Si_6Tip_6

the Largest and Most Complicated Ever Experimental Gas Phase Molecular Structure

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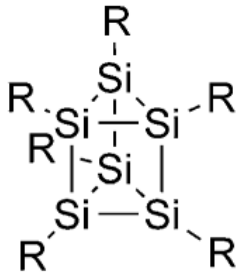
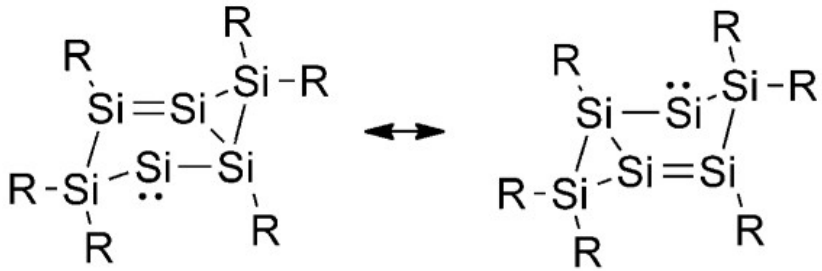
Uni-Bielefeld

2024

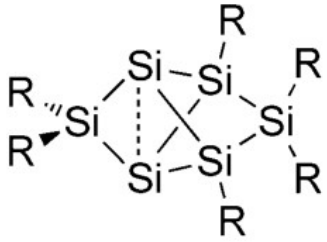
Stable isomers of Si_6R_6



R = Dip = 2,6-*i*$Pr_2C_6H_3$



R = Tip = 2,4,6-*i*$Pr_3C_6H_2$



R = Tip, GED in this work

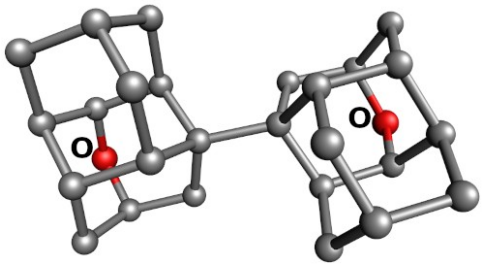
A. Sekiguchi, T. Yatabe, C. Kabuto, H. Sakurai, *J. Am. Chem. Soc.,* 115 (1993) 5853.

K. Abersfelder, A. J. P. White, H. S. Rzepa, D. Scheschkewitz, *Science*, 327 (2010) 564.

K. Abersfelder, A. J. P. White, R. J. F. Berger, H. S. Rzepa, D. Scheschkewitz, *Angew. Chem. Int. Ed.*, 50 (2011) 7936.

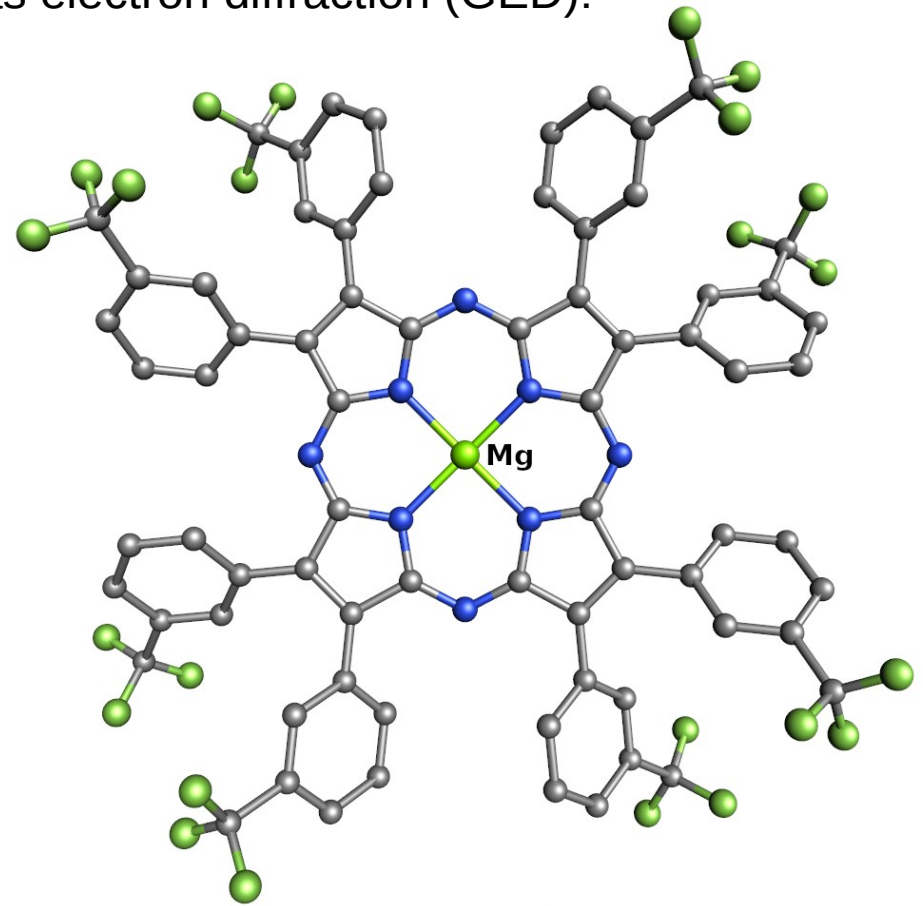
Largest experimental structures in the gas phase

By microwave spectroscopy:



[1]: 378 amu, r = 9.7 Å, C_2, DF = 91

By gas electron diffraction (GED):

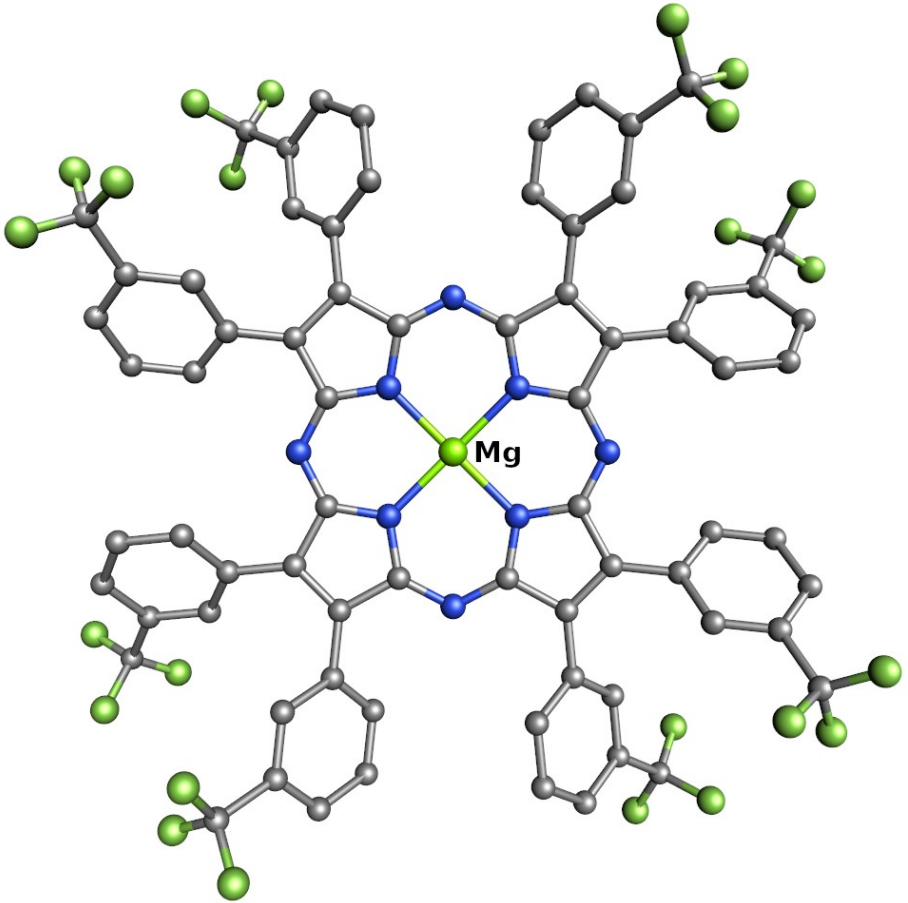


[2]: 1488 amu, r = 18.4 Å, D_4, DF = 50

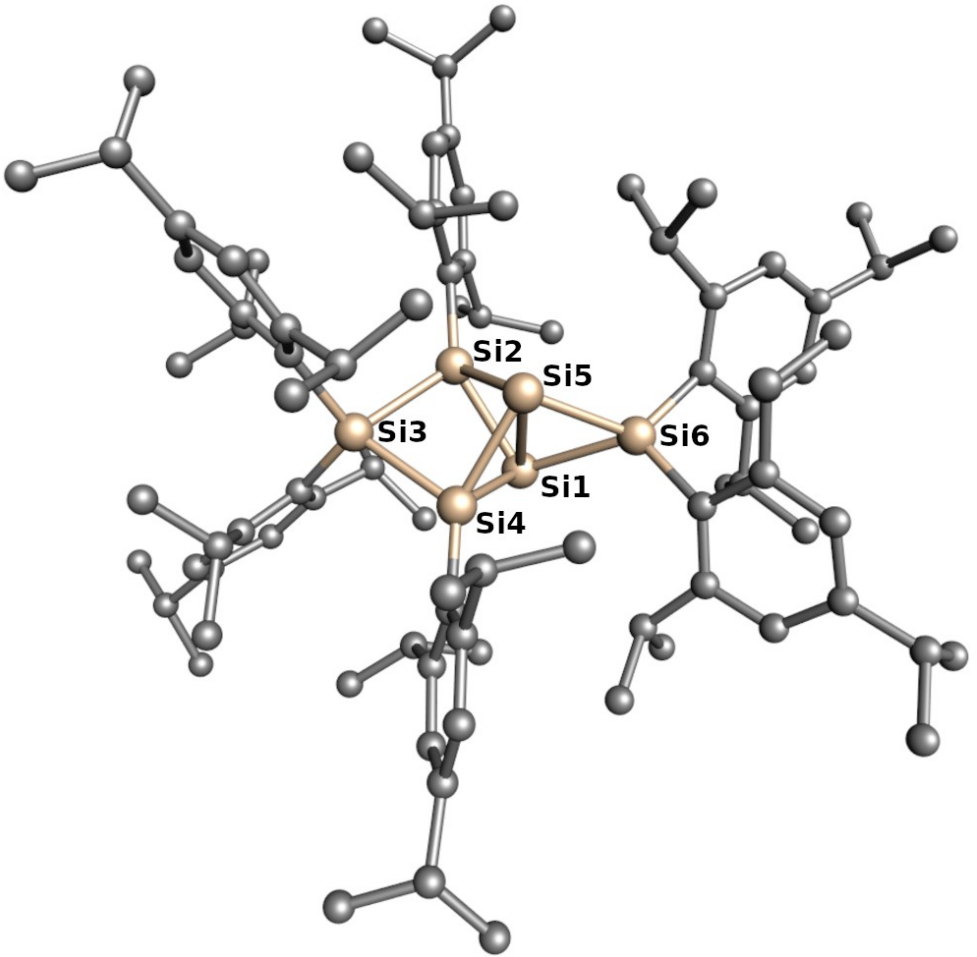
[1] A. Fokin et al., *JACS*, 139 (2017) 16696.

[2] Yu. Zhabanov et al., *J. Mol. Struct.*, 1092 (2015) 104.

Si_6Tip_6 is larger and more complicated



1488 amu, r = 18.4 Å, D_4, DF = 50

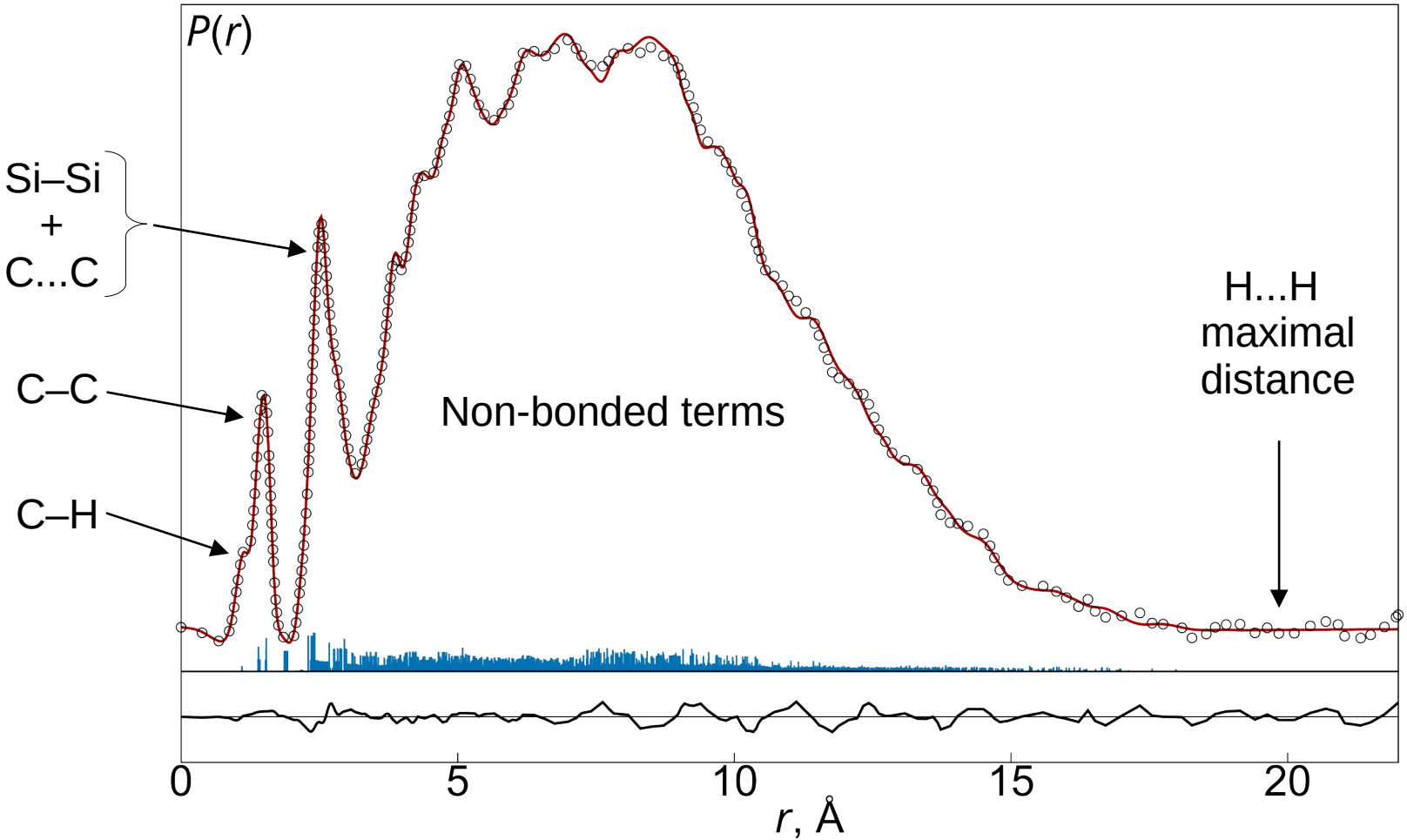


1388 amu, r = 19.9 Å, C_1, DF = 696

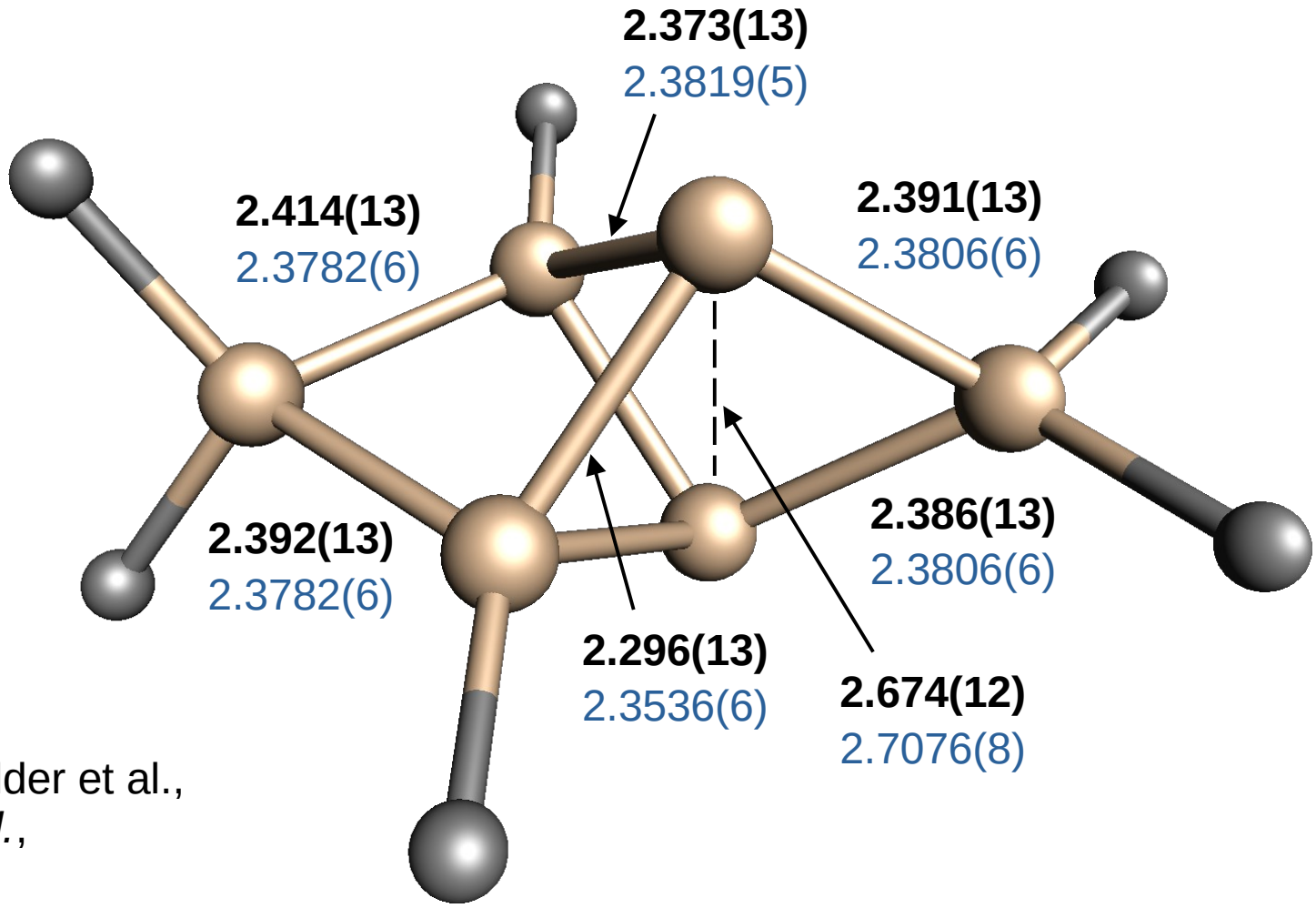
GED @ Uni-Bielefeld: Diffractometer + Mass-spectrometer

GED @ Uni-Bielefeld: Imaging plate scanner

Si_6Tip_6 GED radial distribution function



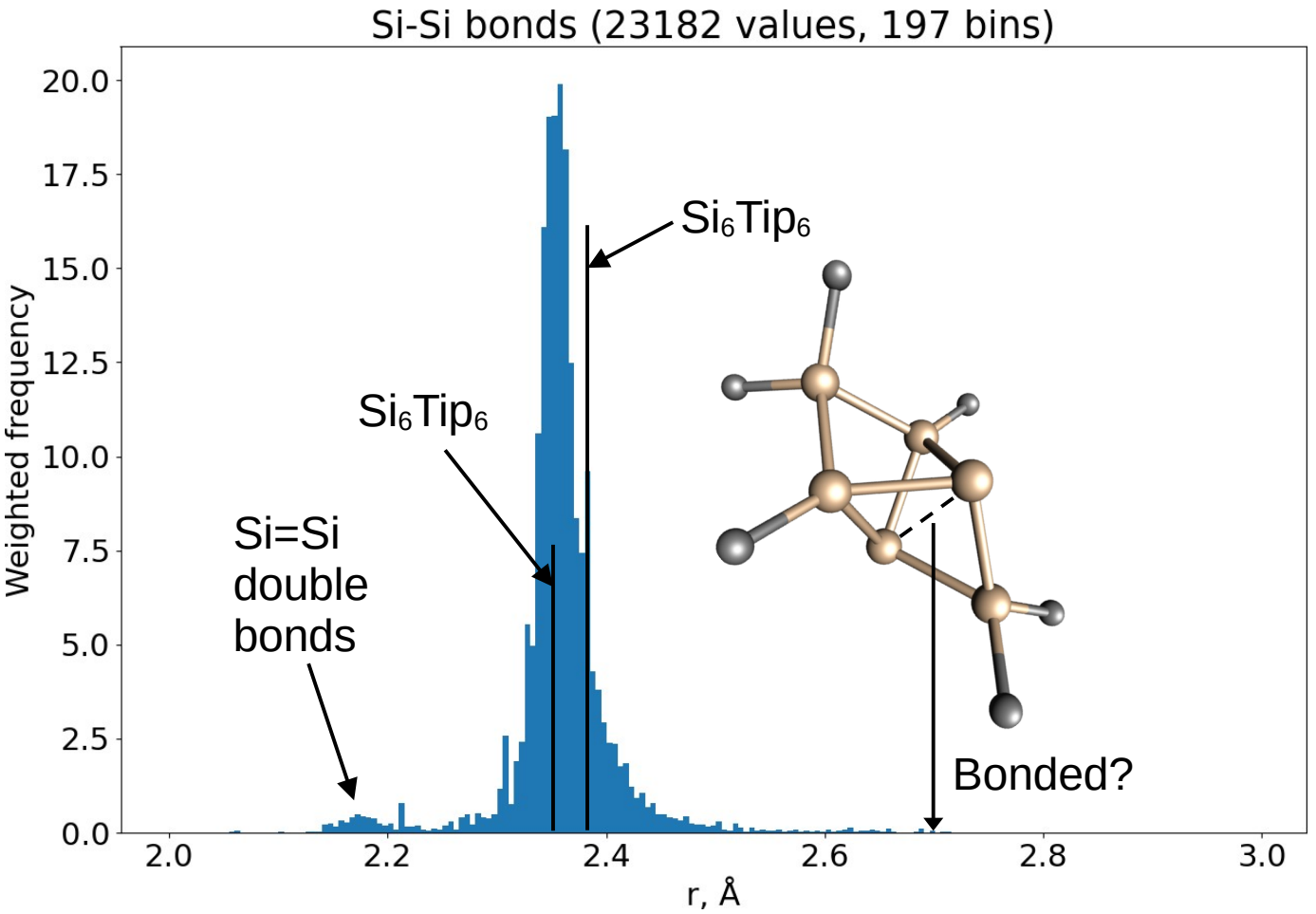
Si_6Tip_6: the structure of the Si_6 core



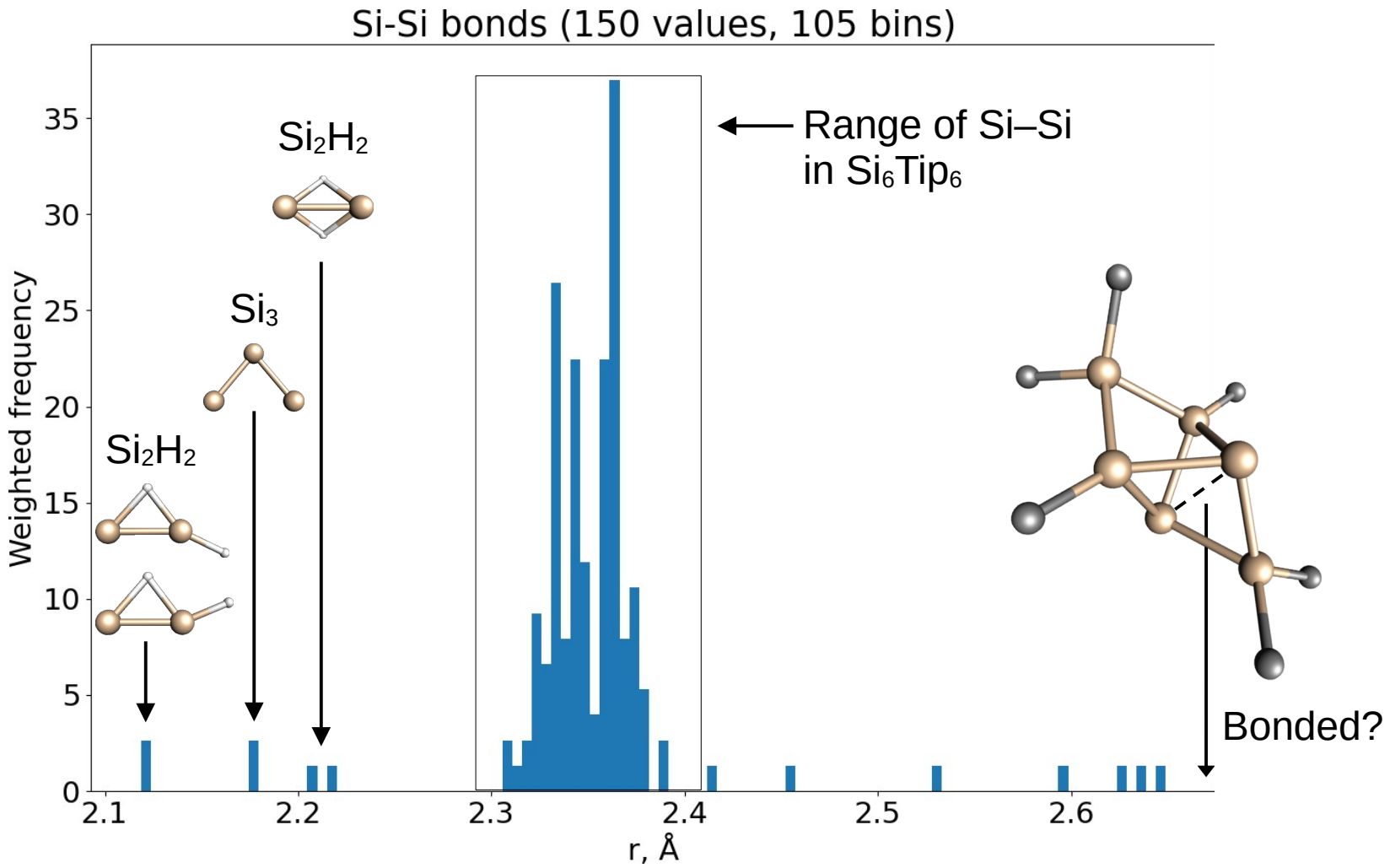
GED r_a [Å] this work.

XRD r_α [Å] K. Abersfelder et al., *Angew. Chem. Int. Ed.*, 50 (2011) 7936.

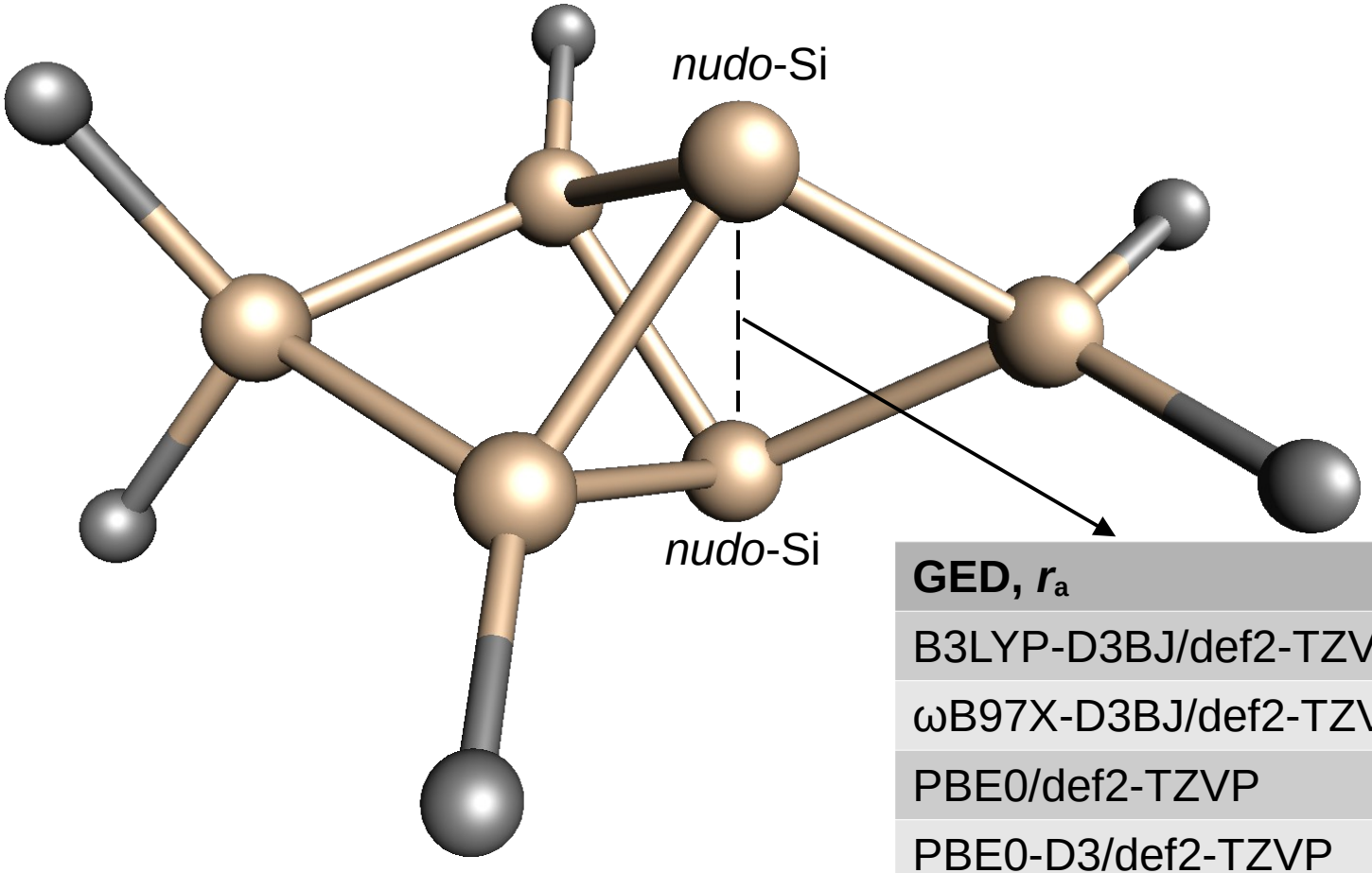
Si–Si bonds in crystals: CSD 2024



Si–Si bonds in the gas phase: MOGADOC 2024



Careful, theoretical structures!



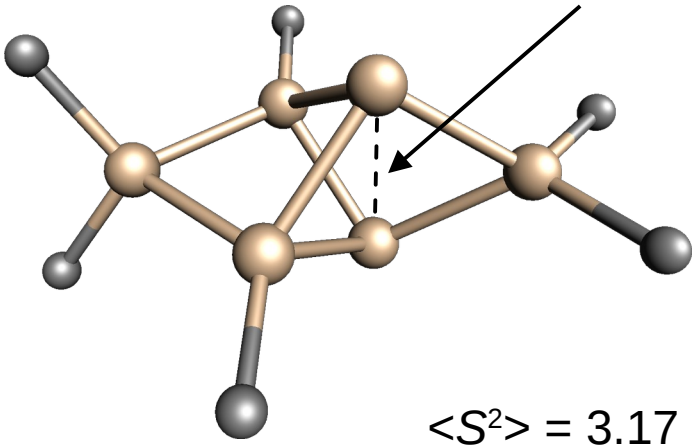
GED, r_a	**2.674(12)**
B3LYP-D3BJ/def2-TZVP	2.799
ωB97X-D3BJ/def2-TZVP	2.785
PBE0/def2-TZVP	2.595
PBE0-D3/def2-TZVP	2.626
PBE0-D3BJ/def2-TZVP	2.665

Electronic structure of Si_6Tip_6

(on the basis of the refined geometry)

Si_6Tip_6: electronic solutions

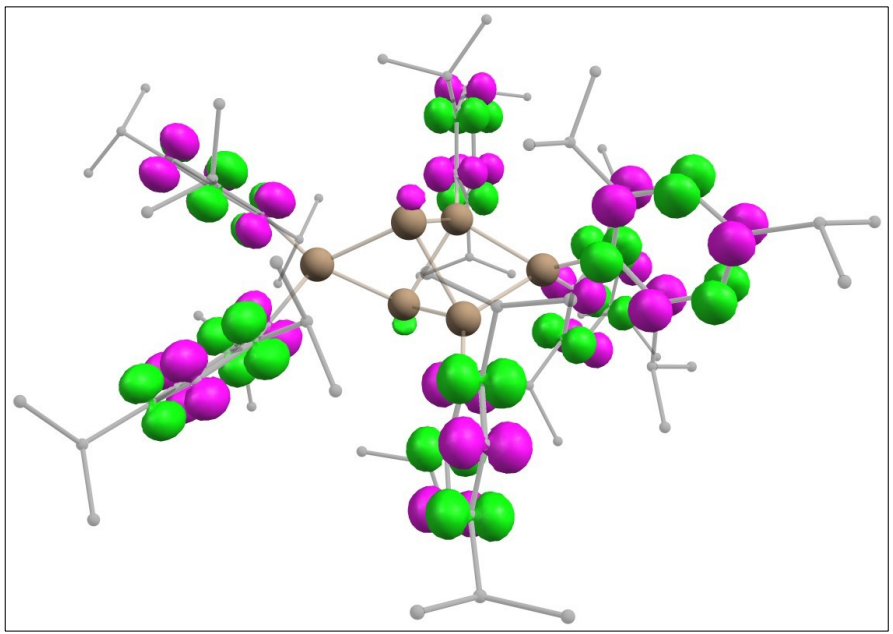
2.639 Å	1st RKS-Singlet, PBEh-3c
2.940 Å	1st UKS-Triplet, +45 kcal/mol, PBEh-3c



$\langle S^2 \rangle = 3.17$

Diradical character
$y = 1$ %

UHF/def2-TZVP broken-symmetry singlet,
spin density (0.02 a.u.):

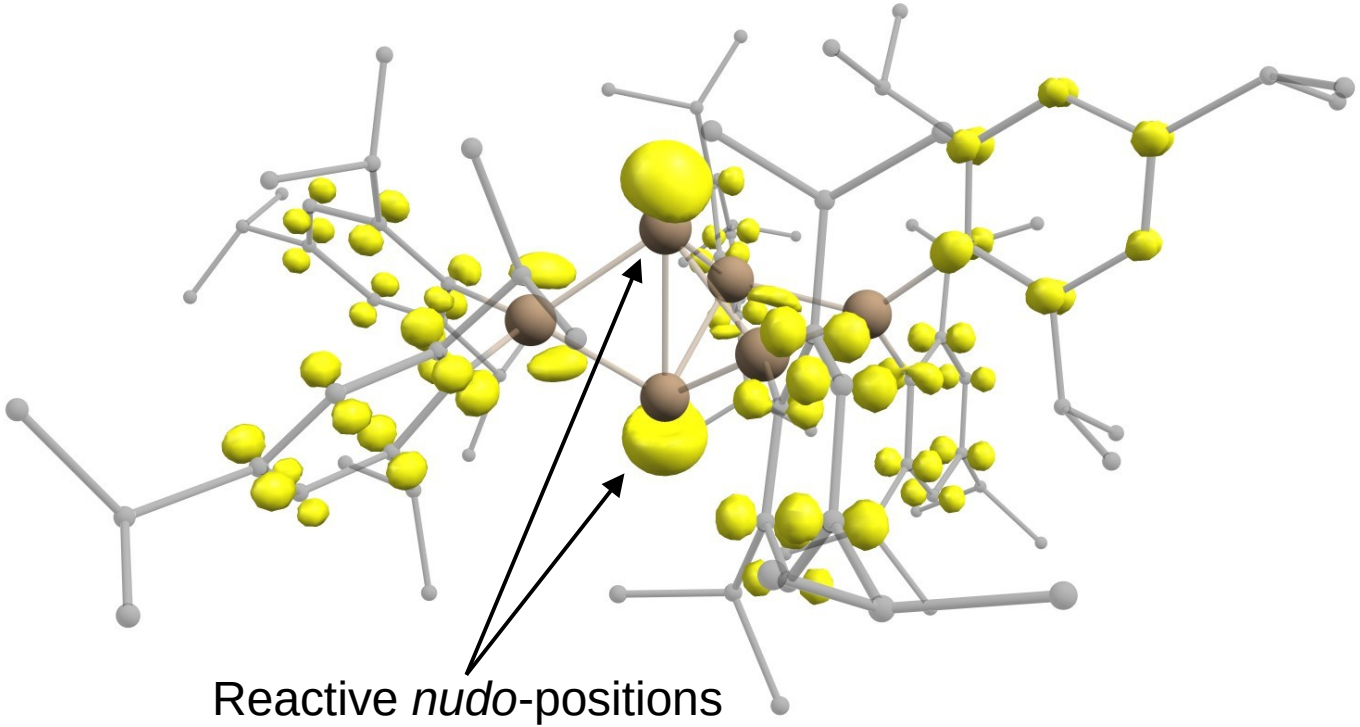


For comparison,
Thiele's HC: $y = 28$ %
Chichibabin's HC: $y = 53$ %

FOD: Fractional Occupation number weighted Density

FT-PBE0/def2-TZVP (T = 10000 K): N_{FOD} = 2.66

FOD distribution (0.003 a.u.): "hot" (strongly correlated and chemically active) electrons:

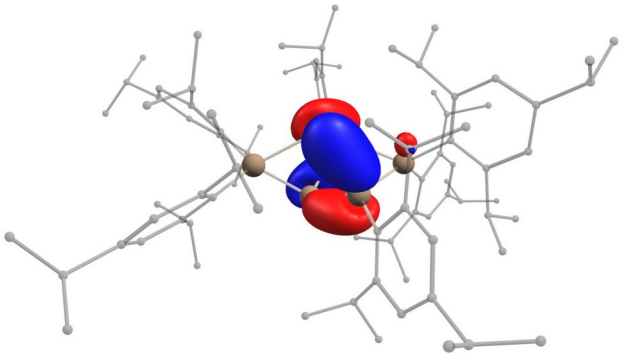


FOD method:
C. A. Bauer et al.,
Chem. Eur. J., 23 (2017) 6150.

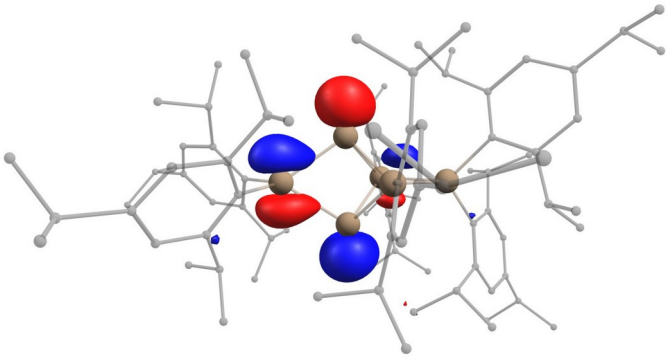
FMO: Frontier Molecular Orbitals

RKS-PBE0/def2-TZVP
canonical orbitals:

Problem with localization.

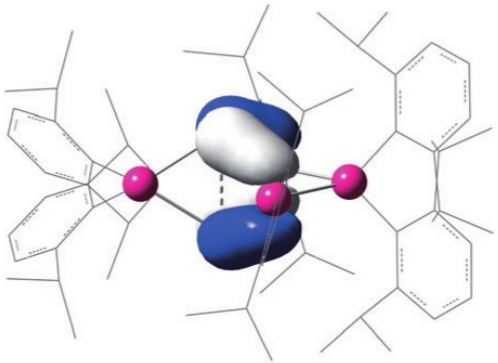


HOMO (-5.59 eV)

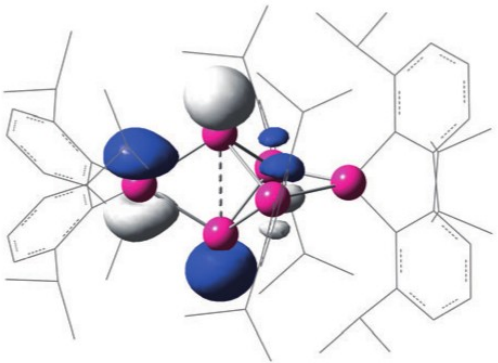


LUMO (-1.73 eV)

Similar to calculated earlier:
K. Abersfelder et al.,
Angew. Chem. Int. Ed.,
50 (2011) 7936.

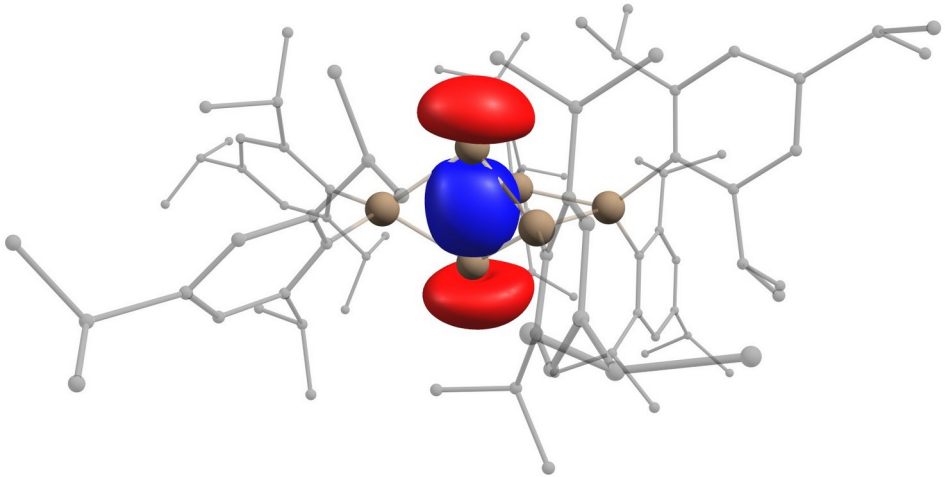


HOMO

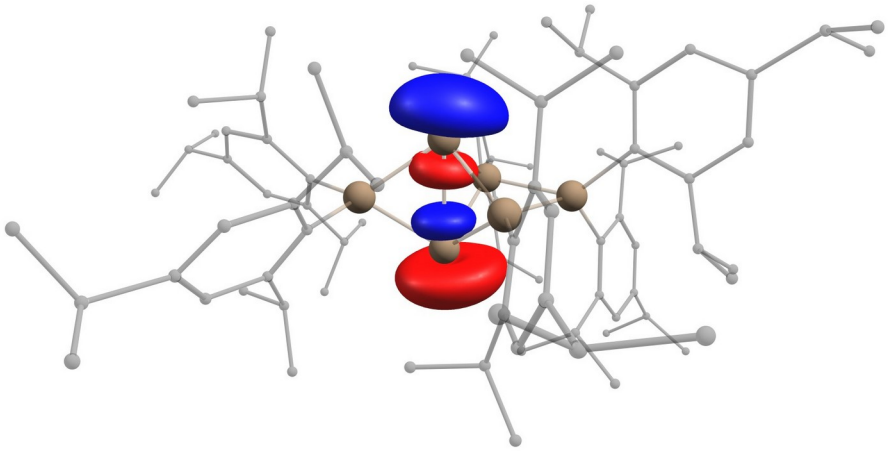


LUMO

NBO: Natural Bond Orbitals



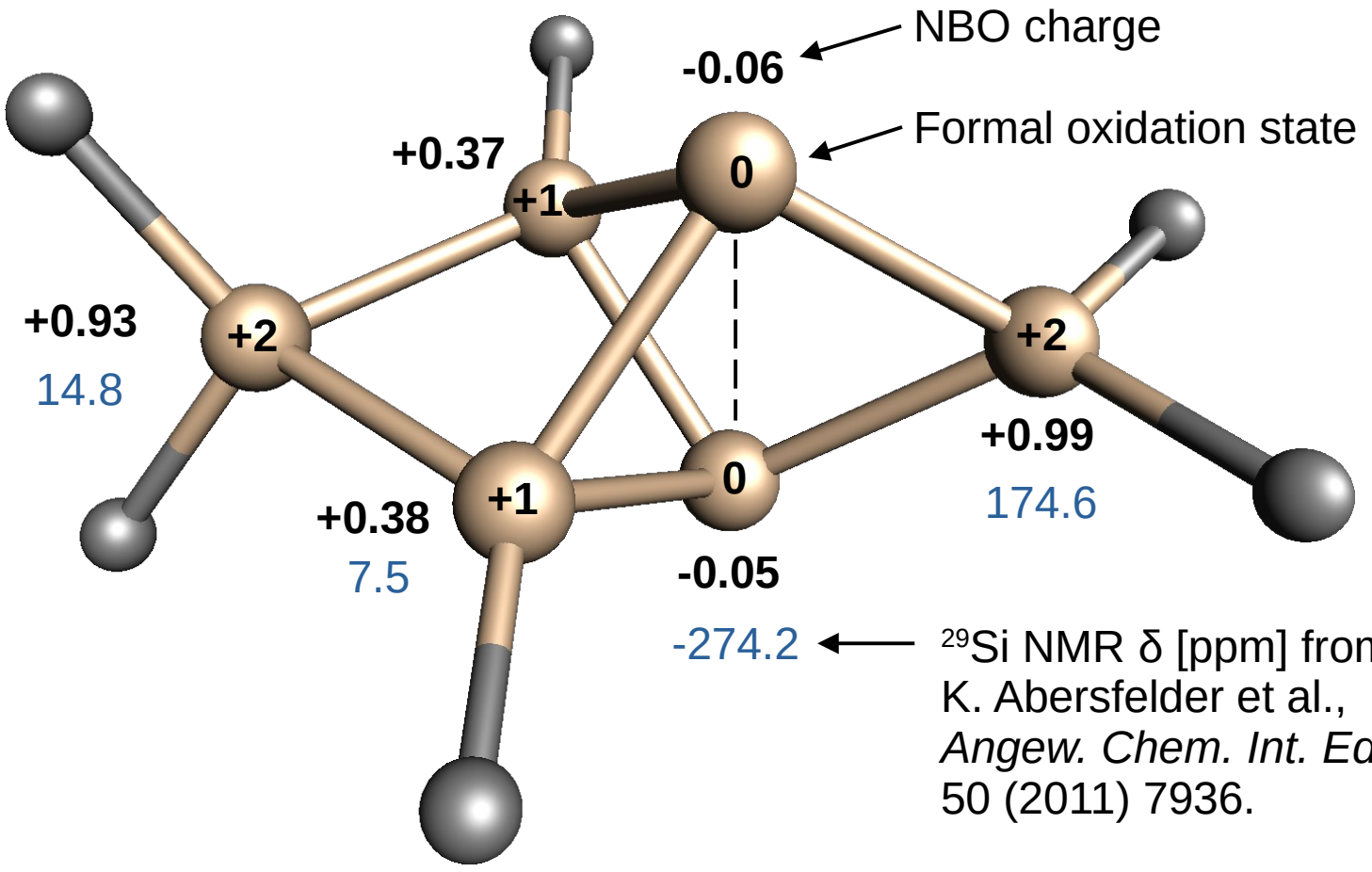
σ(Si1–Si5) [1.75 e]



σ*(Si1–Si5) [0.23 e]

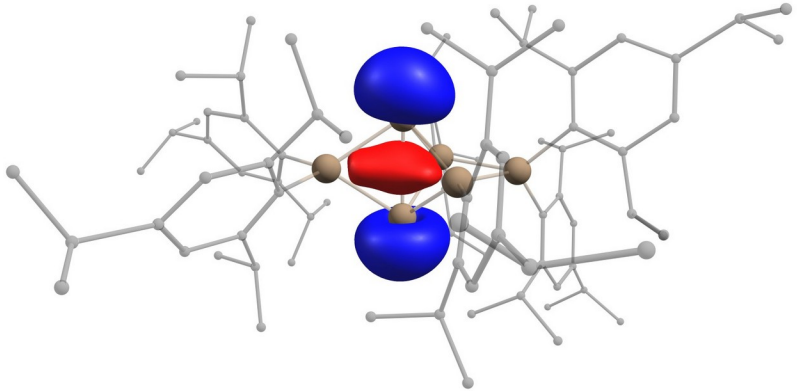
- *nudo*-Si are bonded: Si1–Si5
- Wiberg bond index for (Si1–Si5): 0.60
- Strong interactions σ(Si–Si) → σ*(Si1–Si5)

NBO: natural atomic charges

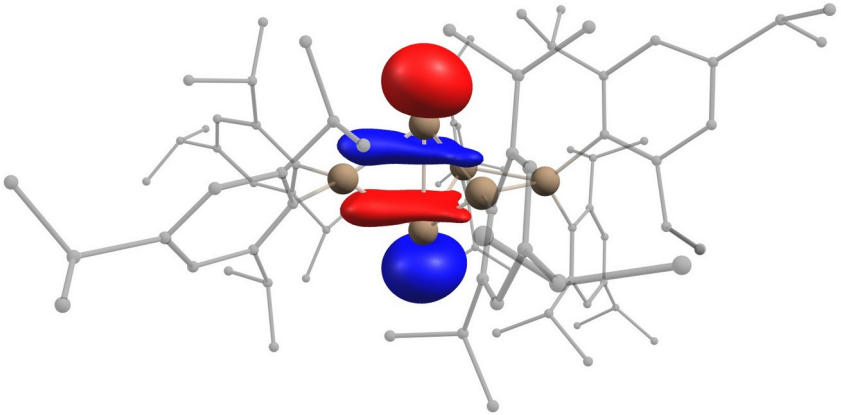


CASSCF: Complete Active Space SCF

SS-CASSCF(6,6)/def2-TZVP:



HOMO (1.89 e)



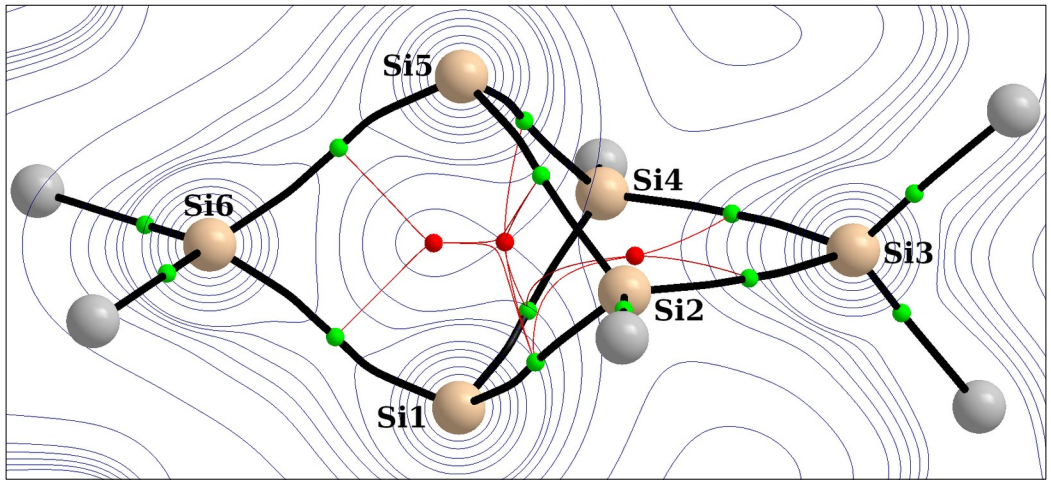
LUMO (0.12 e)

- Solution: 93% “222000”, 5% “220200”
- Löwdin bond order for Si1–Si5: 0.75
- Diradical character β = 11 %

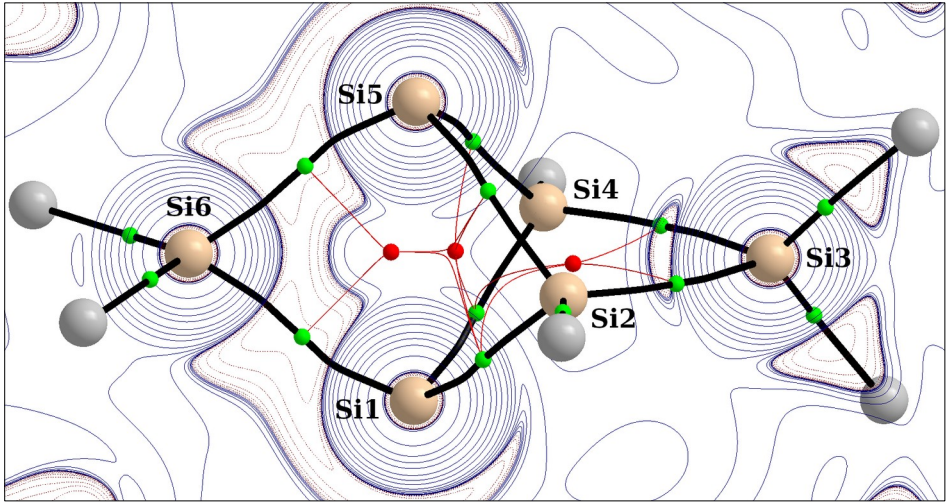
QTAIM: Quantum Theory of Atoms In Molecules

RKS-PBE0/def2-TZVP:

Electron density

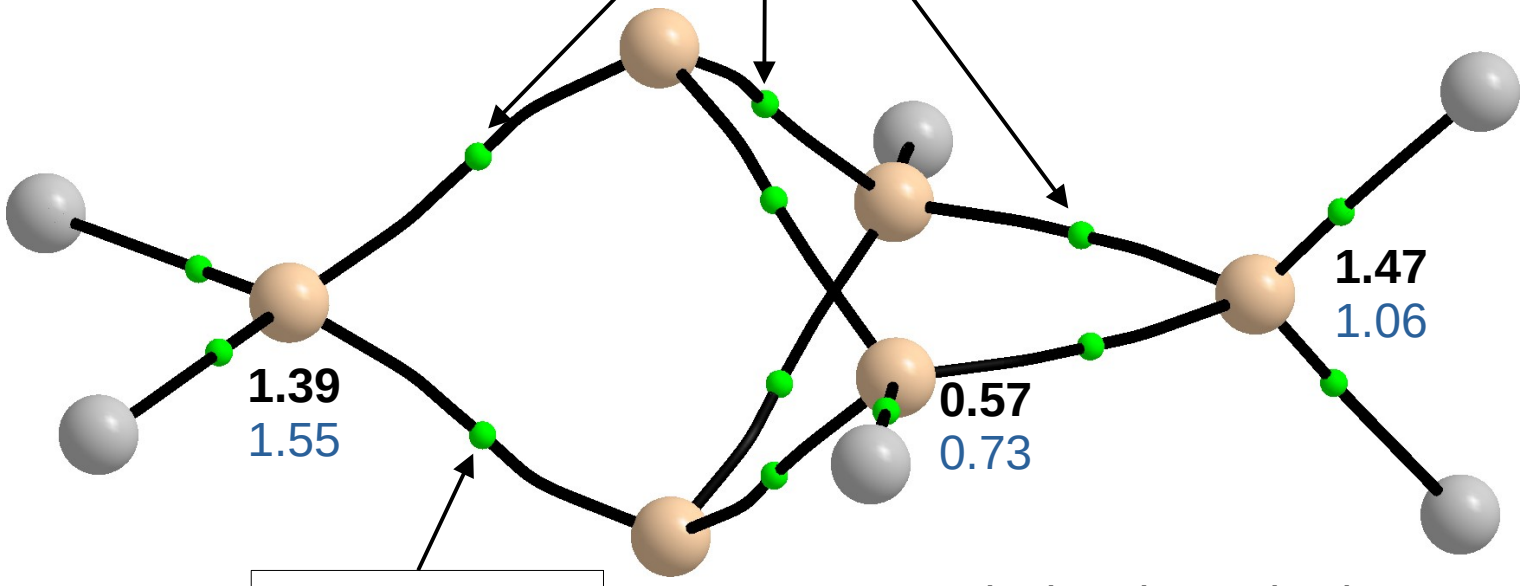


Laplacian of the electron density



- No bond critical point and bond path for Si1–Si5.
- “Bifurcation catastrophe”: BCP coalesce with RCP to produce a new degenerate RCP.
- No cage critical point! Three rings: (Si1–Si2–Si5–Si6), (Si1–Si2–Si5–Si4), (Si1–Si2–Si3–Si4).

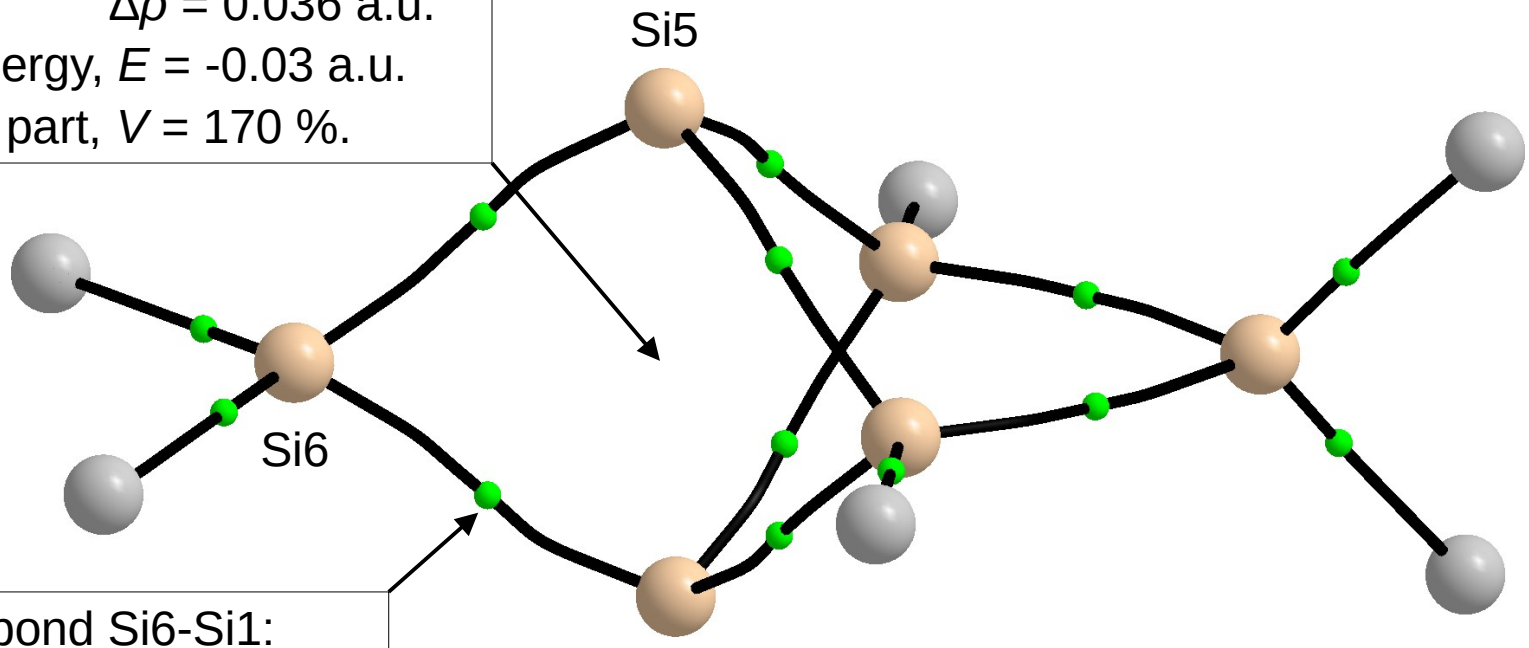
QTAIM theory vs. experiment



[1] D. Kratzert et al., *Angew. Chem. Int. Ed.*, 52 (2013) 4478.

QTAIM + IQA: Interacting Quantum Atoms

In the midpoint between the *nudo*-Si atoms:
Electron delocalization index, f = 0.46
Electron density, ρ = 0.048 a.u.
Laplacian of el. density, $\Delta\rho$ = 0.036 a.u.
IQA Si1-Si5 interaction energy, E = -0.03 a.u.
IQA exchange-correlation part, V = 170 %.



BCP for the definitive bond Si6-Si1:
f = 0.74, ρ = 0.077 a.u., $\Delta\rho$ = -0.09 a.u.,
E = -0.14 a.u., V = 119 %.

IQA result: Si1-Si5 is stabilizing with signatures typical for a weak covalent bond!

Conclusions

- Si_6Tip_6 is the largest and most complicated experimentally determined gas-phase structure.
- Molecules of the size and complexity as in Si_6Tip_6 can definitely be studied by GED.
- However, the accuracy and precision of refined parameters is lowered,
- and the importance of supplementary theoretical data increases significantly.

- Si_6Tip_6 is closed-shell singlet with low diradical character and low static electron correlation.
- Well defined Si–Si bonds are of typical length.
- The Si1–Si5 can be considered as a very weak single covalent bond.
- As such, it is now the longest Si–Si bond determined in the gas phase.