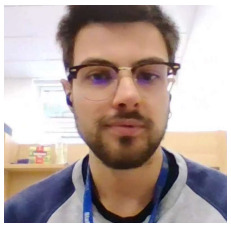
CCP-NC Discussion Meeting 11 May 2023

First-Principles Computation of pNMR Chemical Shifts

Zhipeng Ke, Edoardo Fusco, Daniel Dawson, Sharon Ashbrook
Michael Bühl
School of Chemistry and Centre of Magnetic Resonance,
University of St Andrews

History of Chemical-Shift Calculations

closed shell

1950 Theory (Ramsey)

1966 Coupled Hartree-Fock (Lipscomb)
1974 GIAO (Ditchfield)
1983 IGLO (Kutzelnigg)

} Hartree-Fock level

1990 SOLO (Bouman, Hansen)
1992 GIAO-MP2 (Gauss)
1996 GIAO-CCSD(T) (Gauss)

} including electron correlation

1994 SOS-DFPT-IGLO (Malkin)
1995/96 GIAO-DFT (Ziegler, Cheeseman, Pulay)

} DFT level

1999 ZORA-DFT (Ziegler)

} relativistic level

2001 GIPAW-DFT (Mauri)

} periodic systems

2003/04 paramagnetic NMR, $S = ½$ (Vaara, Patchkovskii)
2007/08 paramagnetic NMR, any S (Kaupp, Vaara)

Theory of pNMR chemical shifts

Milestone papers:

Z. Rinkevicius, J. Vaara, L. Telyatnyk, O. Vahtras, *J. Chem. Phys*. **2003**, *118*, 2550.

S. Moon, S. Patchkovskii, in: *Calculation of NMR and EPR Parameters. Theory and Applications,* M. Kaupp, M. Bühl, V. G. Malkin (Eds.), Wiley-VCH, Weinheim, **2004**, pp. 325-340.

P. Hrobarik, R. Reviakine, A. V. Arbuznikov, O. L. Malkina, V. G. Malkin, F. Koehler, M. Kaupp. *J. Chem. Phys.* **2007**, *126*, 024107.

T. O. Pennannen, J. Vaara*, Phys. Rev. Lett*. **2008**, *100*, 133002

S. A. Rouf, J. Mareš, J. Vaara, *J. Chem. Theory Comput*. **2015**, *11*, 1683.

B. Martin, J. Autschbach, *Phys. Chem. Chem. Phys*. **2016**, *18*, 21051.

G. Mali, M. Mazaj, *J. Phys. Chem. C* **2021**, *125*, 4655.

Theory of pNMR chemical shifts

isotropic magnetic shielding of a nucleus N in a molecule with arbitrary spin multiplicity:

$$\sigma_{iso} = \underbrace{\sigma_{iso(orb)}}_{\text{orbital shielding part}} - \underbrace{S(S+1)\beta_e/(3kTg_N\beta_N)[g_e \cdot A_{FC} + g_e \cdot A_{PC} + \Delta g_{iso} \cdot A_{FC} + {}^1/_3\,\mathrm{Tr}(\Delta g_{aniso} \cdot A_{dip})]}_{\text{paramagnetic part}}$$

S: total spin
T: temperature
β_e,β_N: Bohr and nuclear magnetons
g_e,g_N: free-electron and nuclear g-values
Δg_{iso}, Δg_{aniso}: g-tensor elements ($g = g_e + \mathbf{1}\cdot \Delta g_{iso} + \Delta g_{aniso}$)
A_{FC},A_{PC},A_{dip}: hyperfine coupling tensor elements

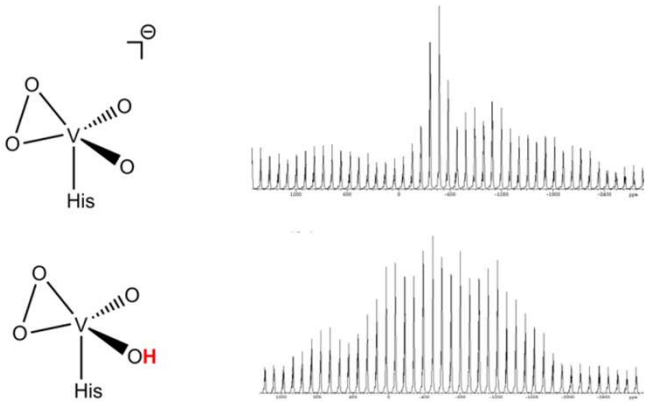
^{13}C and ^{1}H chemical shifts: $\delta_{iso} = \sigma_{iso(orb)}\,(TMS) - \sigma_{iso}$

P. Hrobarik, R. Reviakine, A. V. Arbuznikov, O. L. Malkina, V. G. Malkin, F. Koehler, M. Kaupp. *J. Chem. Phys.* **2007**, *126*, 024107.

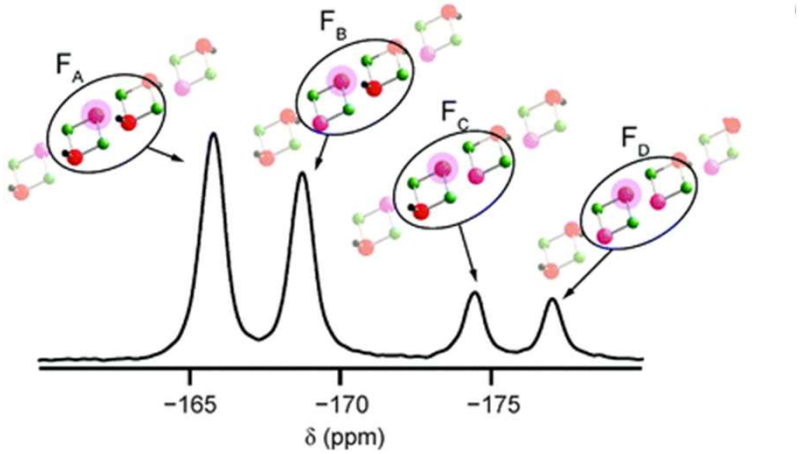
Application of NMR chemical shift computation

- support for signal assignment
- information on (local) structure

well established for diamagnetic molecules and materials



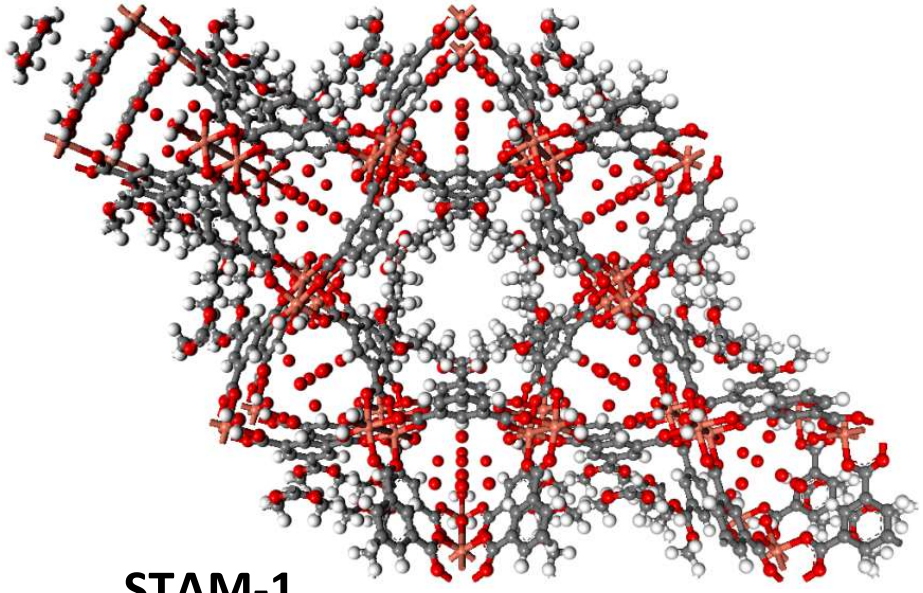
M. Bühl, T. van Mourik, *Wiley Interdisc. Reviews: Comp. Mol. Sci.* **2011**, *1*, 634.



S. E. Ashbrook, D. McKay, *Chem. Commun.* **2016**, *52*, 7186

Metal Organic Frameworks (MOFs)

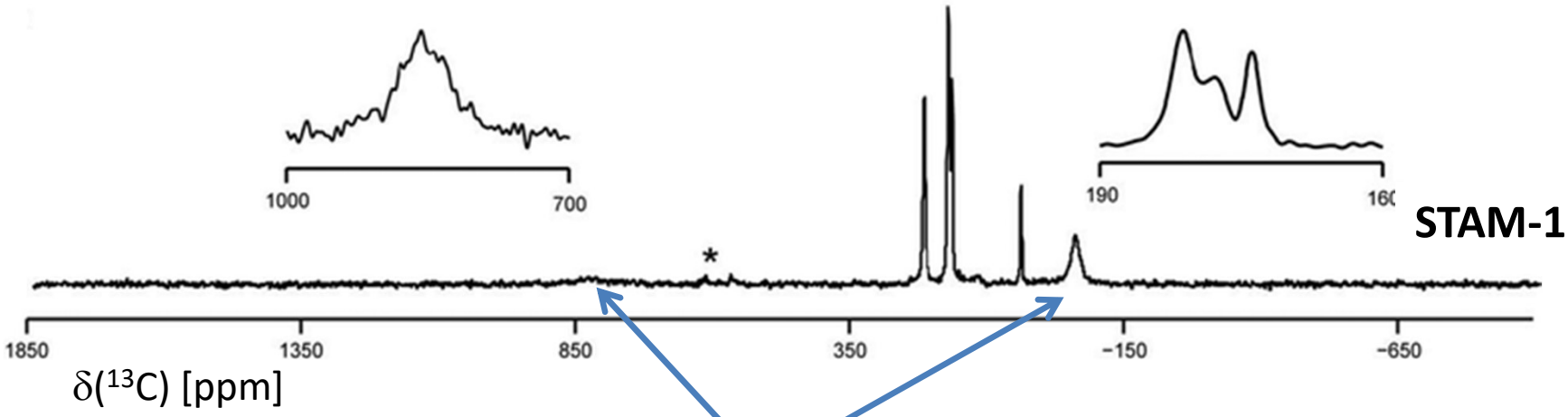
-Gas storage and separation
-Catalysis
-Carrier in medical drug delivery



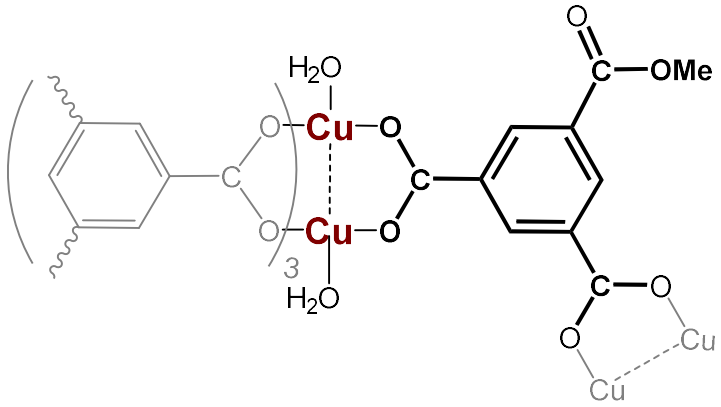
STAM-1

M. I. H. Mohideen, B. Xiao, P. S. Wheatley, A. C. McKinlay, Y. Li, A. M. Z. Slawin, D. W. Aldous, N. F. Cessford, T. Düren, X. Zhao, R. Gill, K. M. Thomas, J. M. Griffin, S. E. Ashbrook , R. E. Morris, *Nat. Chem.* **2011**, *3*, 304.

Solid-state NMR of MOFs



huge paramagnetic shifts due to **Cu(II)** centres



signals assigned through ^{13}C labelling studies

D. M. Dawson, L. E. Jamieson, M. I. H. Mohideen, A. C. McKinlay, I. A. Smellie, R. Cadou, N. S. Keddie, R. E. Morris, S. E. Ashbrook *Phys. Chem. Chem. Phys.* **2013**, *15*, 919.

Methodology

- Density Functional Theory (DFT)
- Optimisation:
  PBE0-D3; basis set: 6-31G*/6-31G**(H^{br})/AE1(Cu) (8s7p4d)
- Orbital shielding, g- and A-tensors:
  PBE, PBE0, PBE0-1/3; basis set: IGLO-II(or III)/AE1(Cu) (9s7p4d)

opt, $\sigma_{iso(orb)}$: Gaussian 09

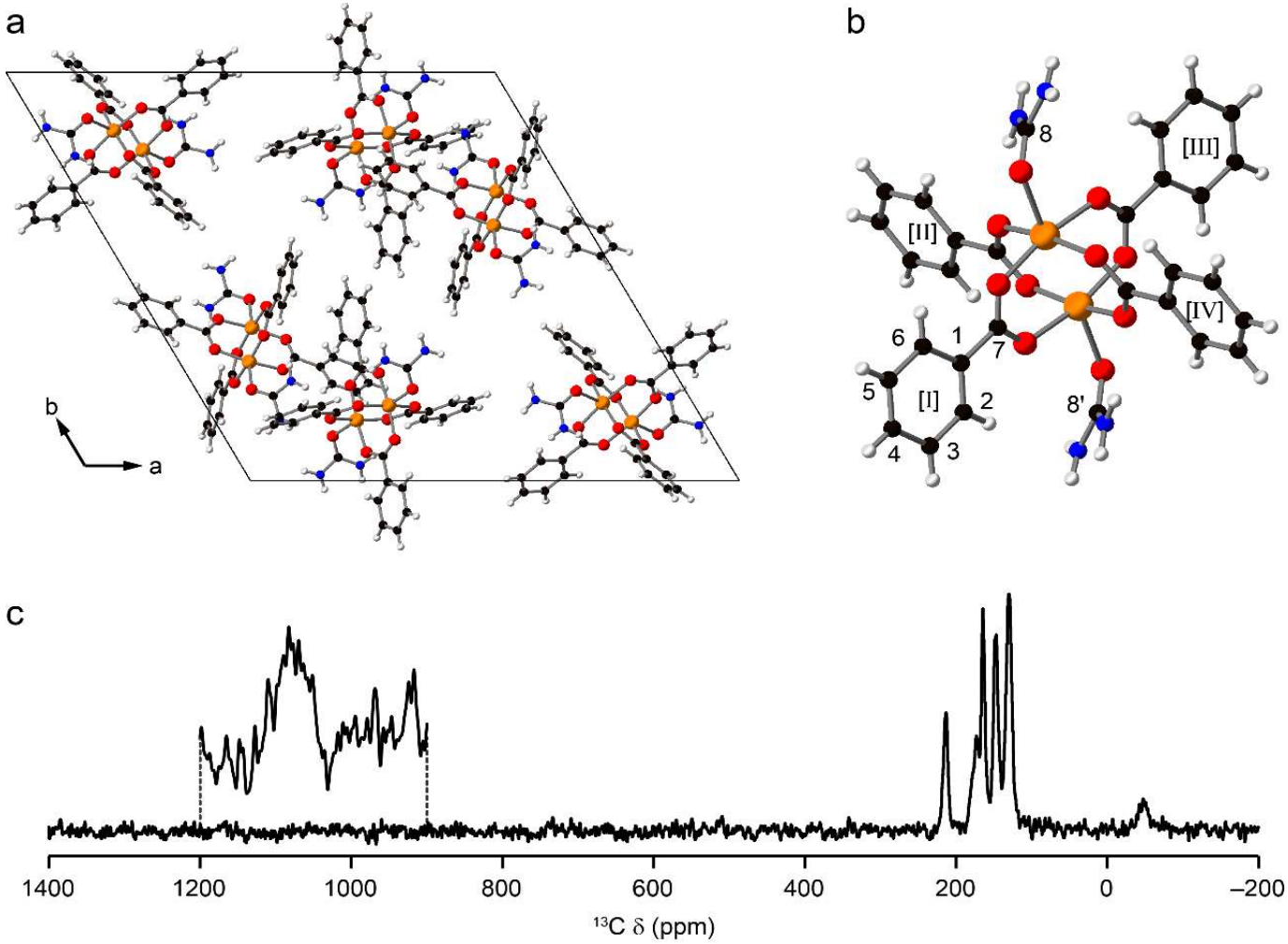
g, A tensors: ORCA

Validated for mononuclear Cu species (phenolic oximes)

M. Bühl, S. E. Ashbrook, D. M. Dawson, R. A. Doyle, P. Hrobarik, M. Kaupp,I. A. Smellie, *Chem. Eur. J.* **2016**, *22*, 15328.
S. E. Ashbrook, G. P. M. Bignami, M. Bühl, D. B. Cordes, D. M. Dawson, R. A. Doyle, Z. Ke, F. M. Mack, A. M. Z. Slawin, I. A. Smellie, *Chem. Commun*. **2017**, *53*, 10512

Molecular model for MOFs

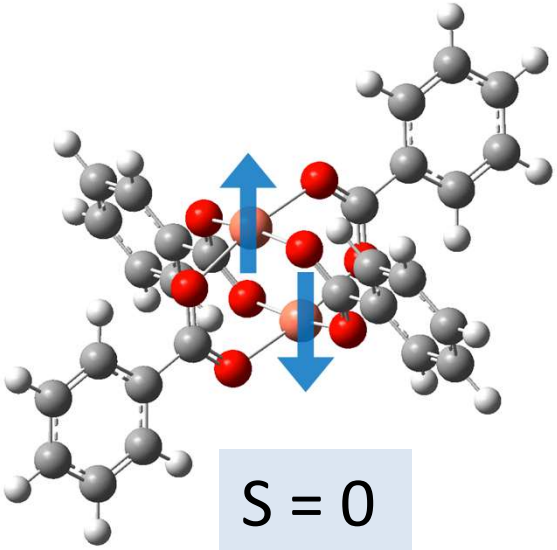
Cu(II) benzoate, isolated paddle-wheel dimers



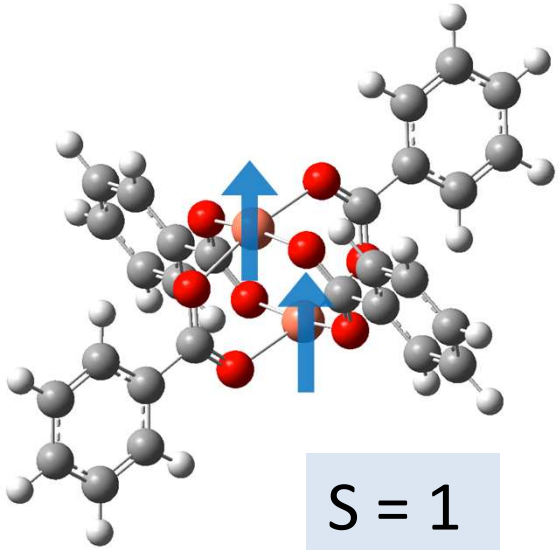
Z. Ke, L. E. Jamieson, D. M. Dawson, S. E. Ashbrook, M. Bühl, *Sol. State Nucl. Magn. Res*. **2019**, *101*, 31.

Molecular model for MOFs

Problem: singlet ground state (no pNMR shifts expected)



S = 0



S = 1

ΔE_{ST} = 134.6 cm^{-1}

(PBE0-⅓/IGLO-II//PBE0-D3/AE1)

Z. Ke, L. E. Jamieson, D. M. Dawson, S. E. Ashbrook, M. Bühl, *Sol. State Nucl. Magn. Res*. **2019**, *101*, 31.

Molecular model for MOFs

Working hypothesis: pNMR shifts arise from thermal population of triplet state

➡ Boltzmann averaging:

$$x_i = N_i/N_{total} = g_i \exp(-\Delta E_i/RT)/\sum_i g_i \exp(-\Delta E_i/RT)$$

$$\delta_{total} = \sum x_i \, \delta_{iso(i)}$$

i = 1(singlet): $\Delta E_1 = 0$, $g_1 = 1$

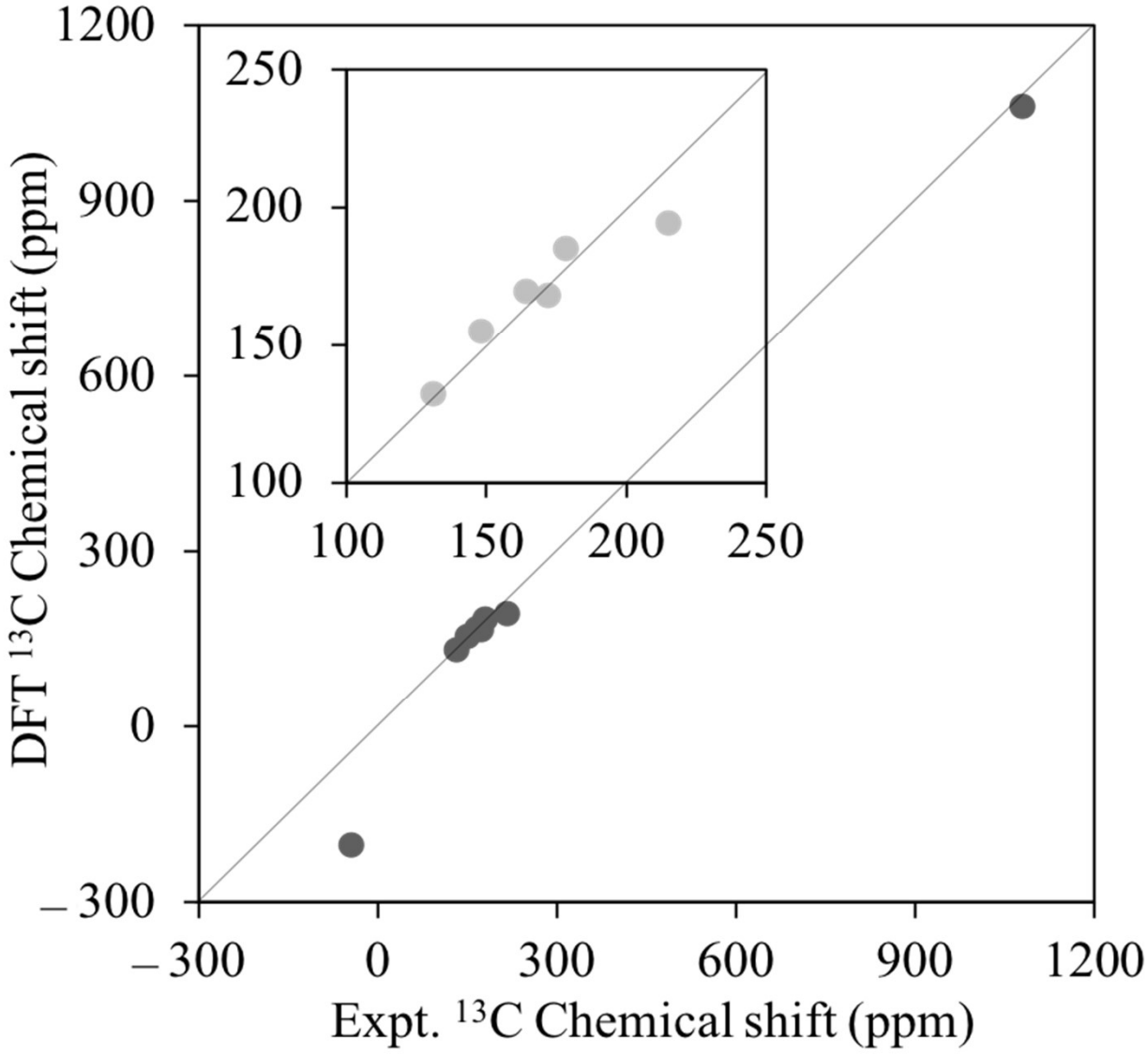
i = 2(triplet): $\Delta E_2 = \Delta E_{ST}$, $g_2 = 3$

σ_{orb} calculated using broken-symmetry Kohn-Sham DFT

Z. Ke, L. E. Jamieson, D. M. Dawson, S. E. Ashbrook, M. Bühl, *Sol. State Nucl. Magn. Res*. **2019**, *101*, 31.

PBE0-$^1/_3$
/IGLO-II

Performance of the model

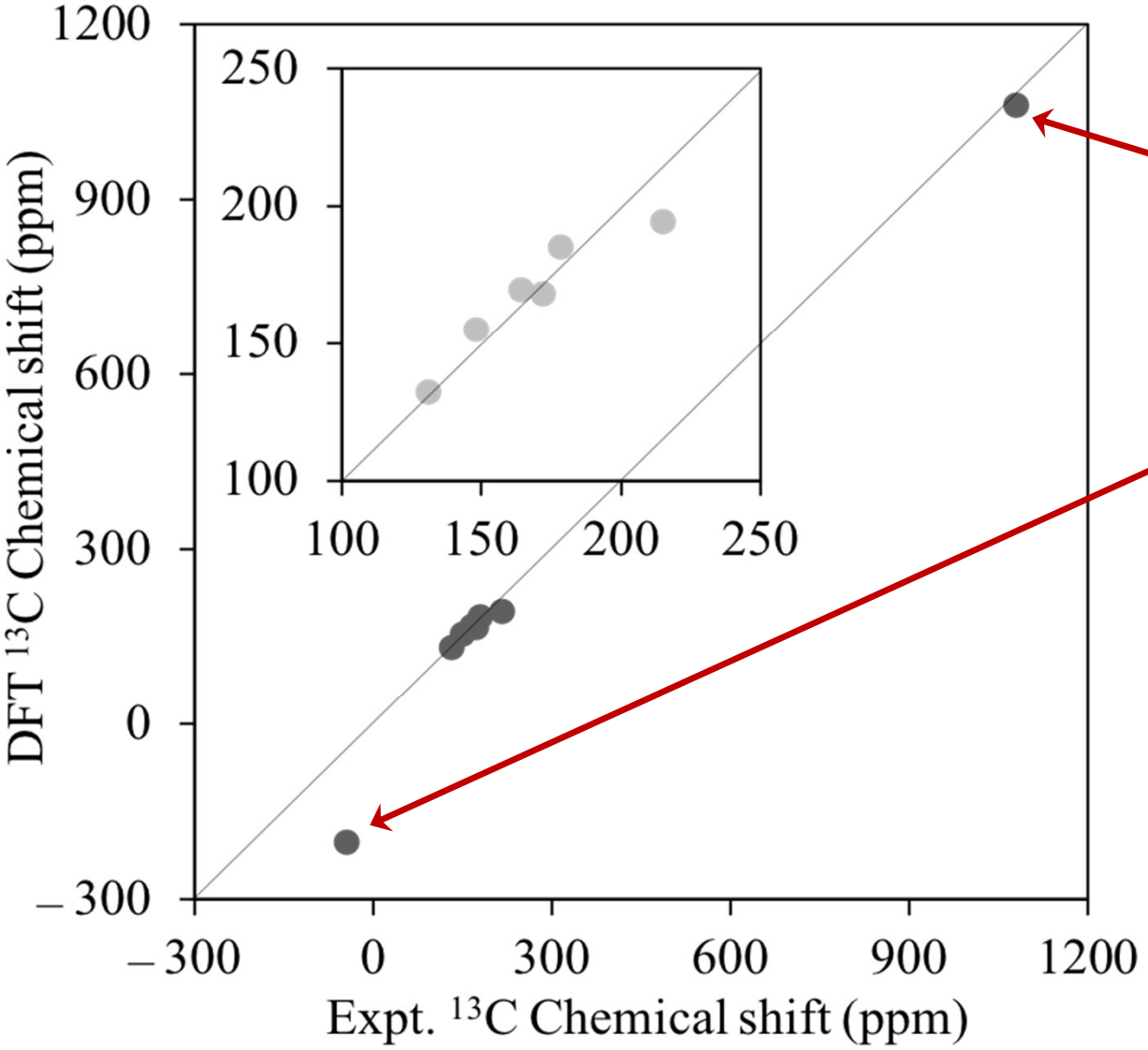


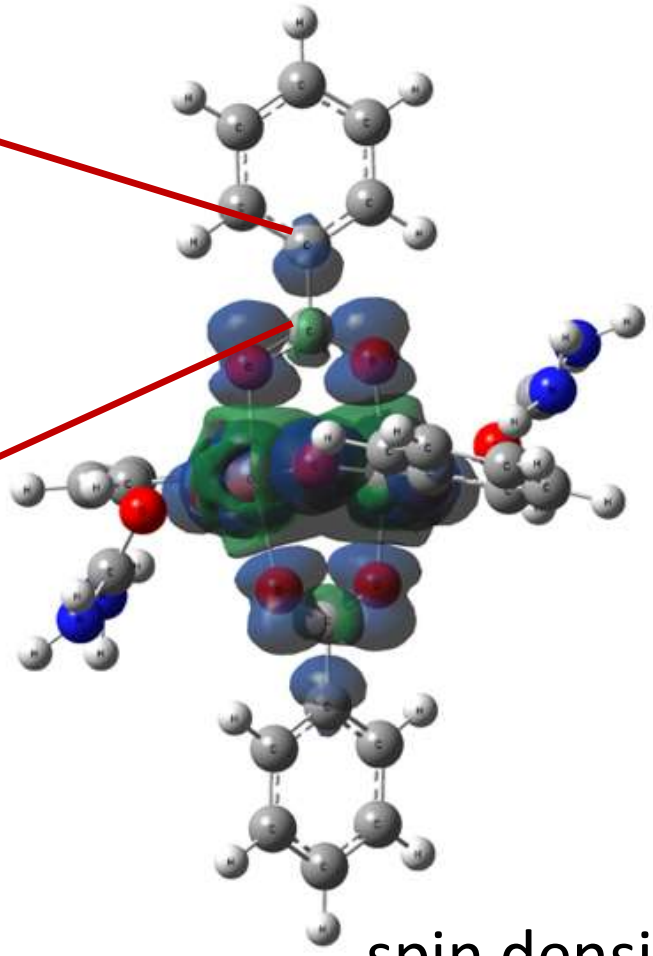
Z. Ke, L. E. Jamieson, D. M. Dawson, S. E. Ashbrook, M. Bühl, *Sol. State Nucl. Magn. Res*. **2019**, *101*, 31.

PBE0-1/3 /IGLO-II

Performance of the model

assignment

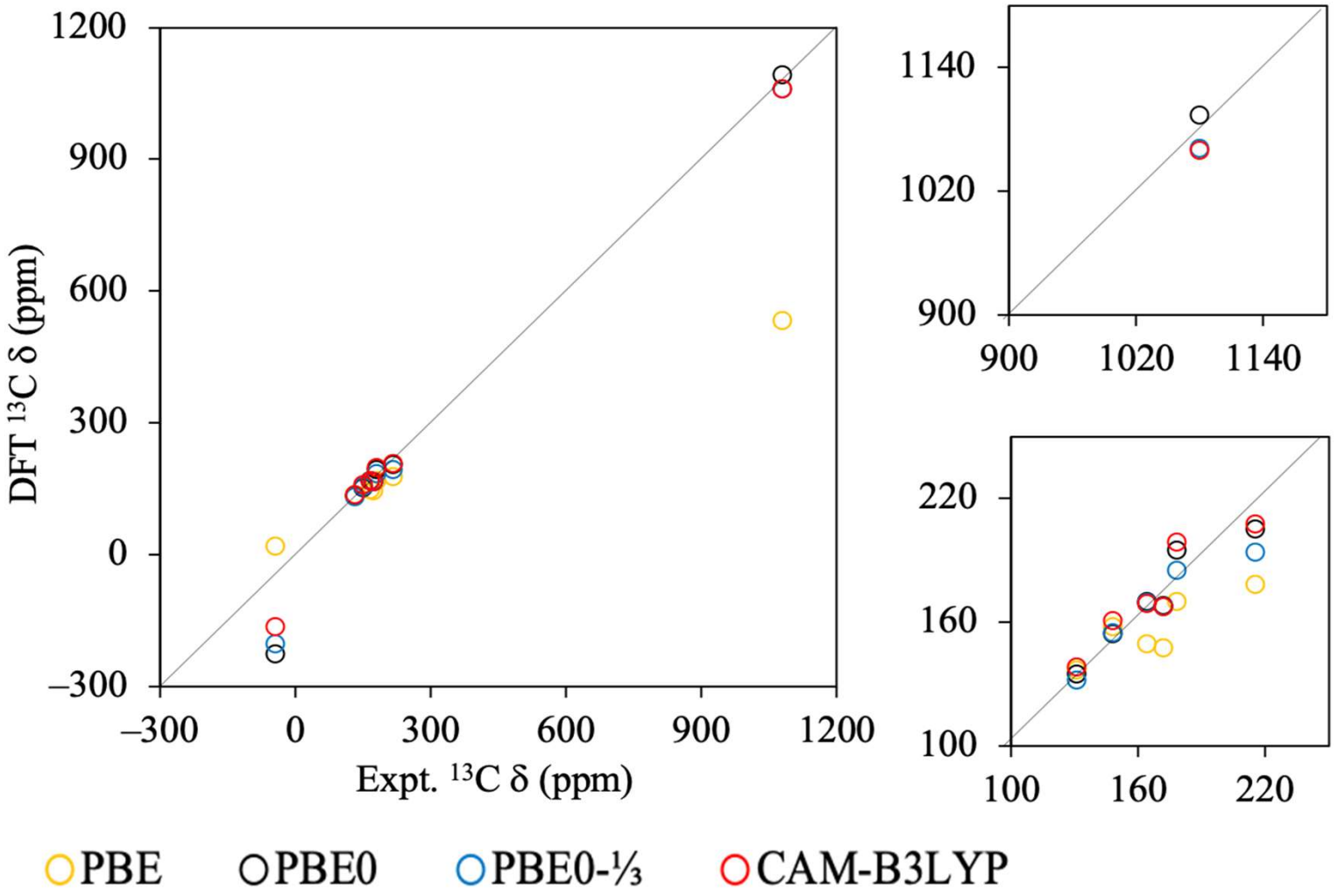




spin density
(PBE0-⅓/IGLO-II)

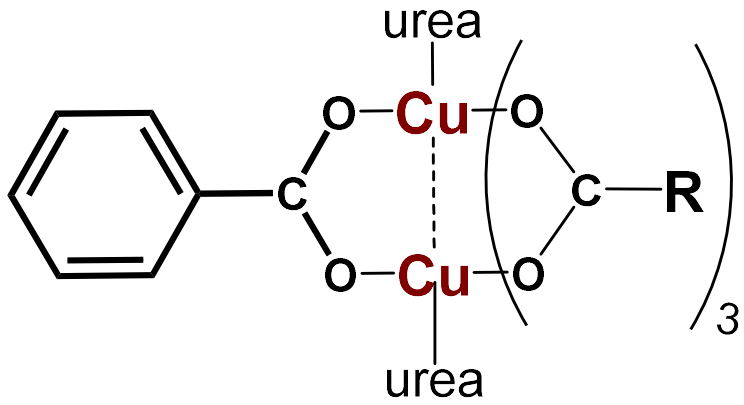
Z. Ke, L. E. Jamieson, D. M. Dawson, S. E. Ashbrook, M. Bühl, *Sol. State Nucl. Magn. Res*. **2019**, *101*, 31.

Effect of DFT functional



CAM-B3LYP slightly superior

Effect of structure



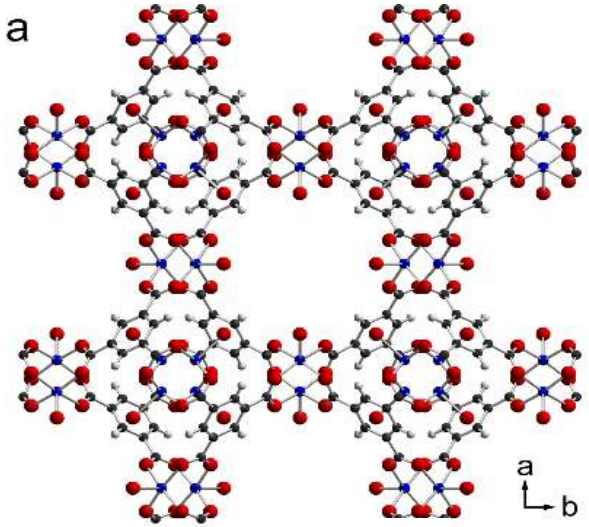
Level of pNMR calculations: CAM-B3LYP/IGLO-II

Level of opt	Substituents	MAD
PBE0-D3	R = Ph	23.0
GFN2-xTB[a,b]	R = Ph	22.6
GFN2-xTB[a,b]	R = Me	21.7

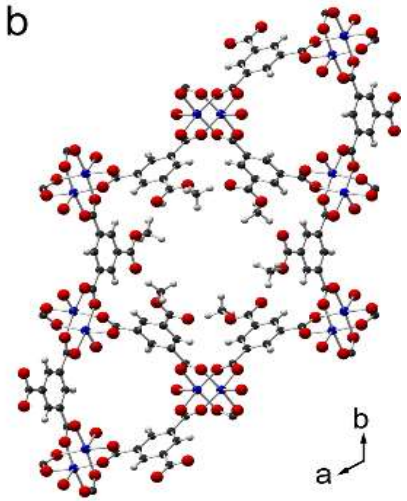
significant computational savings

[a]C. Bannwarth, S.Ehlert, S.; Grimme, *J. Chem. Theory Comput.* **2019**, *15*, 1652.
[b]High-spin structure also used for BS singlet.

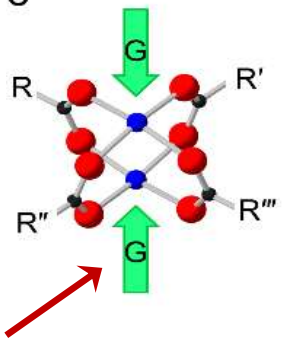
Multinuclear MOF models



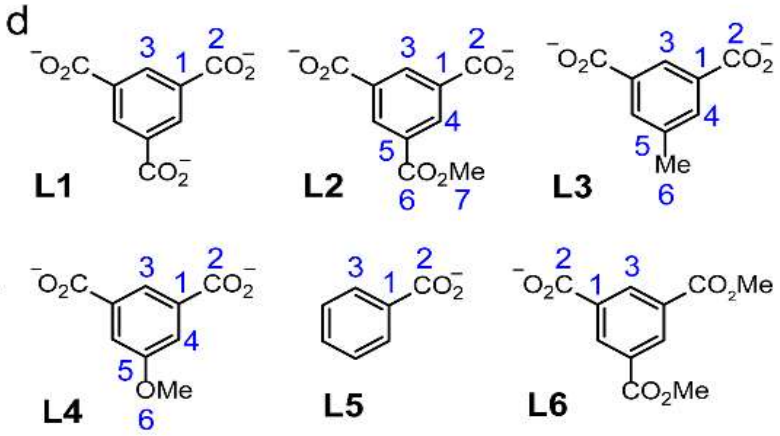
HKUST

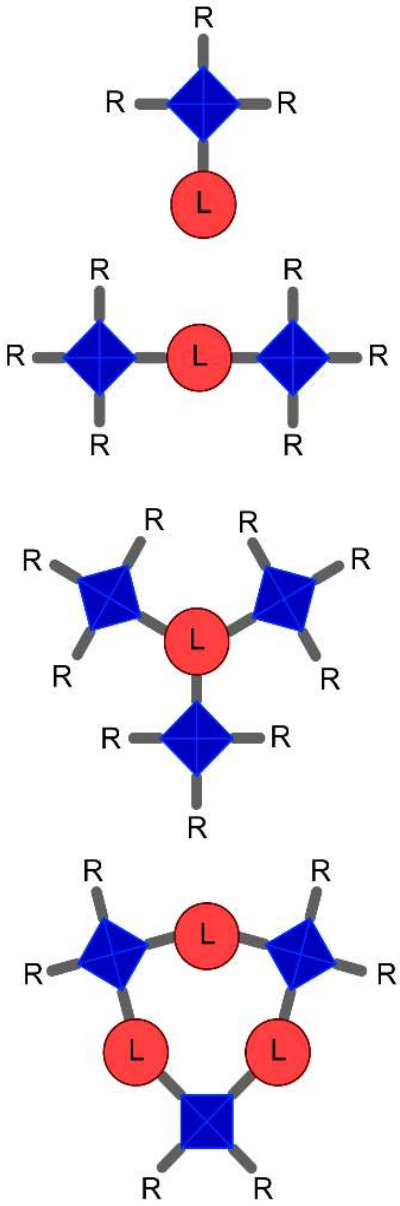


STAM-1



G = H_2O or none

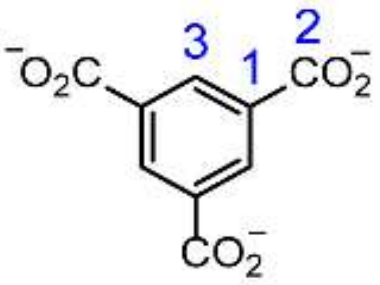




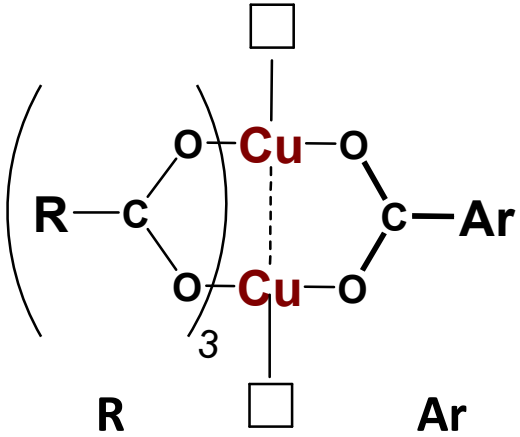
Z. Ke, D. M. Dawson, S. E. Ashbrook, M. Bühl, *Chem. Sci*. **2022**, *13*, 2674.

Single dimer model for activated HKUST

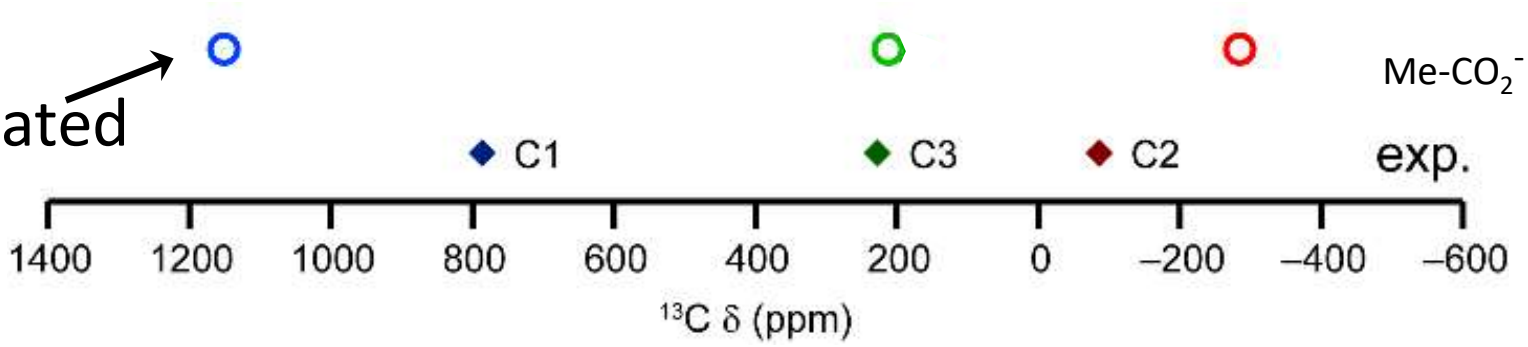
exptl. linker:



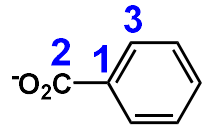
mononuclear models:



o: as calculated



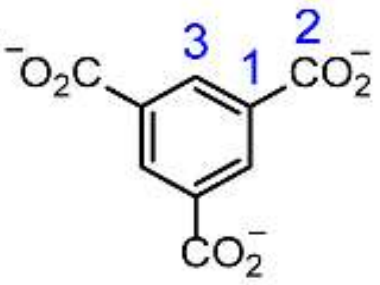
Me-CO_2^-



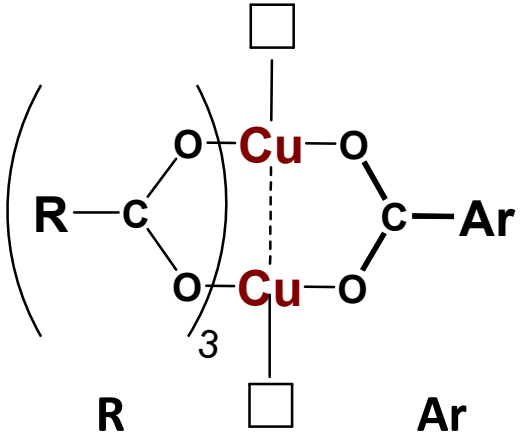
Z. Ke, D. M. Dawson, S. E. Ashbrook, M. Bühl, *Chem. Sci*. **2022**, *13*, 2674.

Single dimer model for activated HKUST

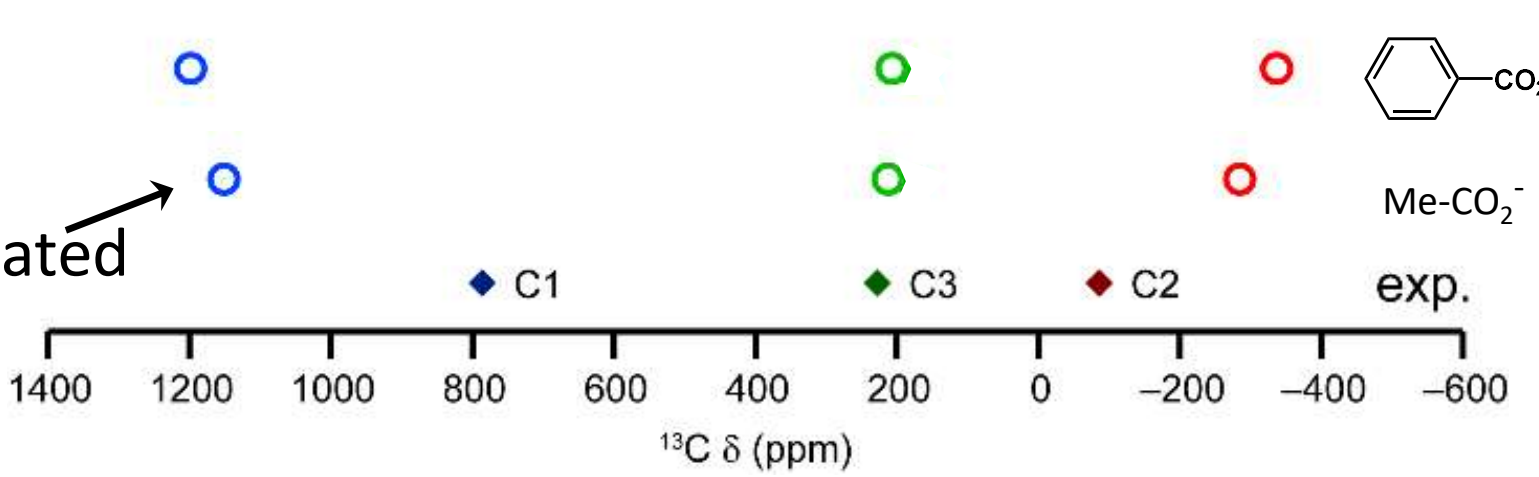
exptl. linker:

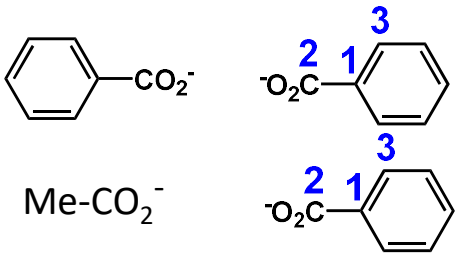


mononuclear models:



o: as calculated

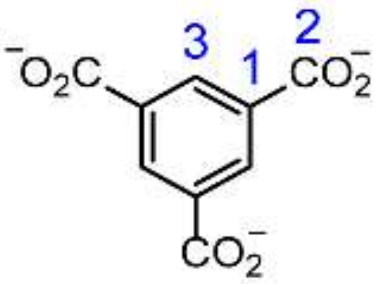




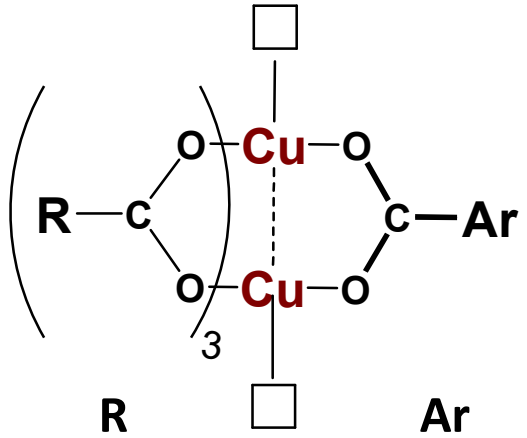
Z. Ke, D. M. Dawson, S. E. Ashbrook, M. Bühl, *Chem. Sci*. **2022**, *13*, 2674.

Single dimer model for activated HKUST

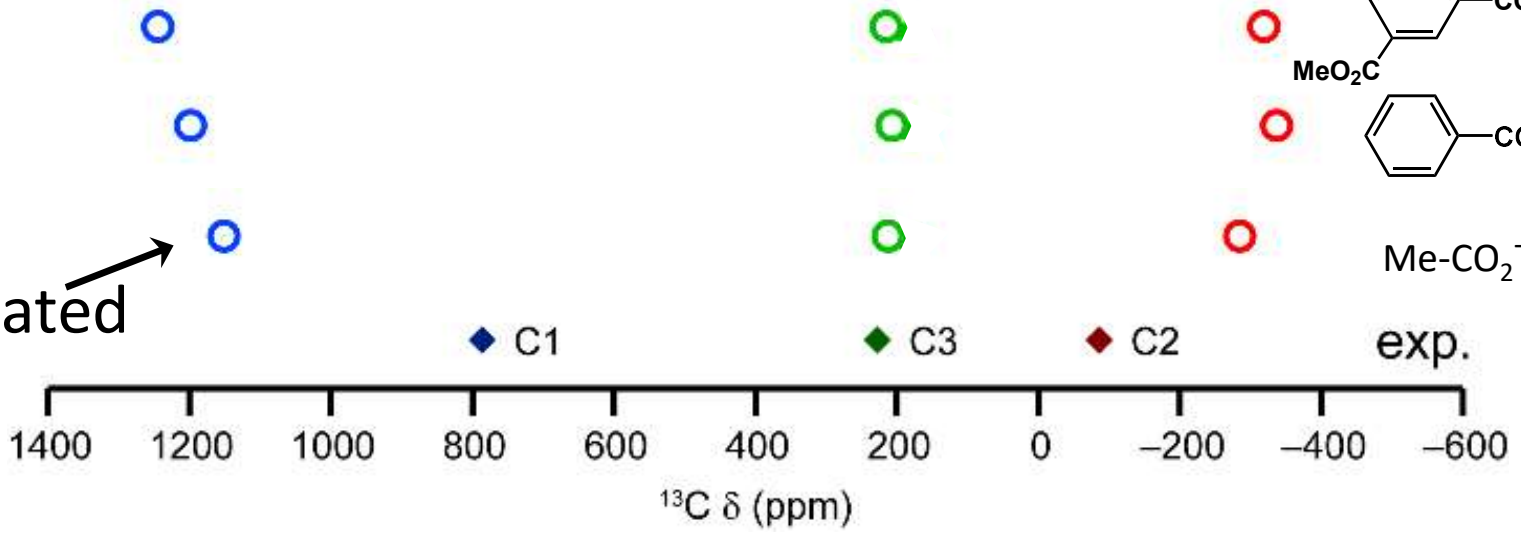
exptl. linker:

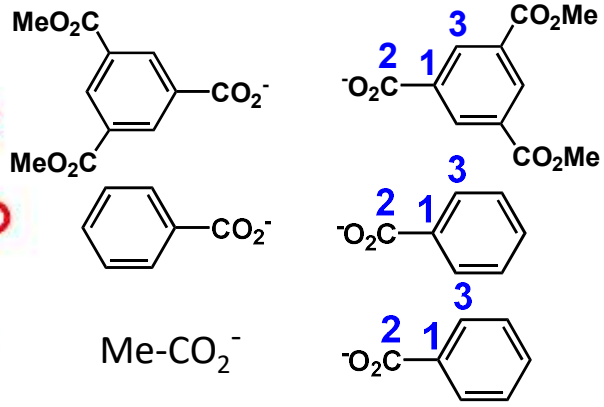


mononuclear models:



o: as calculated





Z. Ke, D. M. Dawson, S. E. Ashbrook, M. Bühl, *Chem. Sci*. **2022**, *13*, 2674.

Single dimer model for activated HKUST

Pragmatic way to reduce contributions from triplet:

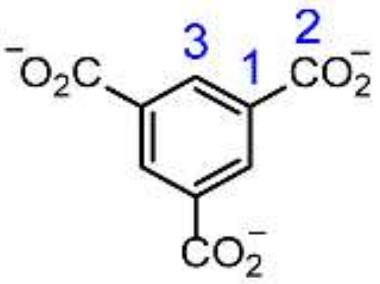
- Scaling of S-T gap (ΔE_{ST}) in Boltzmann distribution

$$x_{trip} = g_{trip} \exp(-s\Delta E_{ST}/RT)/[1 + g_{trip} \exp(-s\Delta E_{ST}/RT)]$$

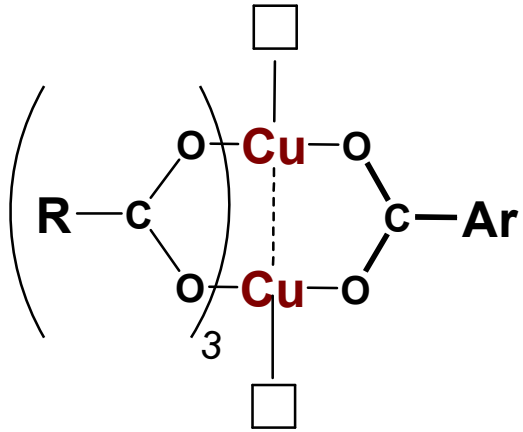
scaling factor **s**

Single dimer model for activated HKUST

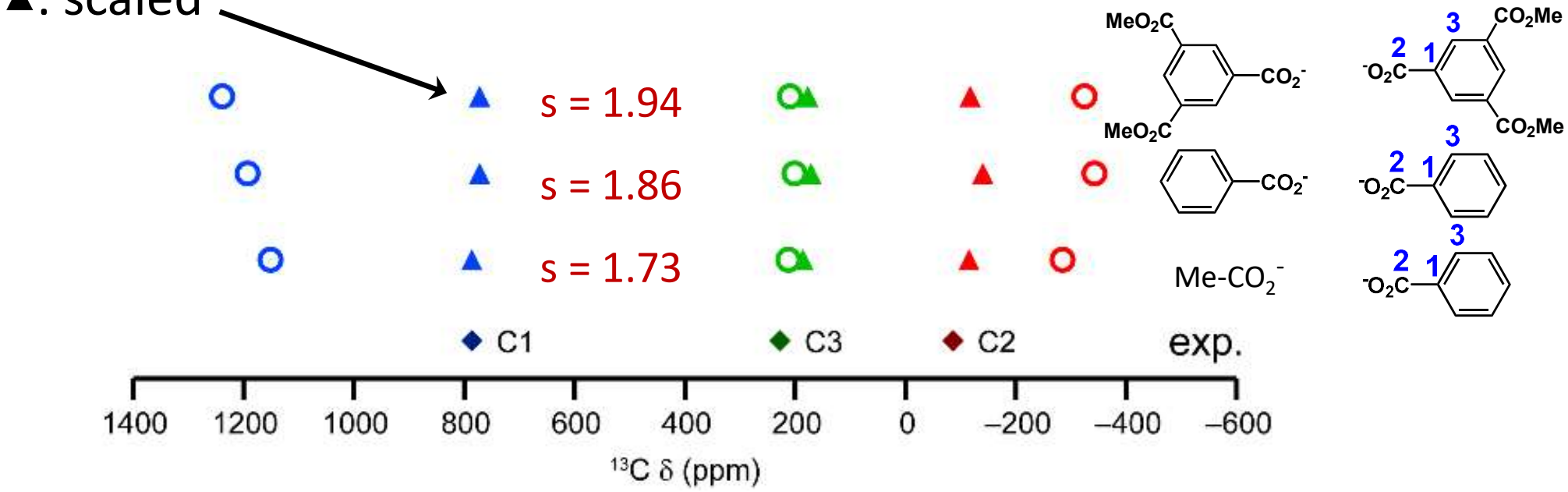
exptl. linker:



mononuclear models:



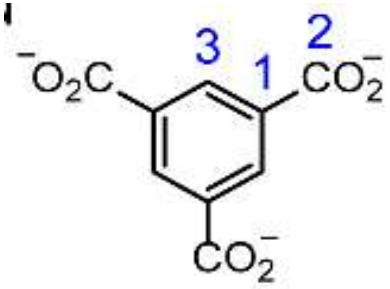
▲: scaled



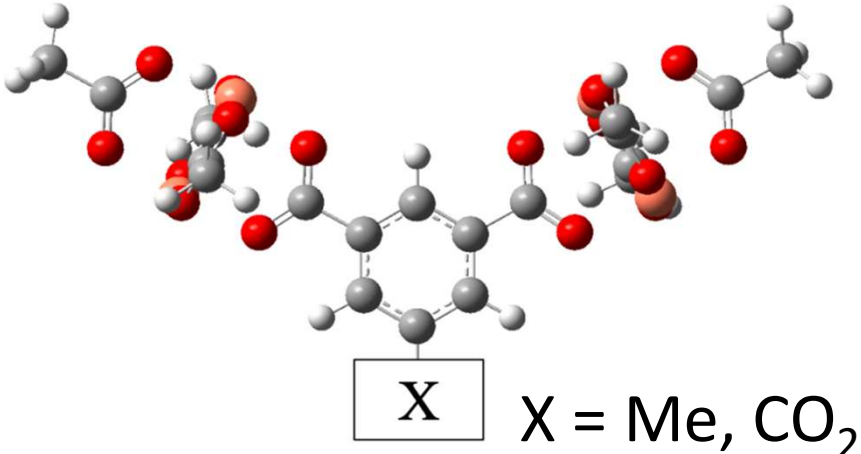
Z. Ke, D. M. Dawson, S. E. Ashbrook, M. Bühl, *Chem. Sci*. **2022**, *13*, 2674.

Double dimer model for activated HKUST

exptl. linker:



dinuclear models:

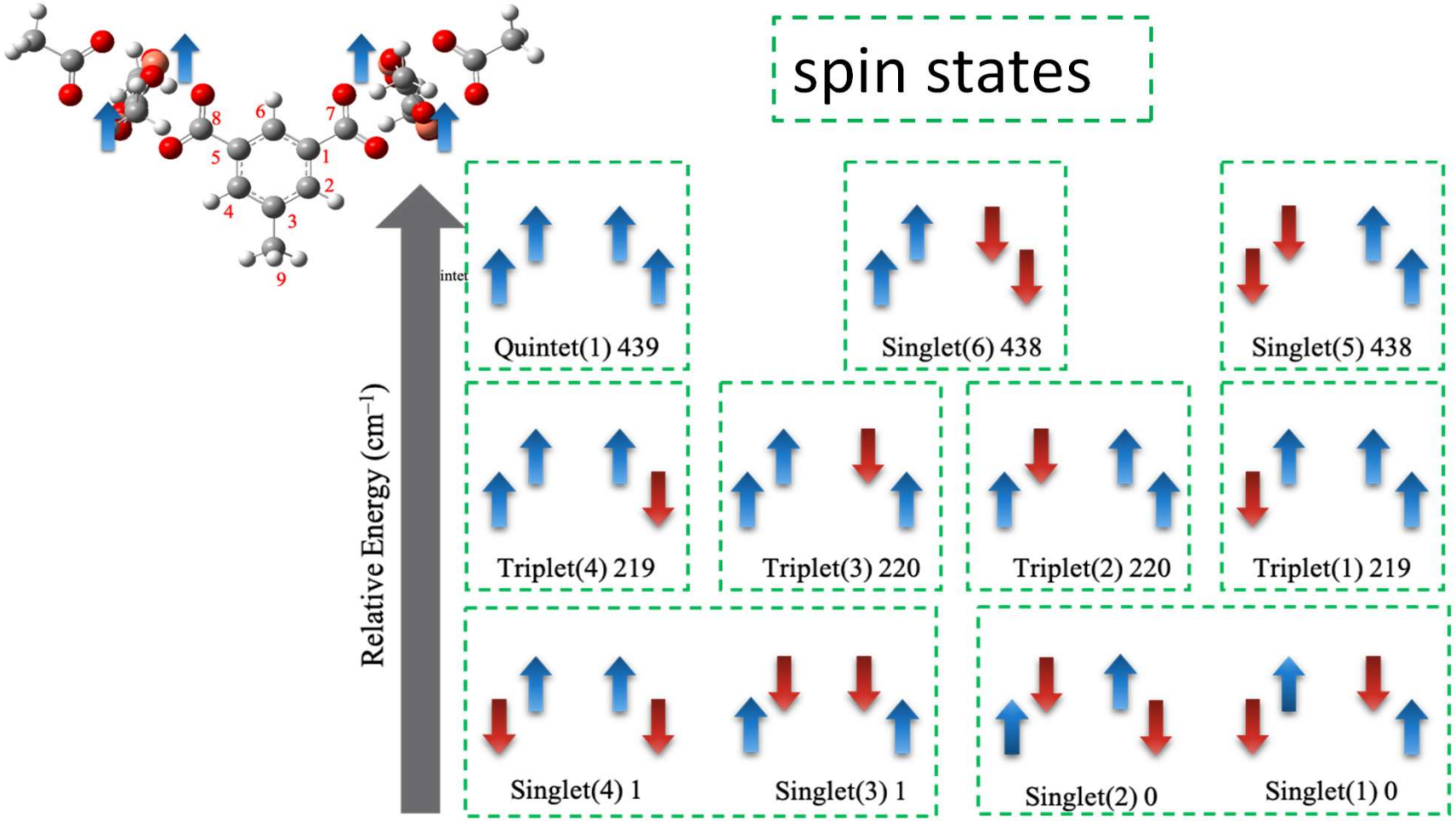


X = Me, CO_2Me

Problem:
Many possible spin configurations
How to combine into spin states?

Z. Ke, D. M. Dawson, S. E. Ashbrook, M. Bühl, *Chem. Sci*. **2022**, *13*, 2674.

Double dimer model for activated HKUST

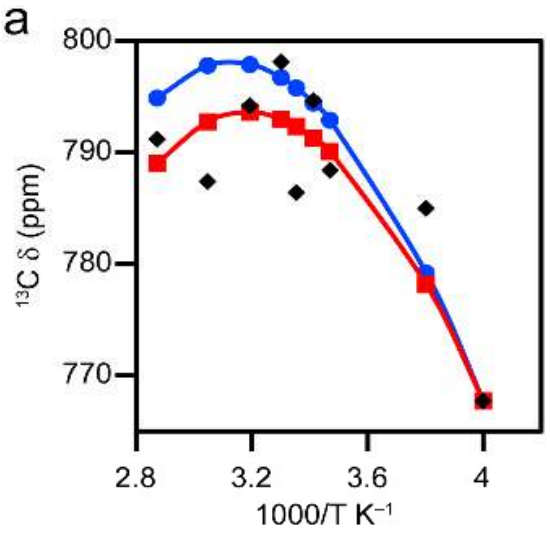


single scale factor: $x_i = g_i \exp(-s\Delta E_i/RT) / \sum_i g_i \exp(-s\Delta E_i/RT)$

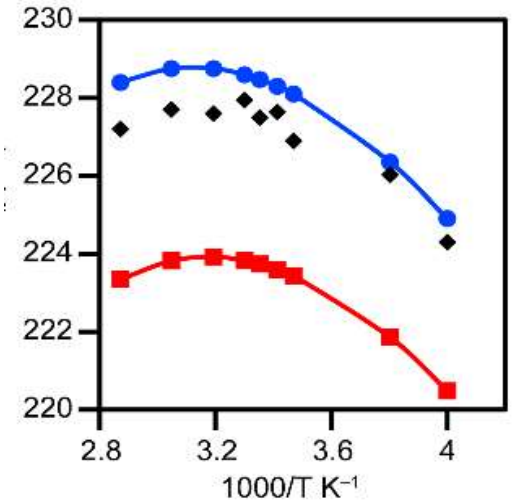
Z. Ke, D. M. Dawson, S. E. Ashbrook, M. Bühl, *Chem. Sci*. **2022**, *13*, 2674.

Temperature dependence

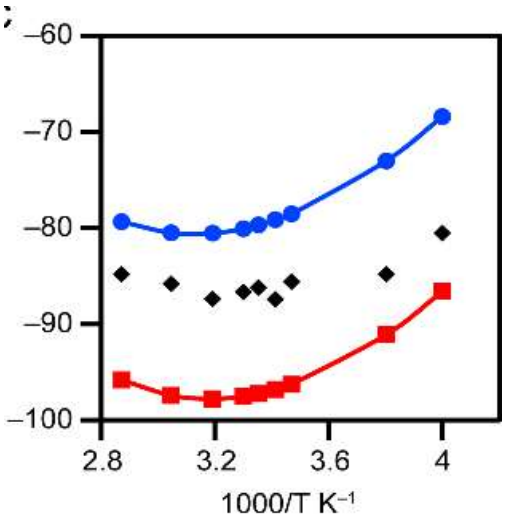
C1

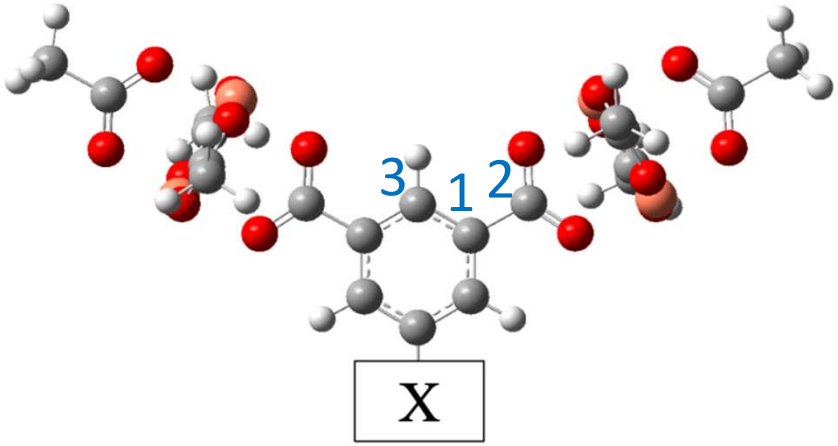


C3



C2





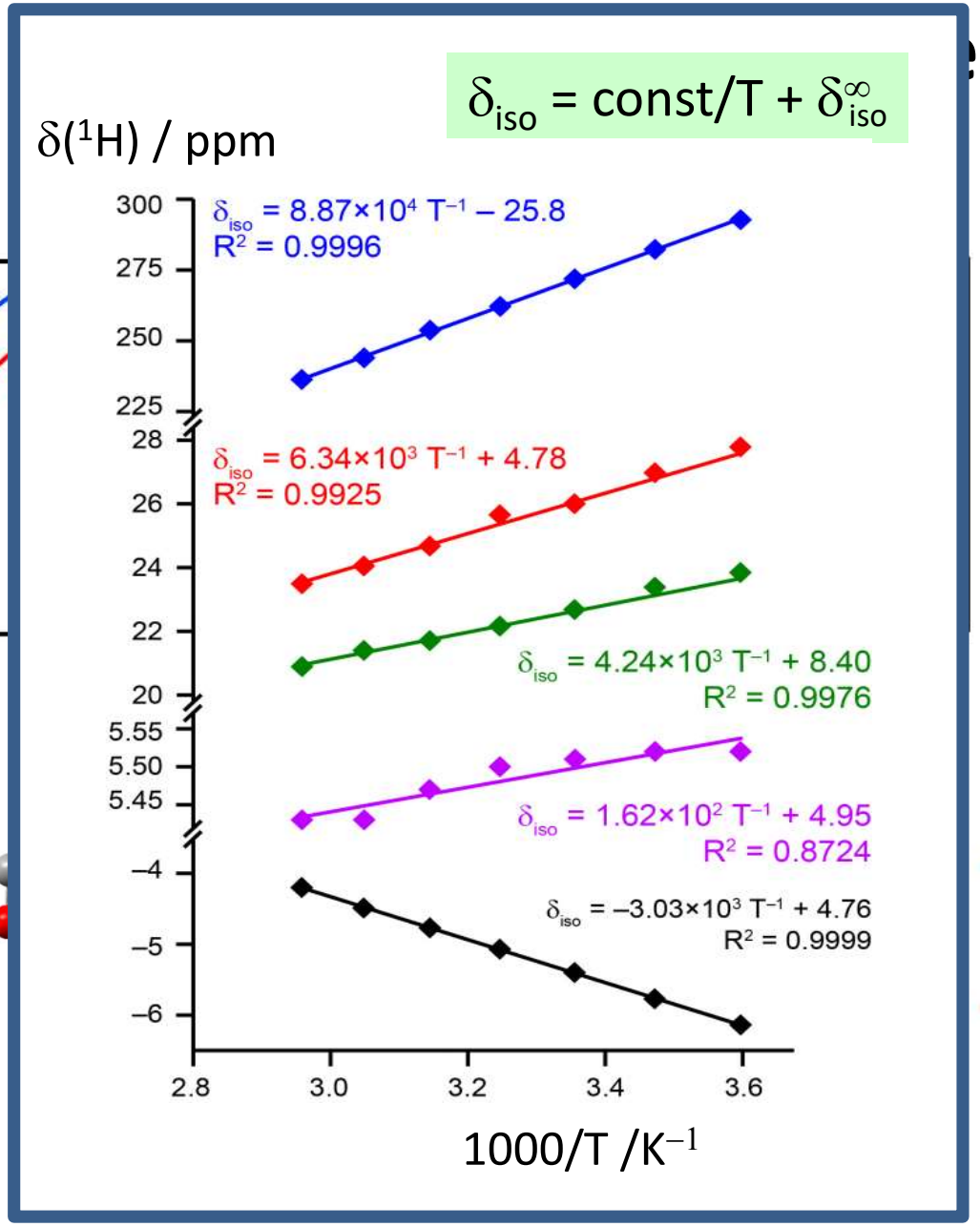
X = CO_2Me (s = 1.33)

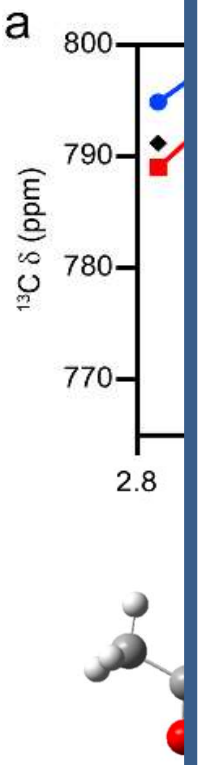
X = Me (s = 1.31)

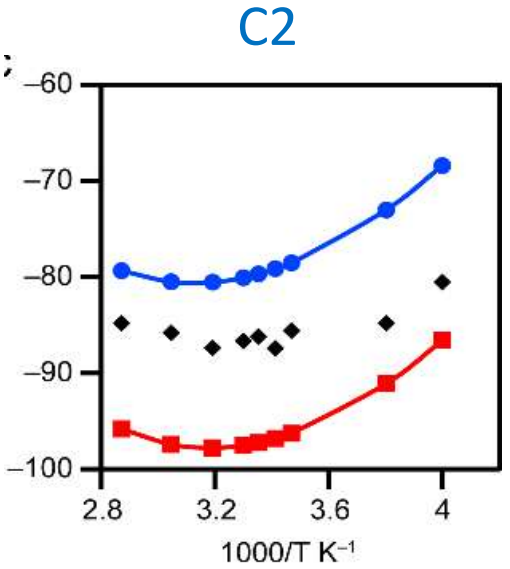
experiment

Z. Ke, D. M. Dawson, S. E. Ashbrook, M. Bühl, *Chem. Sci*. **2022**, *13*, 2674.

ndence







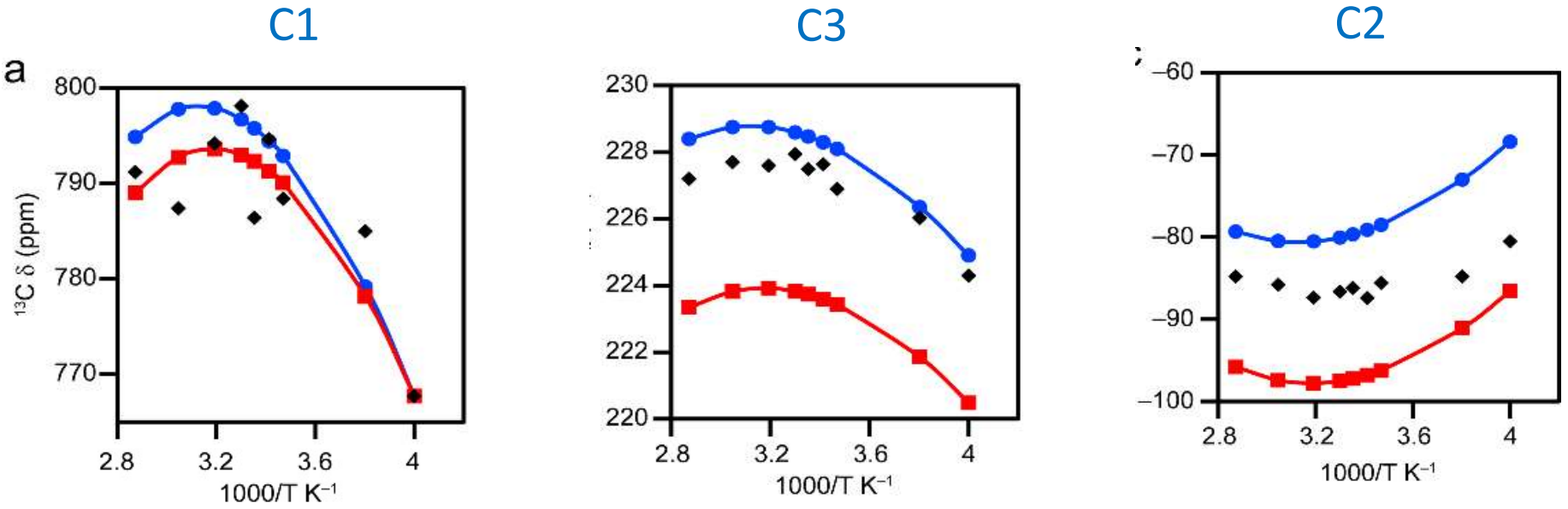
X = CO_2Me (s = 1.33)

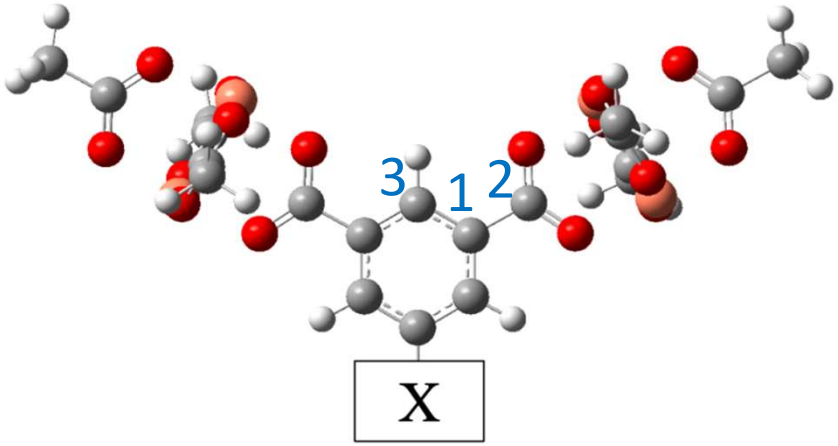
X = Me (s = 1.30)

experiment

Z. Ke, D. M. Dawson, S. E. Ashbrook, M. Bühl, *Chem. Sci*. **2022**, *13*, 2674.

Temperature dependence





X = CO_2Me (s = 1.33)

X = Me (s = 1.31)

experiment

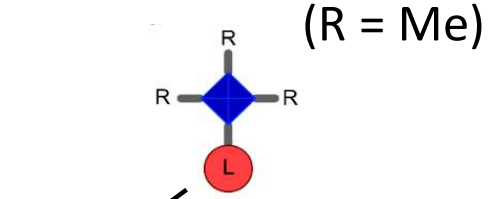
unusual temperature dependence very well reproduced

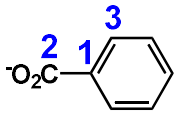
Z. Ke, D. M. Dawson, S. E. Ashbrook, M. Bühl, *Chem. Sci*. **2022**, *13*, 2674.

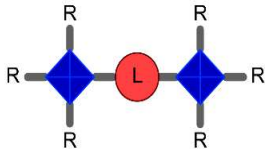
Triple-dimer models for activated HKUST

models:

(R = Me)

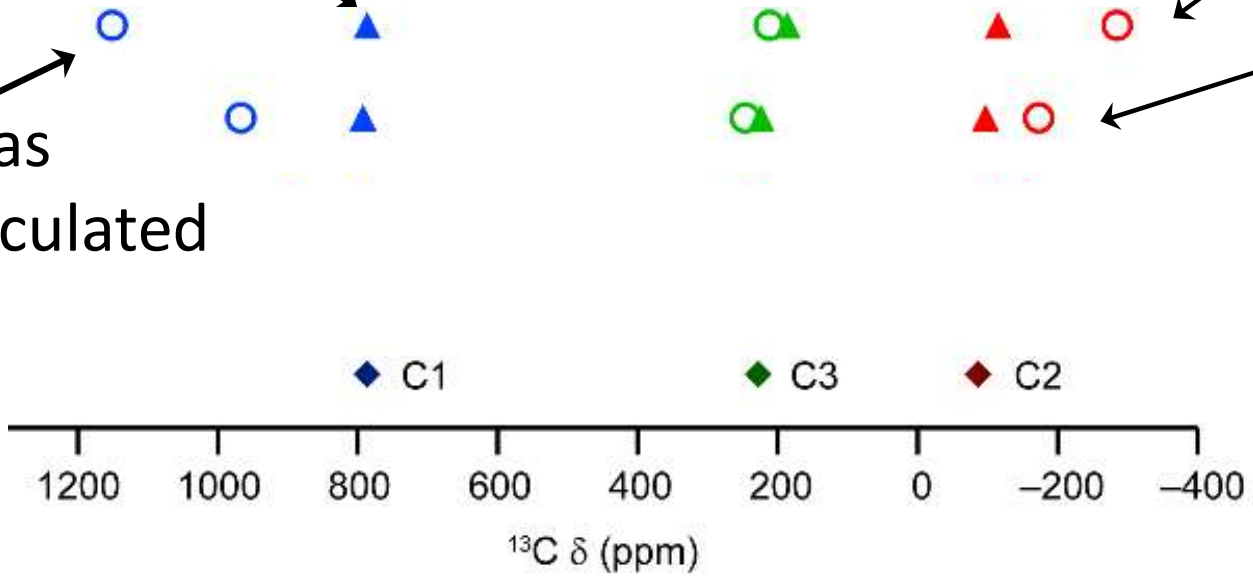






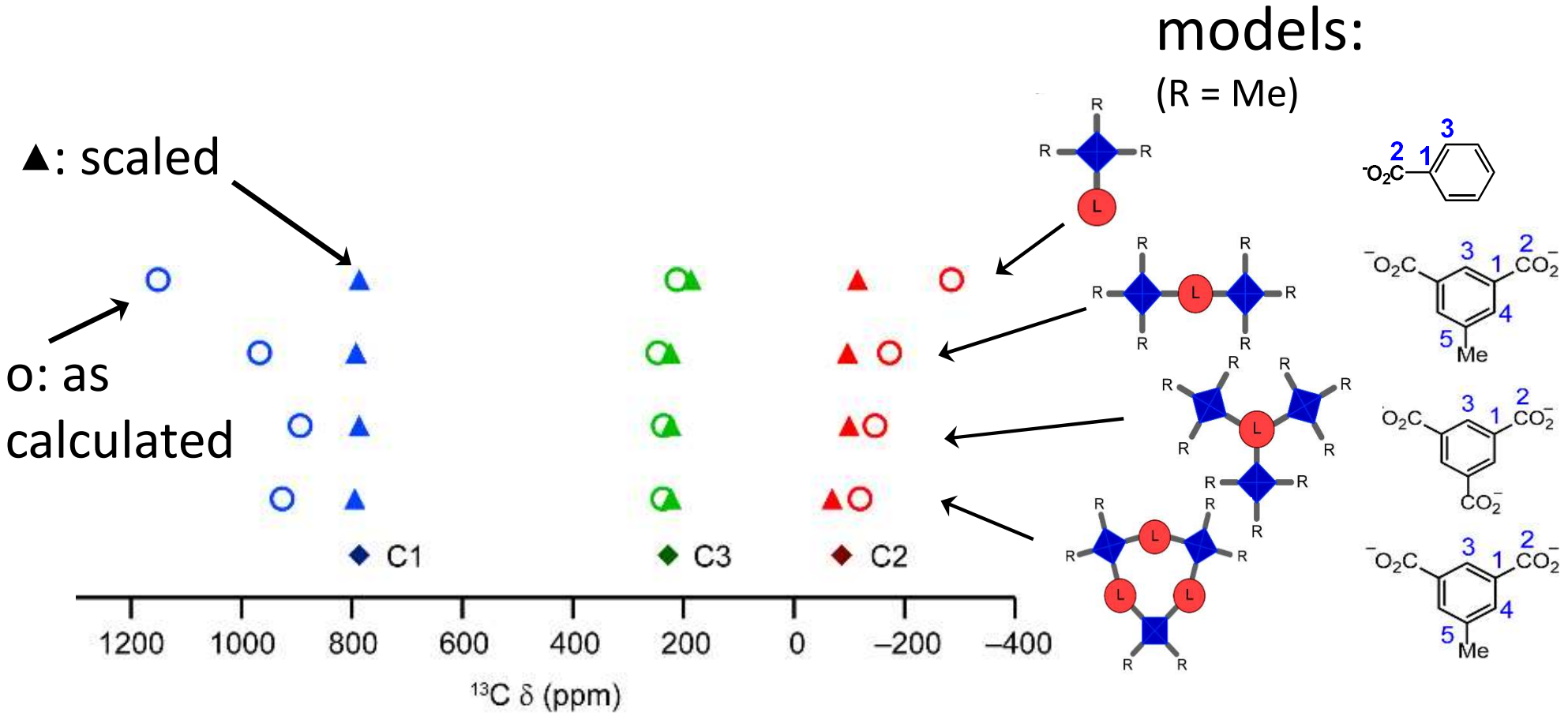
▲: scaled

o: as calculated



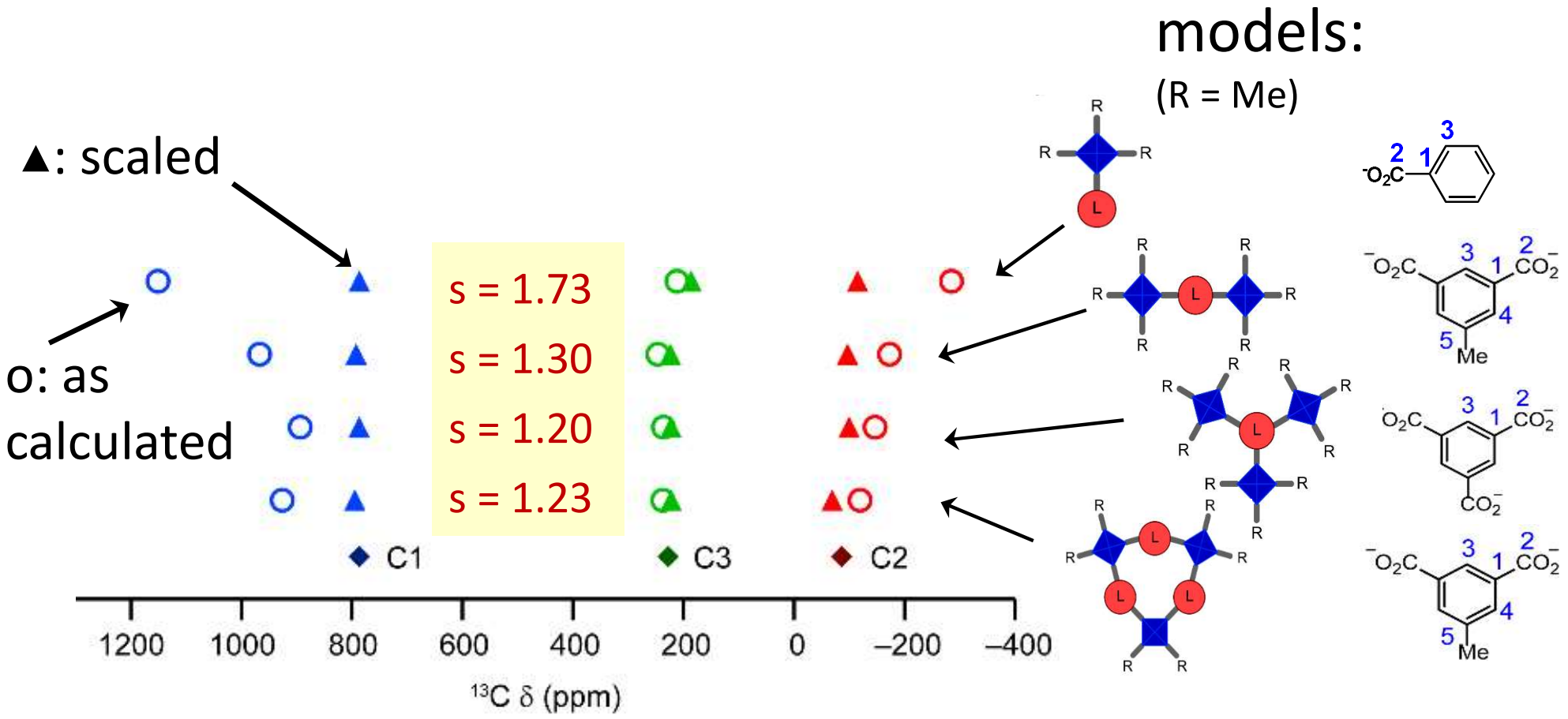
Z. Ke, D. M. Dawson, S. E. Ashbrook, M. Bühl, *Chem. Sci*. **2022**, *13*, 2674.

Triple-dimer models for activated HKUST



Z. Ke, D. M. Dawson, S. E. Ashbrook, M. Bühl, *Chem. Sci*. **2022**, *13*, 2674.

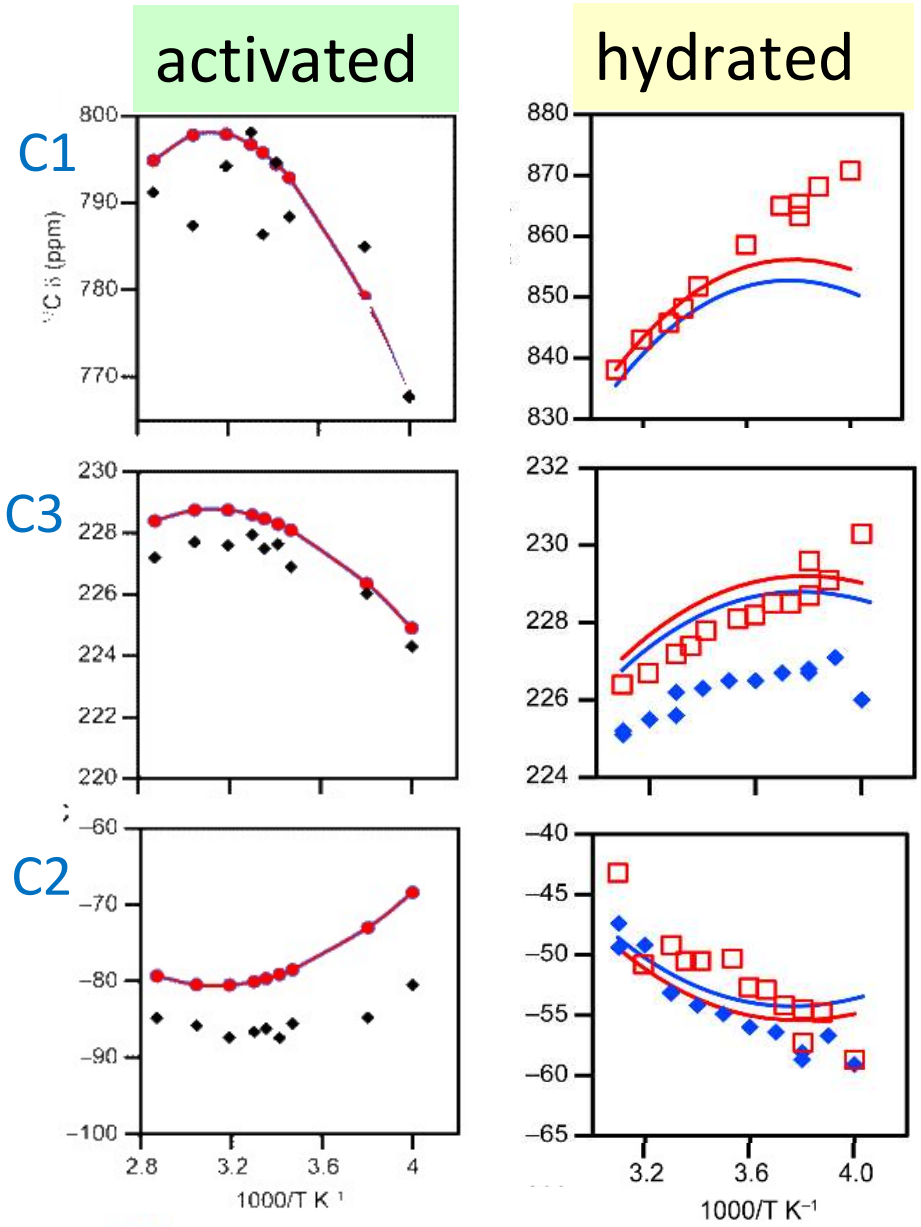
Triple-dimer models for activated HKUST

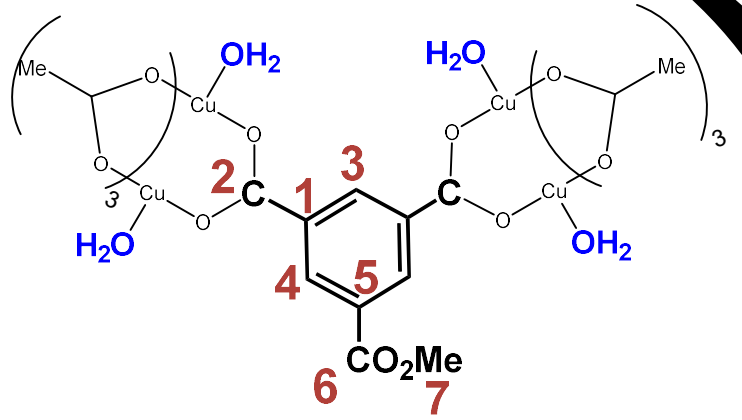


scale factor approaching unity as models become larger

Z. Ke, D. M. Dawson, S. E. Ashbrook, M. Bühl, *Chem. Sci*. **2022**, *13*, 2674.

Hydrated MOFs





double dimer model for STAM-1 (and HKUST)

HKUST calc (s = 1.33) expt

HKUST calc (s = 1.29) expt

STAM-1 calc (s = 1.30) expt

Z. Ke, D. M. Dawson, S. E. Ashbrook, M. Bühl, *Chem. Sci*. **2022**, *13*, 2674.

Conclusion

- Molecular models for MOFs validated in "bottoms-up" approach
- pNMR shifts arise from thermal population of high-spin states
- Uniform scaling of as-calculated energy gaps required
- Temperature dependence of pNMR signals explained

Next challenge:
refinement of models (dynamics, crystal matrix)

Develop pNMR calculations and experiments into structural tool, e.g. to study uptake of guest molecules