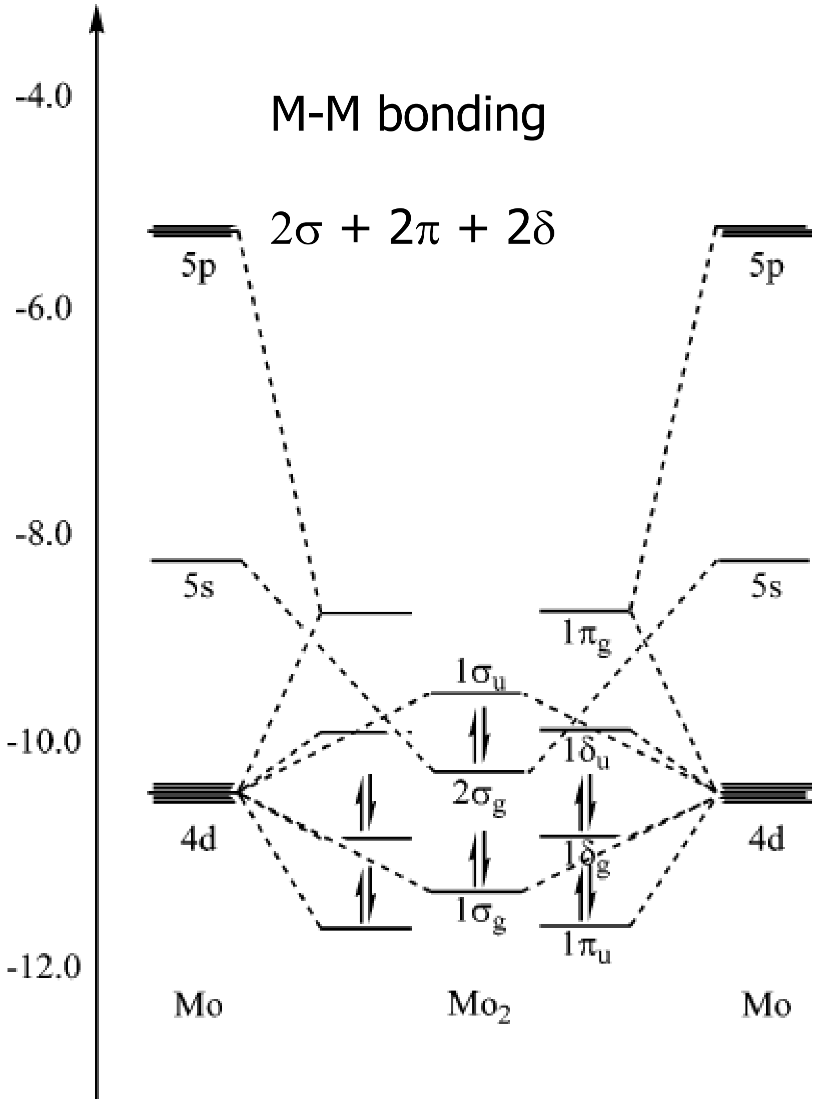
M_2 (M = Cr, Mo, W)

Matrix isolation
IR and UV spectroscopy
Short M-M distances
Singlet ground state

Laser-evaporated Cr_2 in the gas phase
d(Cr-Cr) = 1.68 Å

Spectroscopic studies of Cr_2 generated from pulsed photolysis of $Cr(CO)_6$
d(Cr-Cr) = 1.71 Å

Mo-Mo molecule
in the gas phase at low temperatures
d(Mo-Mo) = 1.93 Å



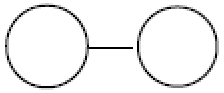
M-M bonding

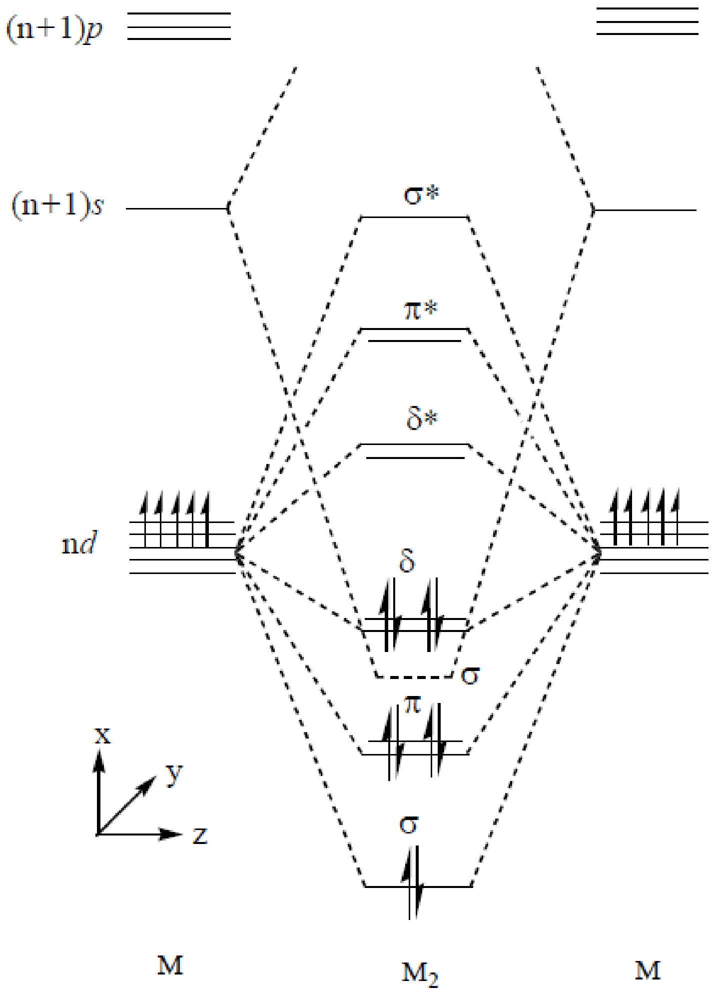
$2\sigma + 2\pi + 2\delta$

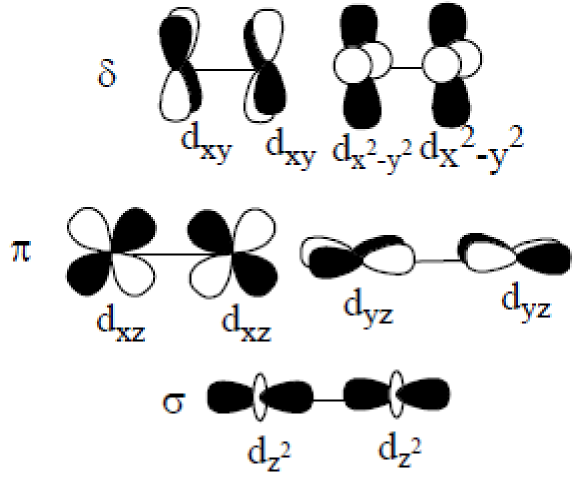
Sextuple Bonding in Gr6 M_2 Dimers

p-orbitals too high in energy

M_2 (M = Cr, Mo, W)





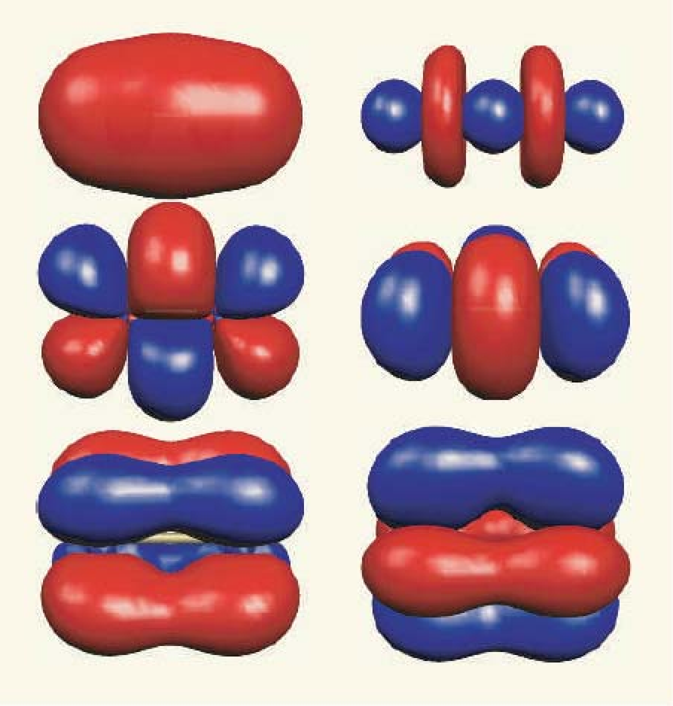


overlap **increases down** a group and can reach the bonding manifold

δ-bonds are weaker than π-bonds due to poor overlap between orbitals

M-M bonding energy increases down a group which is in contrast to the *p*-block

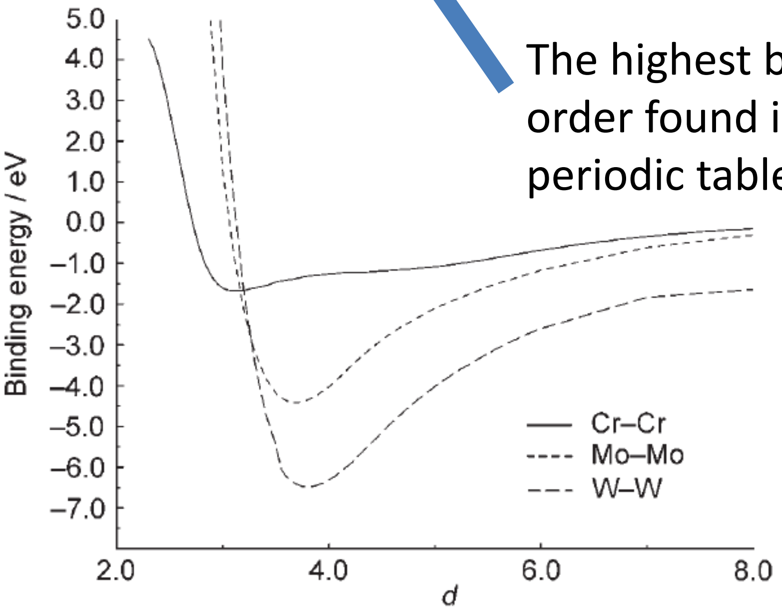
Sextuple Bonding in Gr6 M_2 Dimers



Effective bond order (EBO)
Dissociation energy (DE)

M	EBO	d(M-M), Å	DE, eV
Cr	3.5	1.66	1.65
Mo	5.2	1.95	4.4
W	5.2	2.01	5.4

The highest bond order found in the periodic table



Cr_2 – poor delta bonding, 4 AF coupled electrons, larger 4s orbitals generate a considerably longer bond than the 3d-3d This unbalance weakens the 3d bonds and makes the 4s bond repulsive at equilibrium geometry, the repulsive interaction between the closed 3p, which have about the same radial extension as 3d

Multiple Bonding

The bond energy only 1.65 eV for Cr_2 sextuple bond
but 3.17 eV for quintuple bond in [PhCrCrPh]
= no direct relation between bond order and bond energy, a complex quantity depends on many factors, such as atomic promotion energy, the interplay between attractive nuclear forces and electron repulsion, spin–orbit coupling- decreases the bond energy

Bond orders higher than 6?
Lanthanides – 4f orbitals?
Actinides – 5f orbitals participate in bonding

The EBO is always smaller than the maximum formal bond order (MBO = the number of electrons forming the bond divided by two)

Molecule	**MBO**	**EBO**	**D_0 [eV]**
Cr_2	6	3.5	1.6
[PhCrCrPh]	5	3.5	3.2
Ac_2	3	1.7	1.2
Th_2	4	3.7	3.3
Pa_2	**5**	**4.5**	**4.0**
U_2	6	4.2	1.2

Multiple Bonding Trends In Groups

Main-Group Elements

Tendency to multiple bonding **decreases down the group**
s + 3×p orbitals available
s/p size difference increases and propensity to hybridization decreases down the group

Transition Metals

Multiple bonding **increases down the group**
s + 5×d orbitals available
Difference in size between the smaller nd and larger (n+1)s orbitals decreases down the group

Relativistic effects contract s and p orbitals while d and f are expanded
The s and d orbitals in second- and especially third-row transition metals are more equal in size, this greater equivalency in size considerably enhances the bond strength

Dictionary of Used Terms

Potential well – potenciálová jáma
Stretching vibrations – valenční vibrace
Zero point energy – energie nulového bodu
Rate determining step – krok určující rychlost reakce
Polyhedral vertex/edge/face – vrchol/hrana/stěna polyedru
Parsimony – střídmost, šetrnost
Standard deviation – směrodatná odchylka
Close packed – nejtěsněji uspořádané