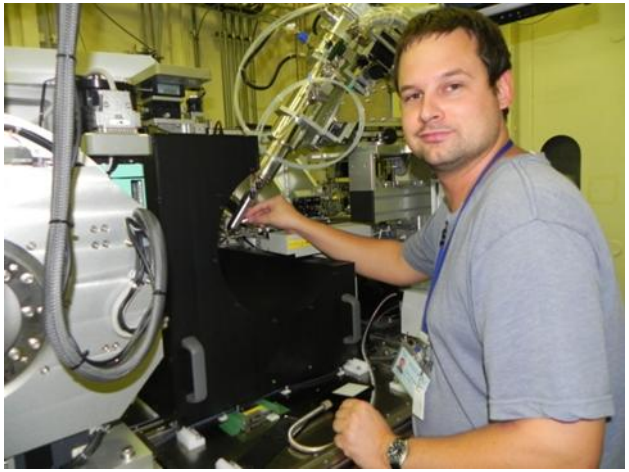
X-ray Wavefunction Refinement

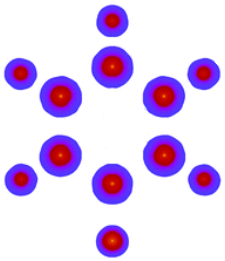


Dr. Simon Grabowsky

Asian Charge Density Workshop
February 2015

Aspherical models

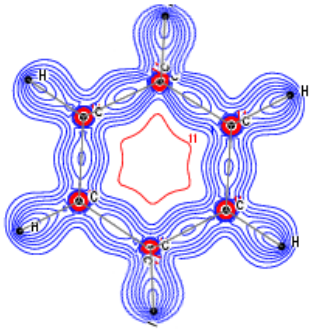
Universität Bremen



IAM
(spherical model)

aspherical model

Multipole-based techniques

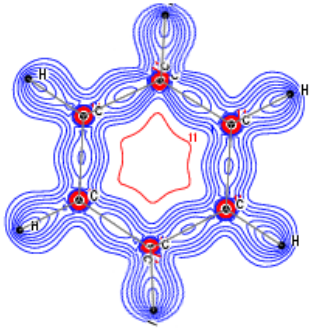


aspherical model

Maximum entropy methods

aspherical model

Wavefunction-based techniques



Multipole model

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- **Independent Atom Model (e.g. shelx or olex2.refine)**

  Neglecting valence density by just adding up spherical atomic electron densities.

  Refinement: x, y, z, 6 U_{ij}'s = 9 par.

  → atom types and atomic positions

- **Multipole Model (e.g. XD or MoPro)**

  Accounting for valence density by assuming aspherical atomic densities.

  Refinement: x, y, z, 6 U_{ij}'s, 30 multipole par. = 39 par.

  → atom types, positions AND the total electron density

Multipole model

Universität Bremen

- **Independent Atom Model**

  Neglecting valence density by just adding up spherical atomic electron densities.

  Refinement: x, y, z, 6 U_{ij}'s = 9 par.

  → atom types and atomic positions

- **Multipole Model**

  Accounting for valence density by assuming aspherical atomic densities.

  Refinement: x, y, z, 6 U_{ij}'s, 30 multipole par. = 39 par.

  → atom types, positions AND the total electron density

→ High-resolution experiments needed for an acceptable ratio of reflections over parameters

MM vs. IAM

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Two major **advantages** of the MM over the IAM:

- More accurate geometry
- Chemical electron-density analysis

Two major **disadvantages** of the MM over the IAM:

- High resolution needed
- Modelling procedure is complicated

XWR vs. MM

Universität Bremen

Two major **advantages** of XWR over the MM:

- Hydrogen atoms are accurately detectable
- Chemical analysis beyond electron density

Two major **disadvantages** of the MM over the IAM **disappear** by using XWR:

- **No** high resolution needed
- Modelling procedure is **not** complicated

XWR vs. MM

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New **disadvantages** of XWR over the MM:

- Refinement and fitting take much longer
- Currently not available for every system
  - No disorder treatment
  - Only molecular species: no network compounds
  - Large compounds such as proteins

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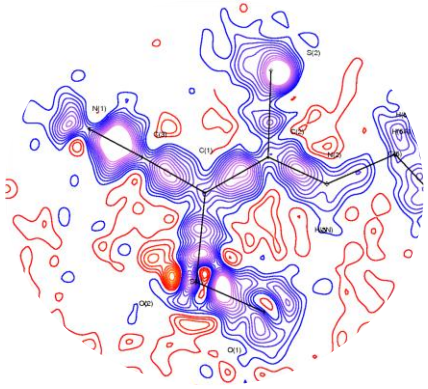
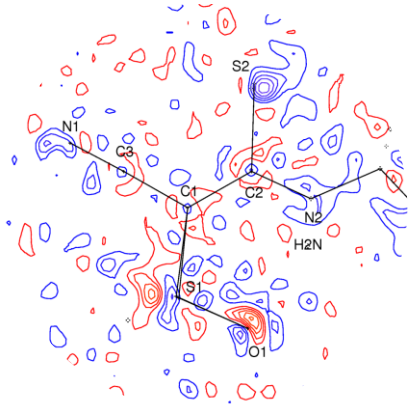
IAM MM XWR

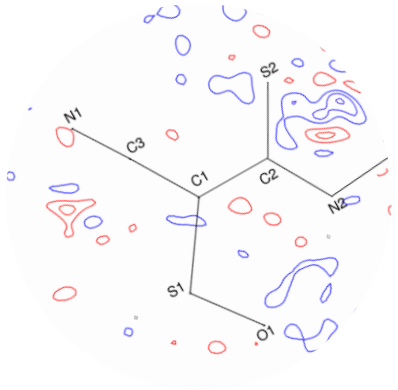
“Level of theory included”

and

“Agreement with experiment”







R_1: **3.7%** **1.9%** **1.5%**

XWR vs. MM

Universität Bremen

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XWR vs. MM

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IUCrJ (2014). 1, 361–379

research papers

IUCrJ
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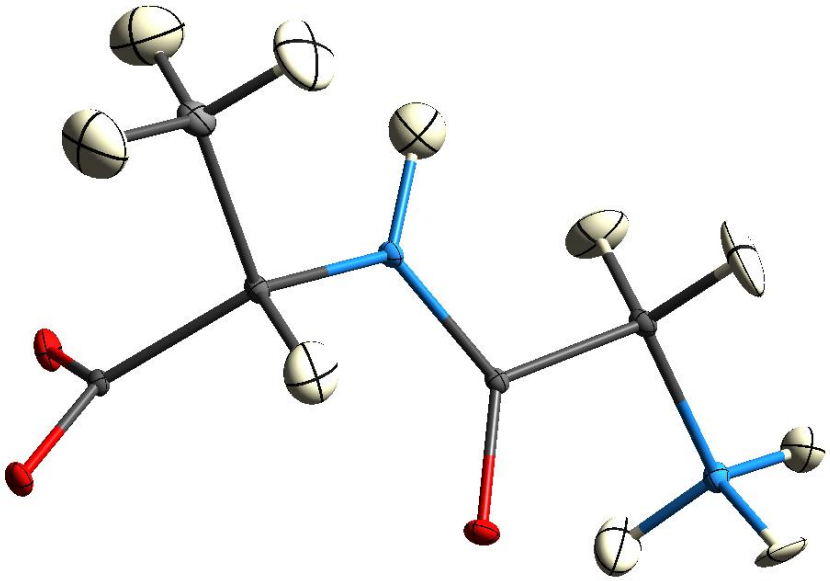
Hirshfeld atom refinement

Silvia C. Capelli,[a] Hans-Beat Bürgi,[b,c] Birger Dittrich,[d,e] Simon Grabowsky[f] and Dylan Jayatilaka[f]*



glycyl-L-alanine

Synchrotron X-ray data:

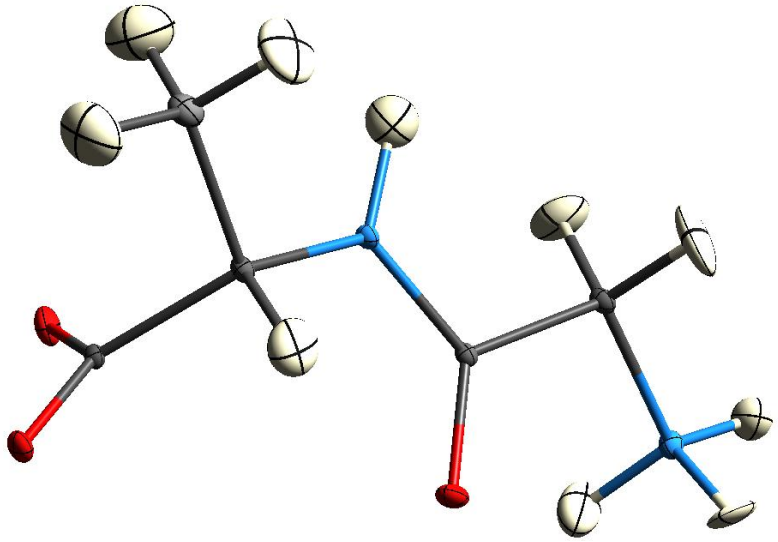
ESRF Grenoble
d = 0.65 Å

Neutron data:

ILL Grenoble
d = 0.7 Å

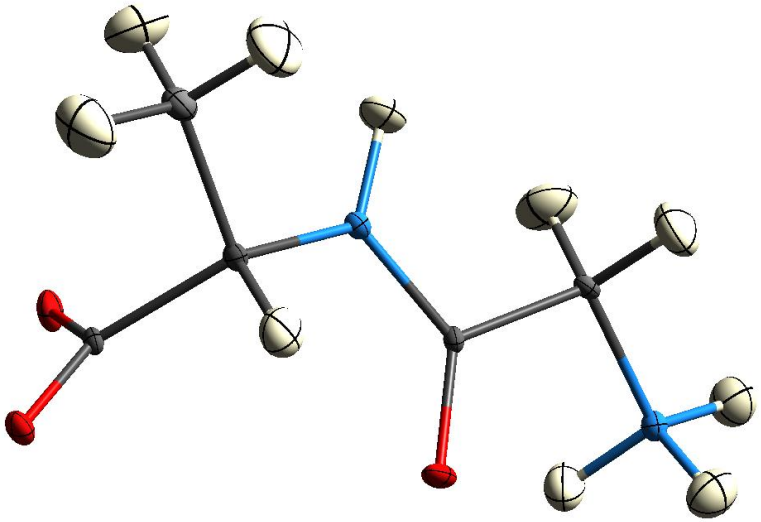
Hydrogen atom treatment

Universität Bremen



XWR

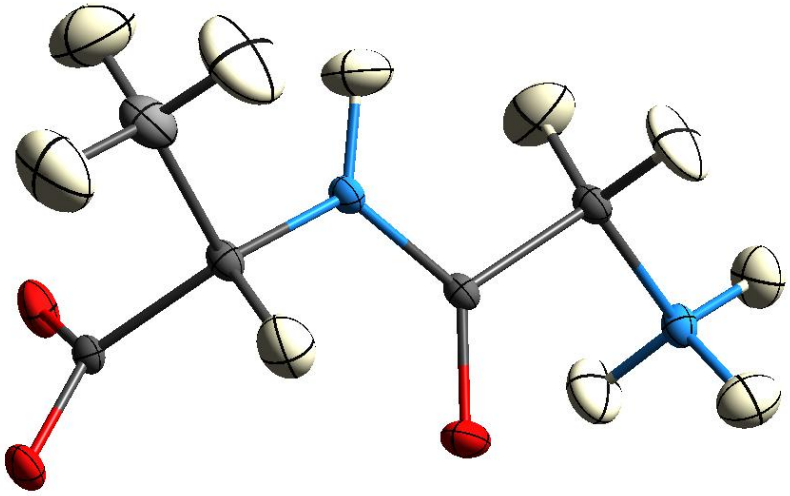
50 K



Neutron

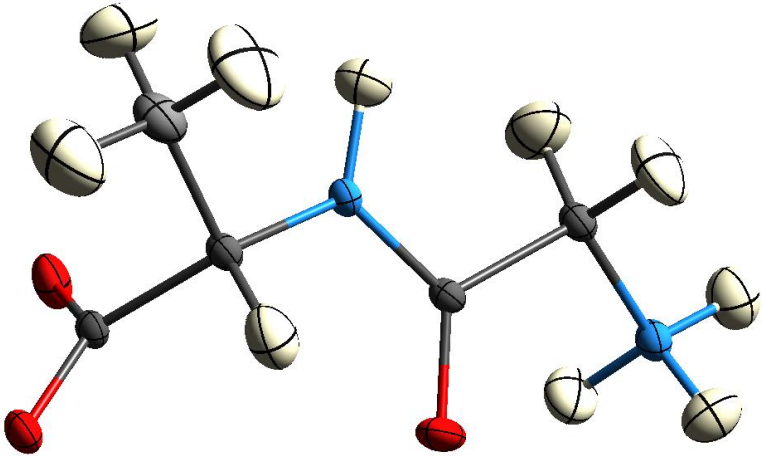
Hydrogen atom treatment

Universität Bremen



XWR

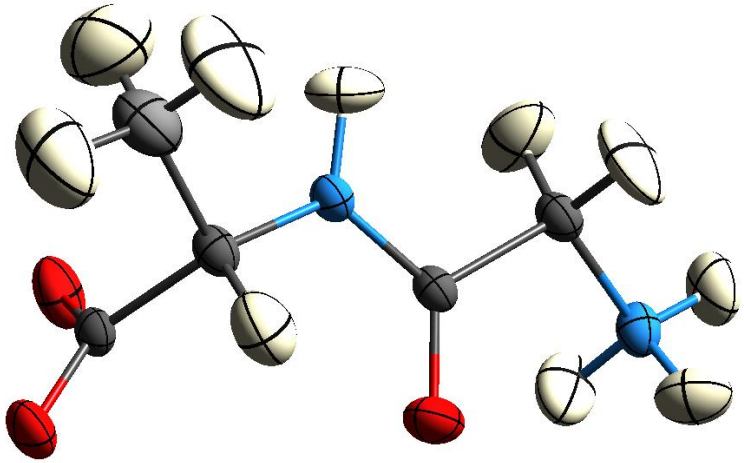
150 K



Neutron

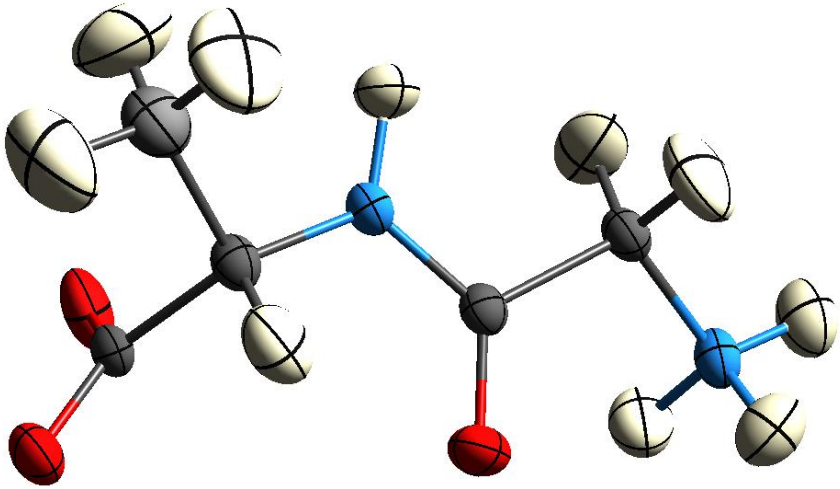
Hydrogen atom treatment

Universität Bremen



XWR

295 K



Neutron

Hydrogen atom treatment

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50K

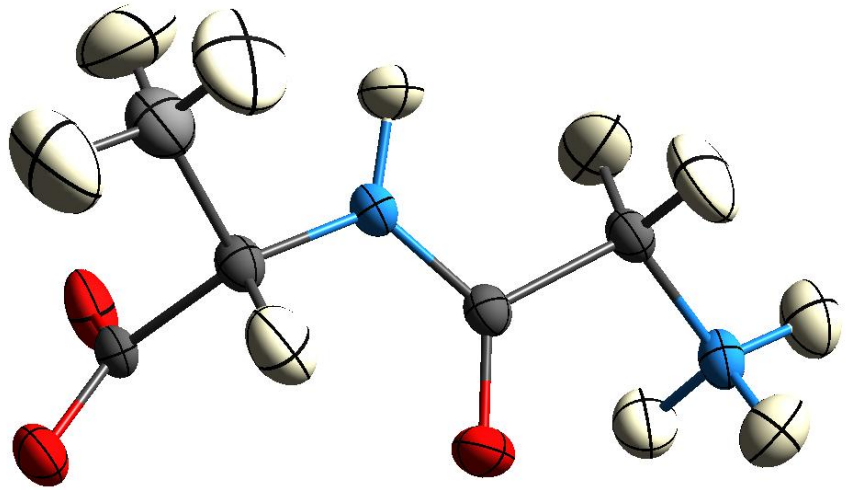
150K

295K

X

IAM/

MM



Neutron

Hydrogen atom treatment

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T in K	X-H lengths in Å		H ADPs (U_{ij}) in Å^2	
	$\|\Delta\|$	RMSD/s.u.	$\|\Delta\|$	RMSD/s.u.
50	0.0093	1.8	0.0040	1.3
150	0.0087	1.8	0.0037	1.4
295	0.0089	1.9	0.0075	1.6

IAM ~ 0.1

MM ~ 0.02

MM ~ 2.3

V. V. Zhurov, E. A. Zhurova, A. I. Stash, A. A. Pinkerton, Acta Cryst A 2011, 67, 160.

Hydrogen atom treatment

Universität Bremen

T in K	X-H lengths in Å		H ADPs (U_{ij}) in Å^2	
	$\|\Delta\|$	RMSD/s.u.	$\|\Delta\|$	RMSD/s.u.
50	0.0093	1.8	0.0040	1.3
150	0.0087	1.8	0.0037	1.4
295	0.0089	1.9	0.0075	1.6

Most accurate structural results ever obtained from X-rays for hydrogen atoms.

Hydrogen atom treatment

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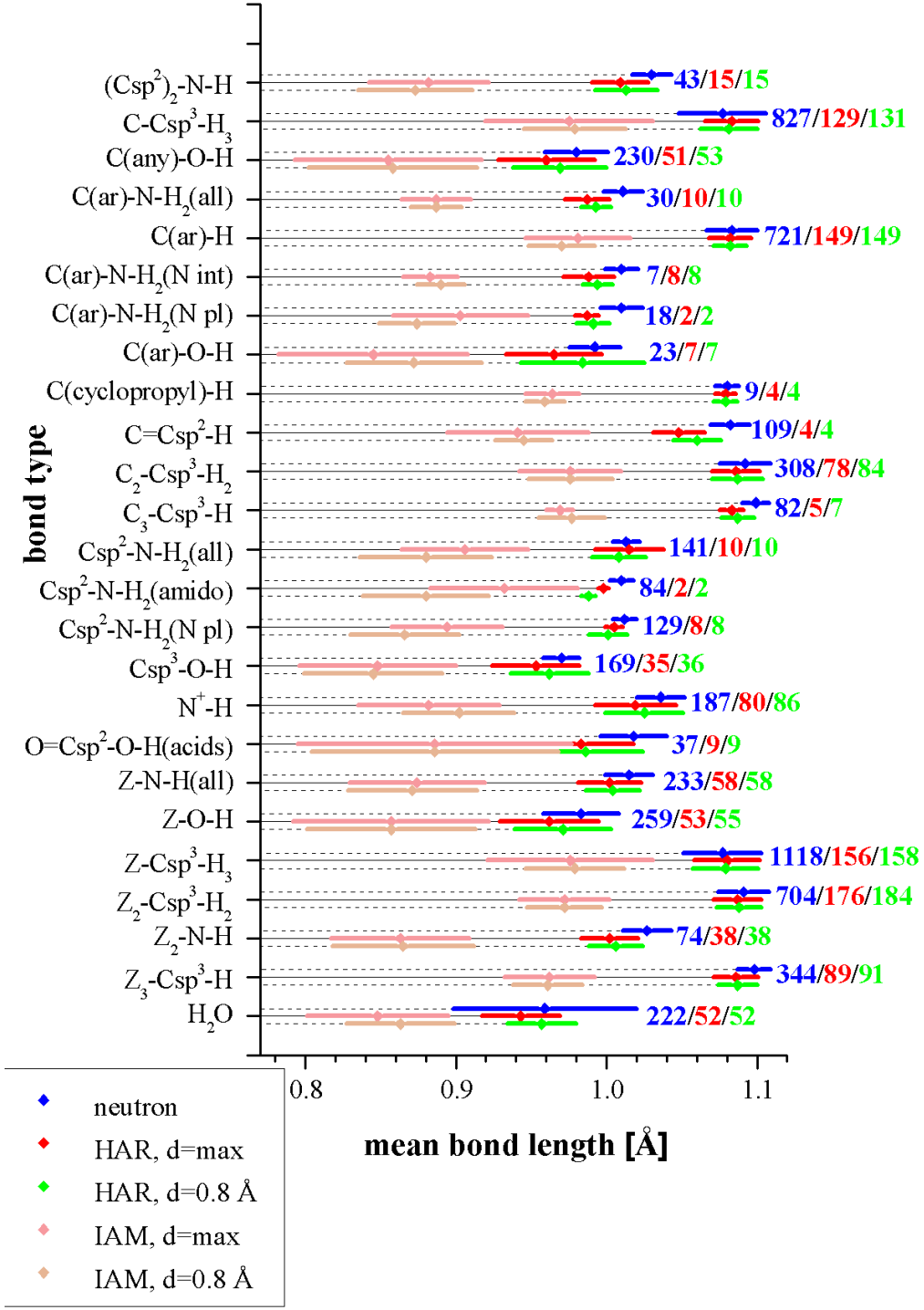
Establishing X-H bond lengths from HAR.

Do we need neutrons at all?

Can we use routine X-ray structures instead?

- over 80 organic compounds (own data sets, from Acta A/B, collaboration with Wozniak/Dominiak)
- resolution d = 0.5 Å to 0.3 Å.
- T < 140 K
- run HAR at different resolutions: d_{max}, d = 0.5, 0.6, 0.7, 0.8 Å
- comparison to averaged X-H distances from neutron diffraction separated into bond-type classes taken from

  F. H. Allen, I. J. Bruno, Acta Cryst. B 2010, 66, 380-386



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$|\Delta|$ = 0.009 to 0.022 Å

RMSD/s.u. = 1.8 to 2.2

Hydrogen atom treatment

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Conclusions:

- Statistical agreement between HAR and neutron results
- obtained at low resolution, suitable for routine data sets
- anisotropic treatment of hydrogens necessary
- level of theory HF/cc-pVDZ sufficient, feasible on normal desktop computer

Strong hydrogen bonds

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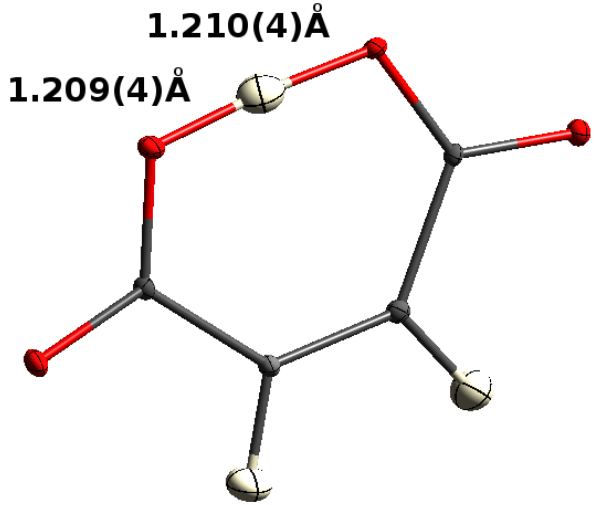
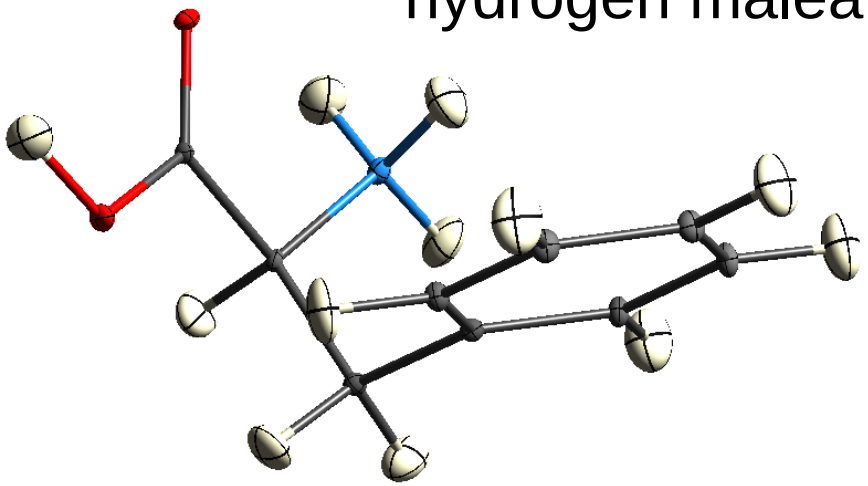


L-phenylalaninium hydrogen maleate



Synchrotron X-ray data:

SPring-8, Japan d = 0.30 Å T = 25 K

Neutron data:

KOALA, ANSTO d = 0.65 Å T = 12 K

Strong hydrogen bonds

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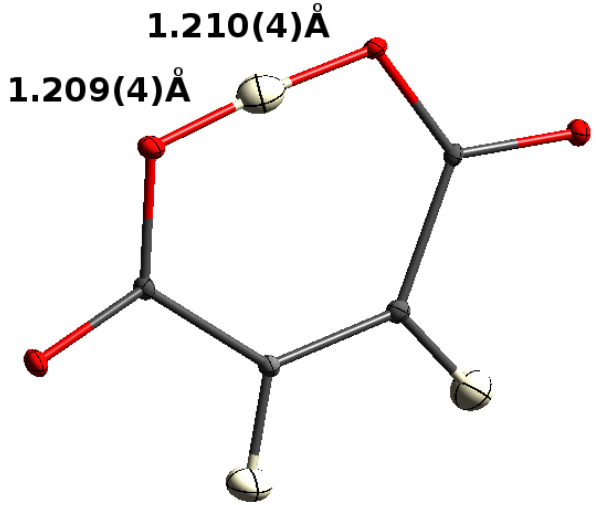
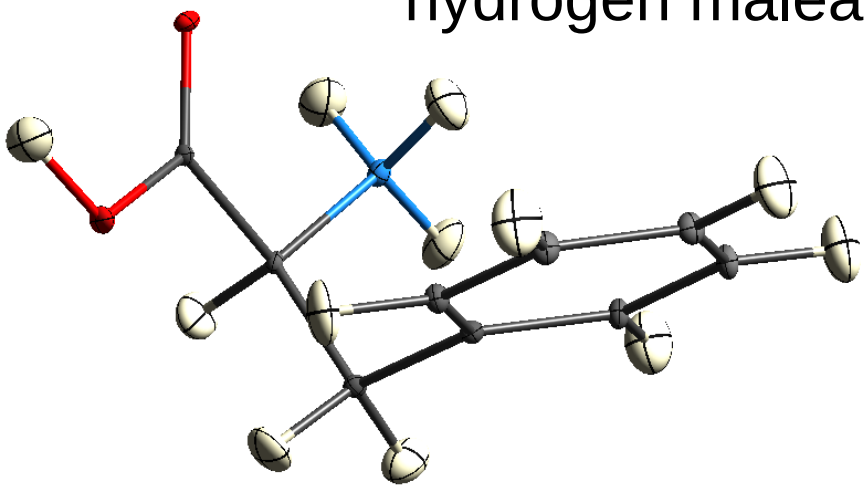


L-phenylalaninium hydrogen maleate



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research papers

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Foundations and Advances
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Hirshfeld atom refinement for modelling strong hydrogen bonds

Magdalena Woińska,[a,b] Dylan Jayatilaka,[b] Mark A. Spackman,[b] Alison J. Edwards,[c] Paulina M. Dominiak,[a] Krzysztof Woźniak,[a] Eiji Nishibori,[d] Kunihisa Sugimoto[e] and Simon Grabowsky[b]*

Strong hydrogen bonds

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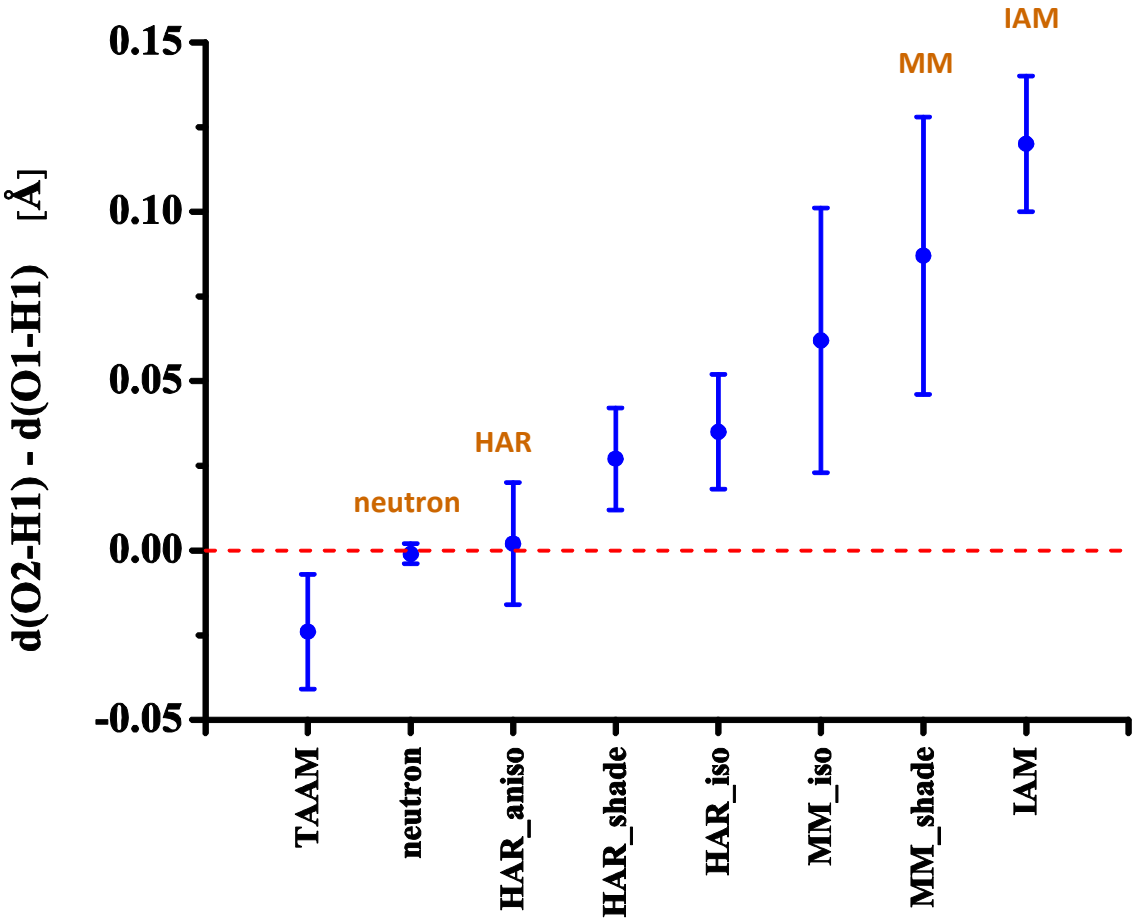

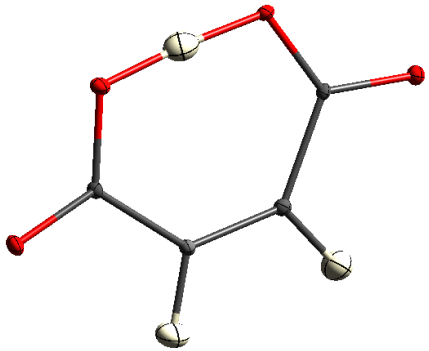

- Deviation from the symmetric hydrogen position
- Precision of the determination

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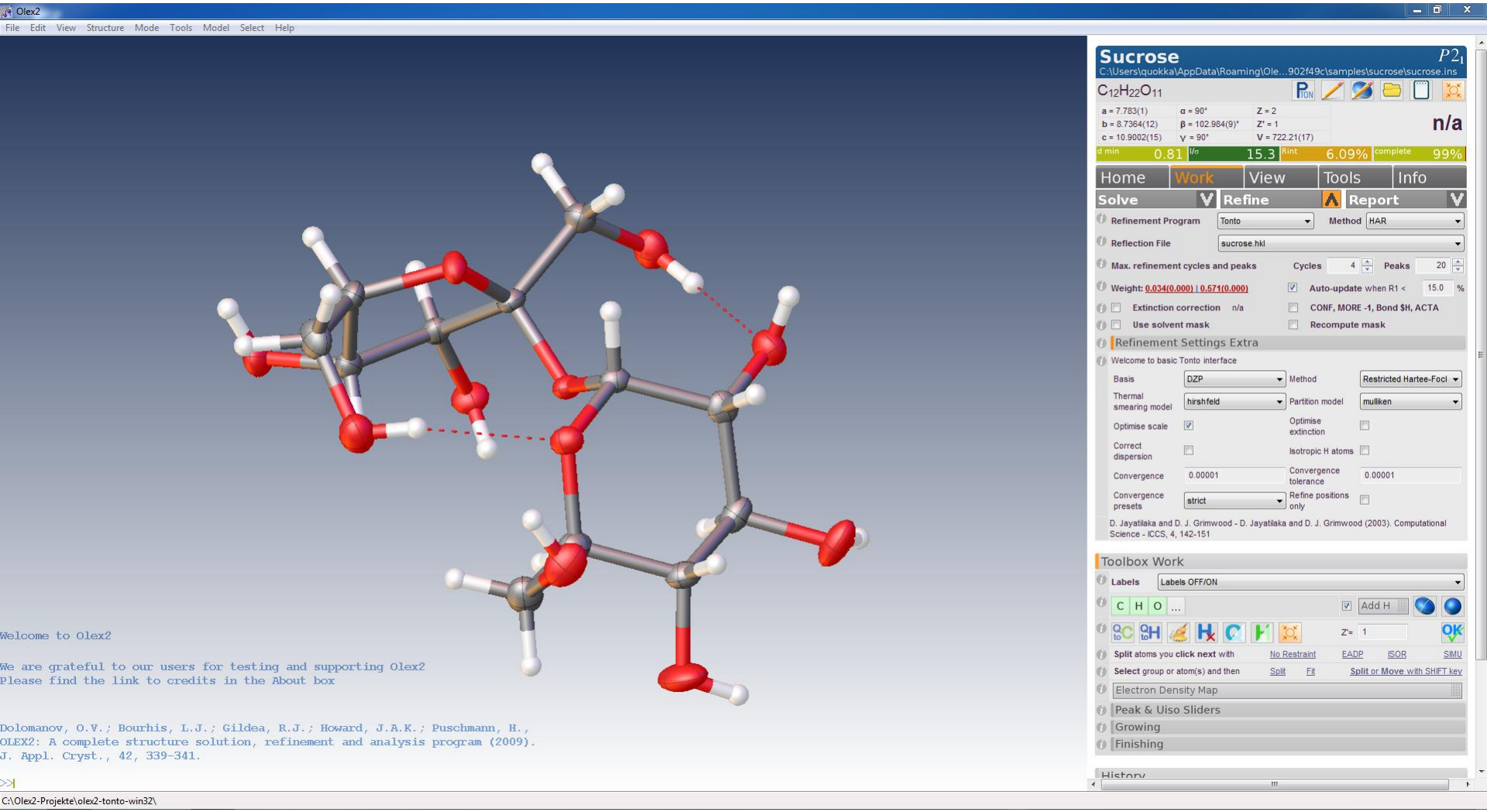

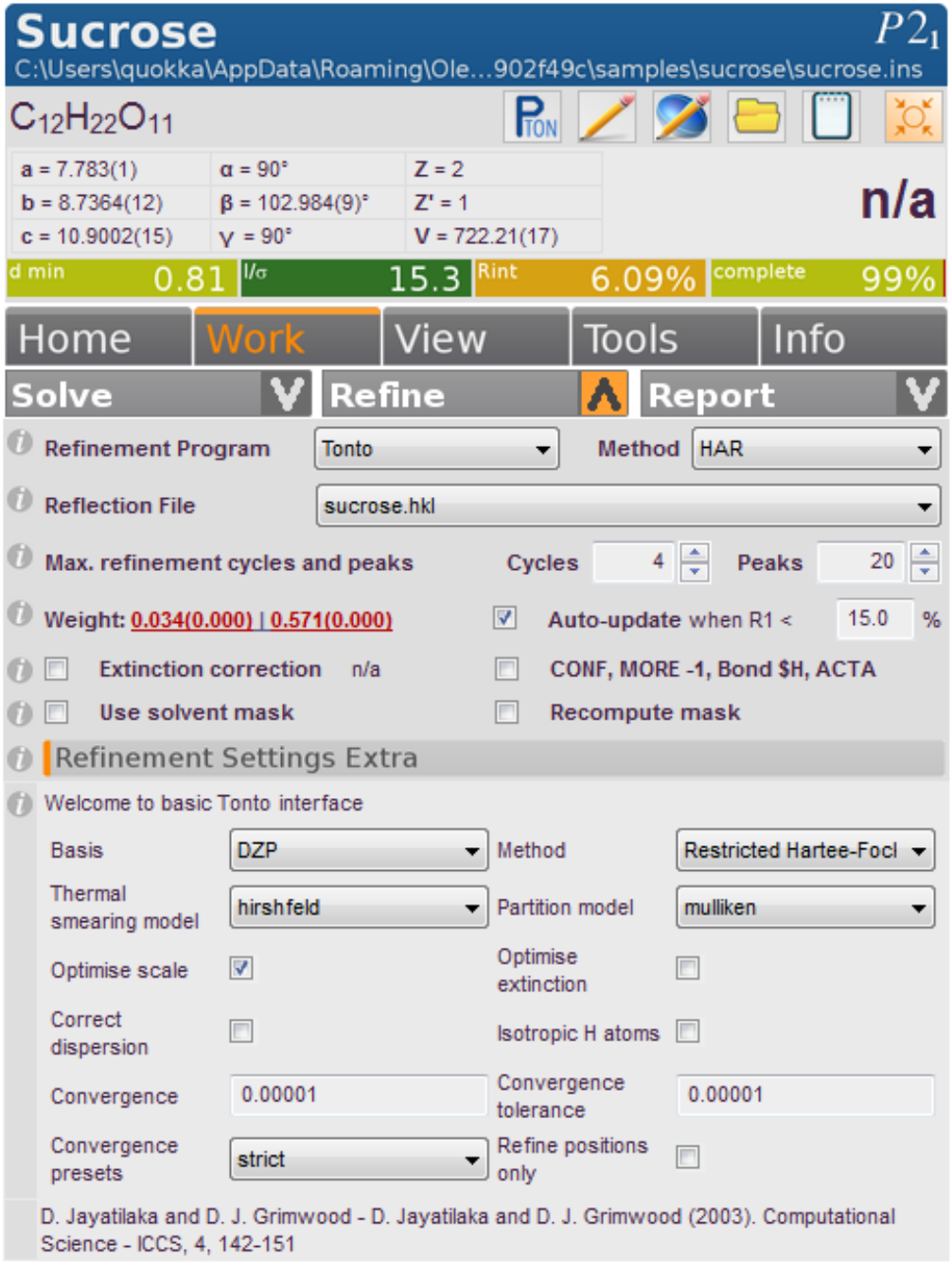

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Tutorial part 1: HAR

- ammonia and epoxide
- compare X-H bond lengths and hydrogen ADPs

XWR vs. MM

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Two major **advantages** of XWR over the MM:

- Hydrogen atoms are accurately detectable
- Chemical analysis beyond electron density

XWR vs. MM

Universität Bremen

Two major **advantages** of XWR over the MM:

- Hydrogen atoms are accurately detectable
- **Chemical analysis beyond electron density**

Defect density =

Exchange-correlation interaction density
plus noise

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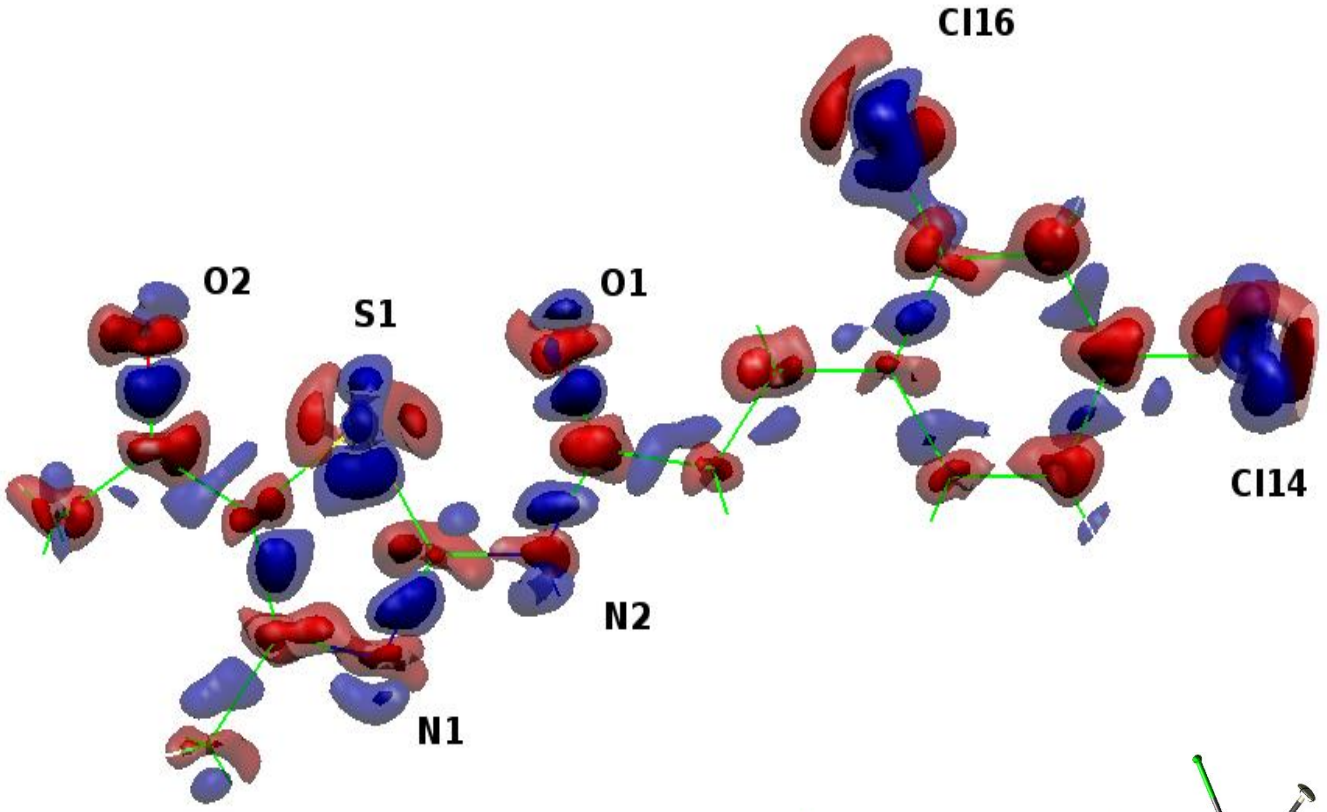
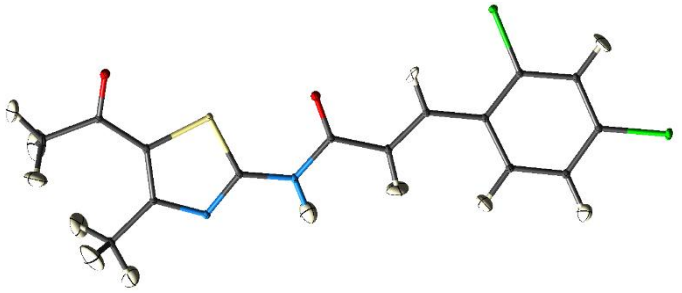
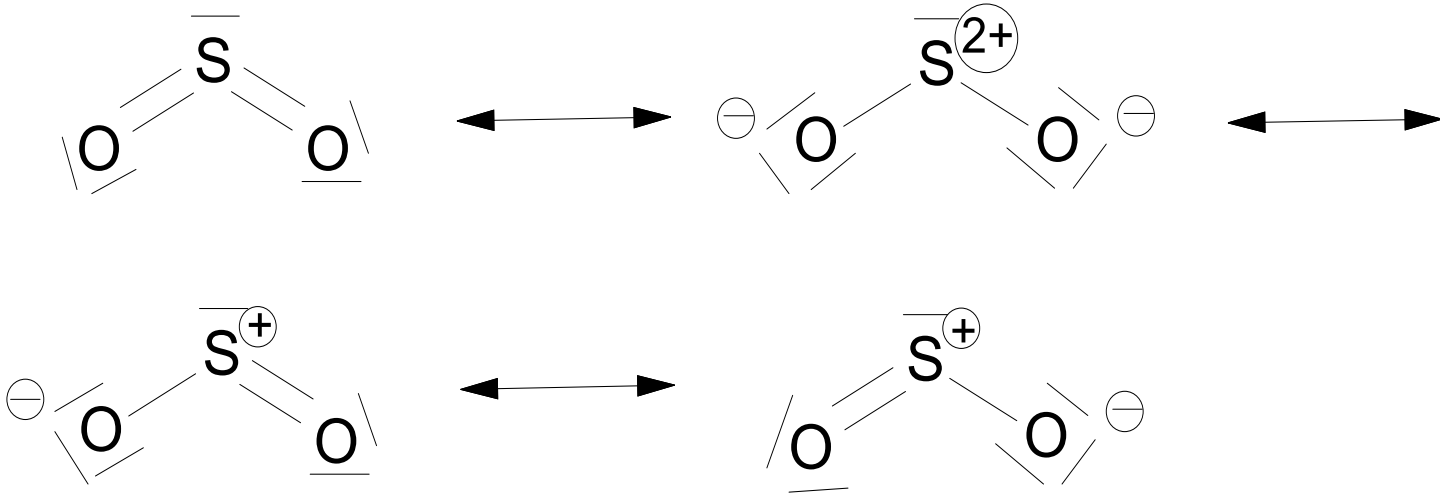




isovalues: 0.05 eÅ^{-3} (solid),
0.025 eÅ^{-3} (faint)

Bond order?



Some widely used textbooks and educational literature state: bond order of 2 (or even higher), sulfur d-orbital participation, hypervalency. **G. H. Purser, J. Chem. Educ. 1989, 66, 710**

Gas-phase experiments and NBO analyses suggest a bond order lower than 2 and no sulfur d-orbital involvement.

D. Powers, H. G. Olson, J. Chem. Phys. 1980, 73, 2271

A. E. Reed, P. Von Rague-Schleyer, J. Am. Chem. Soc. 1990, 112, 1434

Bond order

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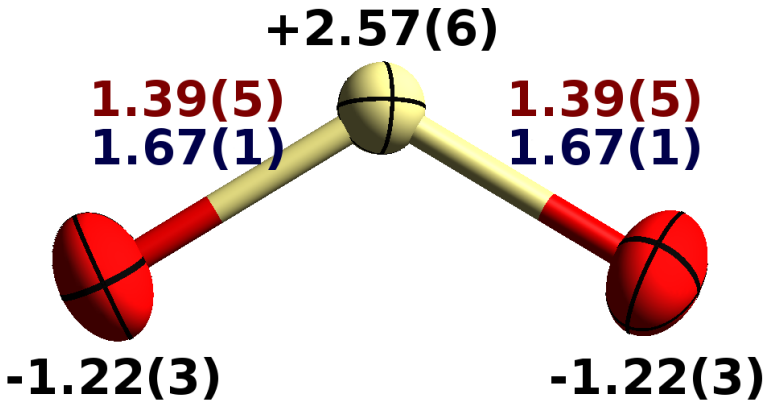
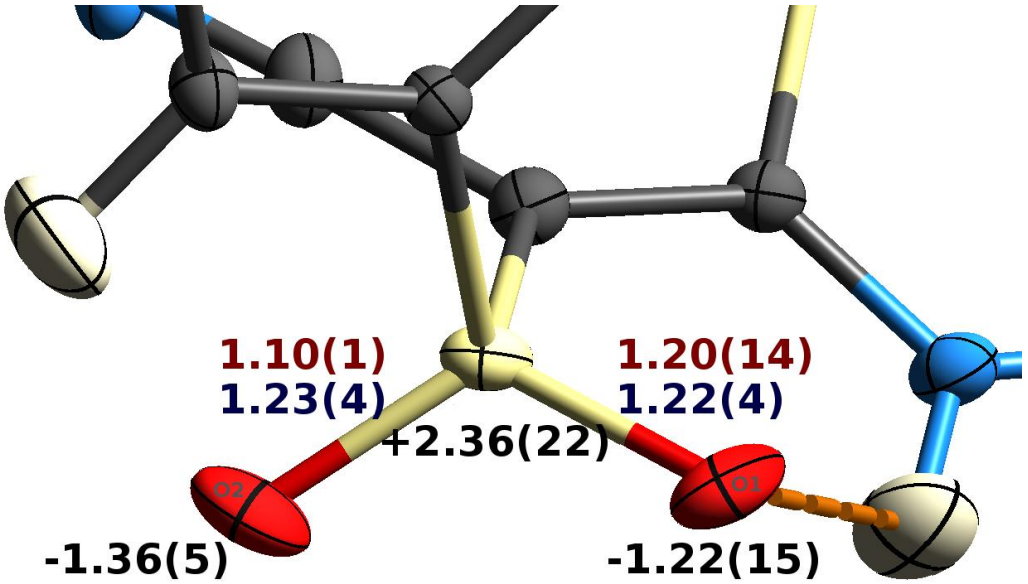
Sulfur dioxide



Sulfonyl group



Delocalization index R. F. W. Bader, M. E. Stephens, J. Am. Chem. Soc. 1975, 97, 7391

Roby bond index M. D. Gould, C. Taylor, S. K. Wolff, G. S. Chandler, D. Jayatilaka, Theor. Chem. Acc. 2008, 119, 275

Electron-pair localization

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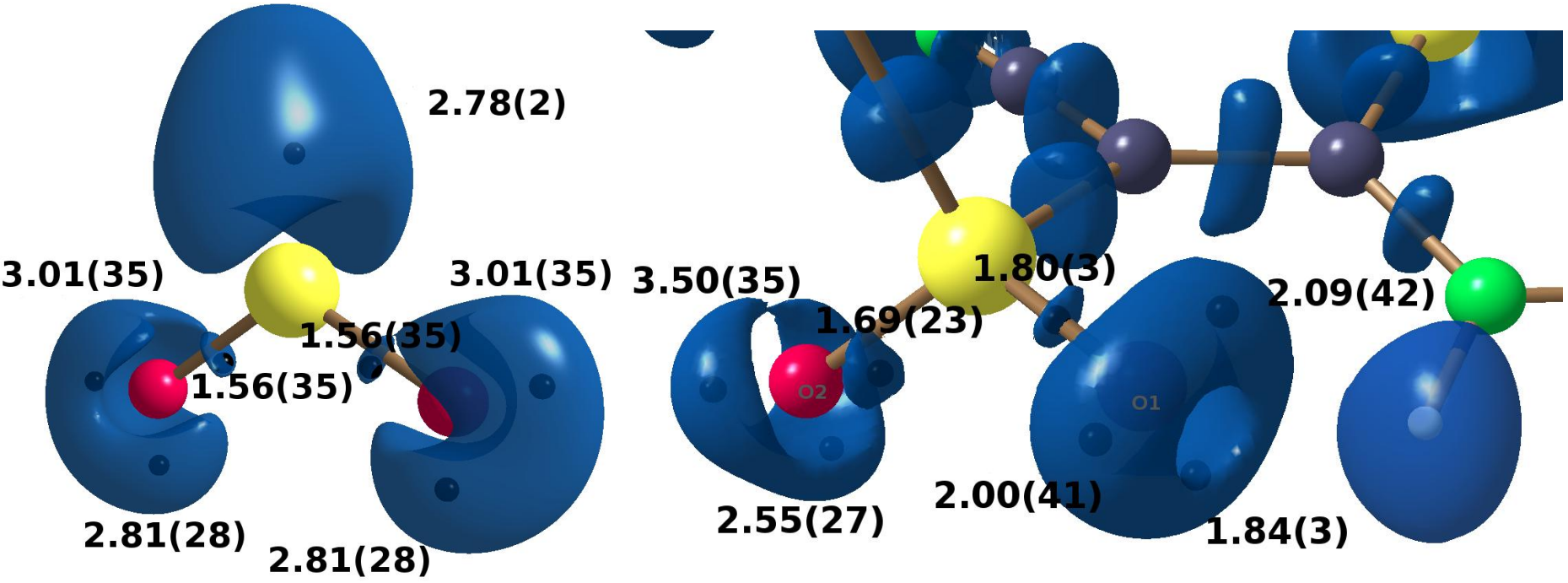
Sulfur dioxide

Sulfonyl group



Valence Populations (Electron Localizability Indicator ELI)

M. Kohout, Int. J. Quant. Chem. 2004, 97, 651

Conclusions

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Angewandte Communications

Angew. Chem. Int. Ed. 2012, 51, 6776 –6779
DOI: 10.1002/anie.201200745

Experimental Bond Orders

The Significance of Ionic Bonding in Sulfur Dioxide: Bond Orders from X-ray Diffraction Data**

Simon Grabowsky, Peter Luger, Jürgen Buschmann, Thomas Schneider, Tanja Schirmeister, Alexandre N. Sobolev, and Dylan Jayatilaka*

- SO_2 is not hypervalent. There are no S=O double bonds. To avoid hypervalency, an ionic description of the S-O bonds prevails.
- Density-matrix derived properties are needed, the electron density itself cannot finally answer the question.
- Experimental data changes the topology.

Tutorial part 2: XCW fitting on epoxide

- running Tonto on Windows
- constructing input and understanding output files

Tutorial part 3: Analysis of structure and constrained wavefunction of epoxide

- Atoms in Molecules topological analysis
- Roby bond index
- 2D maps of electron density and beyond