RUHR-UNIVERSITÄT BOCHUM

Stereochemistry & Chiroptical Spectroscopy
MERTEN LAB

RUB

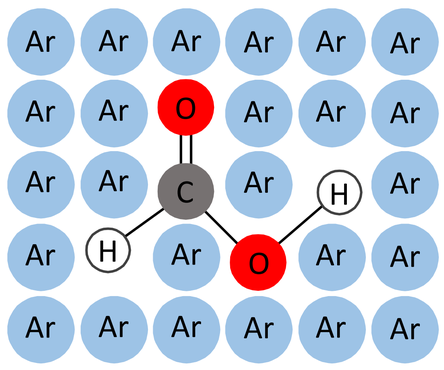
MATRIX EFFECTS IN MI-VCD SPECTRA

THE EFFECT OF TEMPERATURE AND CONCENTRATION

Corentin Grassin, Christian Merten

MATRIX ISOLATION

- Trapping of molecules/reactive intermediates in a non-interacting environment (inert gas)
- Cryogenic temperature (3-70K)
- Study of structure, clustering behaviour and photochemistry[a]
- Coupled with spectroscopy (IR/VCD)



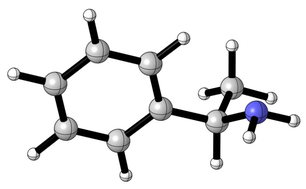
Advantages of MI
- No solvent interference
- Narrow bandwidth
- Detailed analysis possible

Challenges of MI
- Optical quality of matrix
- Conformational cooling
- Analysis can be tricky

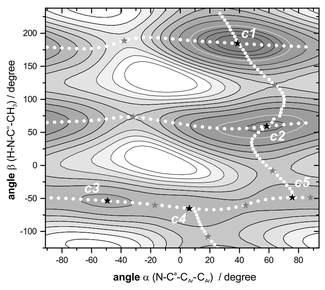
[a] C. H. Pollok, T. Riesebeck, C. Merten *Angew. Chem. Int. Ed.* **56** (2017) 1925-1928

MATRIX EFFECTS

- Unexpected phenomenon[c]
- Frequency shift
- Depolarization
- Physical/Chemical/Cage effects



(R)-α-phenylethyl amine



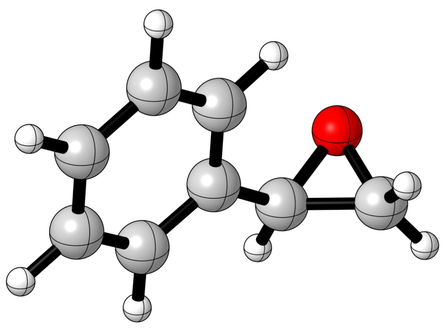
[c] C. H. Pollok, C. Merten *Phys. Chem. Chem. Phys.* **18** (2016) 13496-13502

STYRENE OXIDE

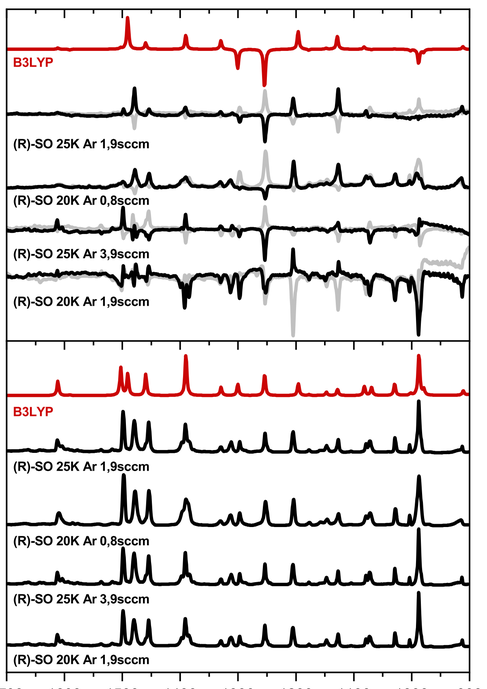
Observations:

- Temperature dependence (5K difference)
- Concentration dependence (0,8-2sccm difference)
- Glassy/blurry deposition[e]

[e] J. W. Nibler, D. A. Coe, *J. Chem. Phys.* **55** (1971) 5133-5134

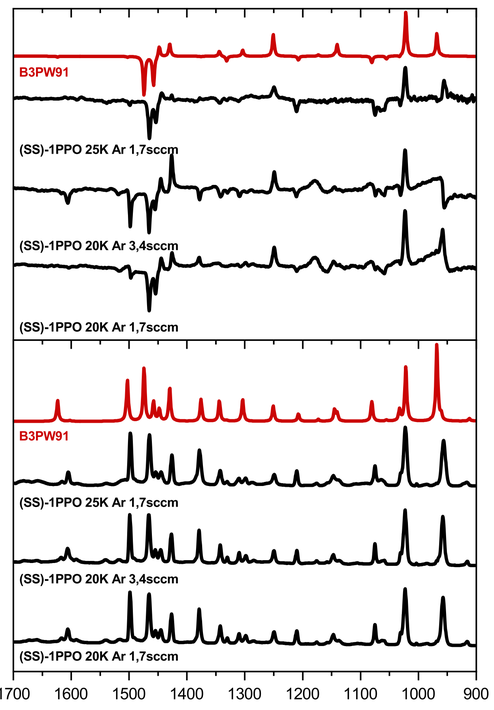


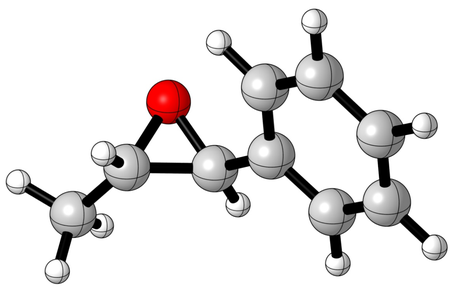
(R)-styrene oxide



Assumptions:

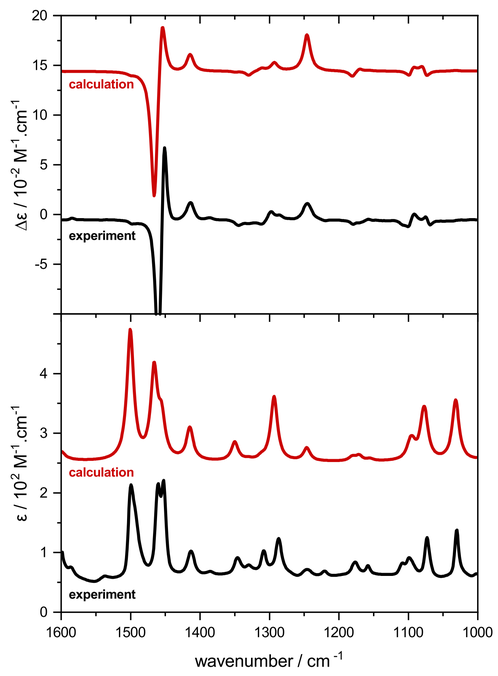
- Artefacts from depolarization
- Preferential stacking of phenyl rings leading to a non-random orientation of guests in Argon lattice





(1S,2S)-1-phenylpropylene oxide

VIBRATIONAL CIRCULAR DICHROISM

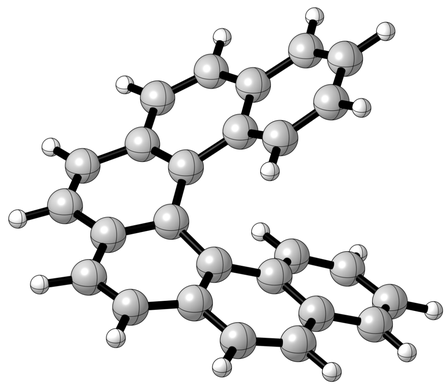


$$VCD = A_{LCP} - A_{RCP}$$

- Chiral version of IR spectroscopy
- AC determination
- Conformational analysis
- Intermolecular interactions[b]
- DFT comparison
- All conformers considered
- example: (SS)-trans-stilbene oxide in CCl_4 bottom: IR spectra ; top: VCD spectra computation: B3LYP/6-311++g(2d,p)

[b] C. Merten *Phys. Chem. Chem. Phys.* **19** (2017) 18803-18812

HEXAHELICENE



(M)-hexahelicene

Observations:

- Temperature dependence (5K difference)
- VCD spectra influenced
- IR spectra unchanged
- New unexpected signals
- Depolarization

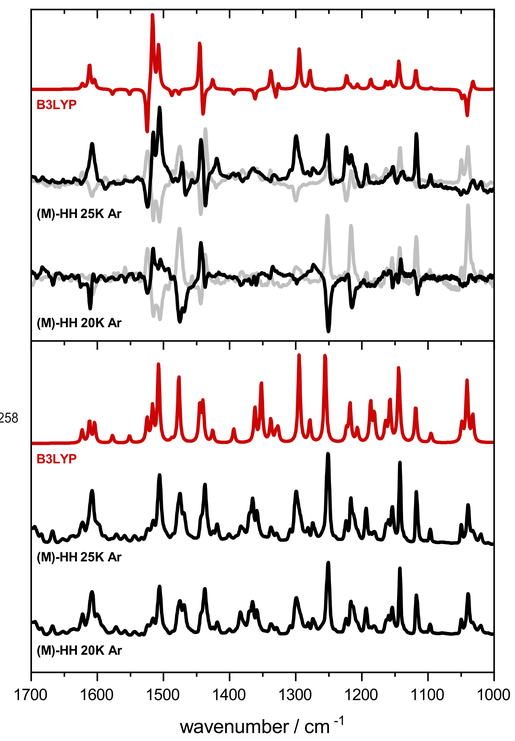
Computational attempts:

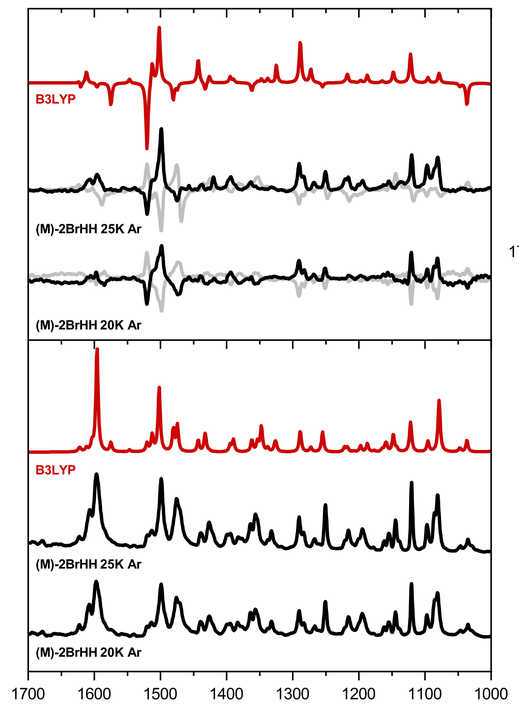
- Dimers/Explicit dispersion forces
- Explicit Argon solvation

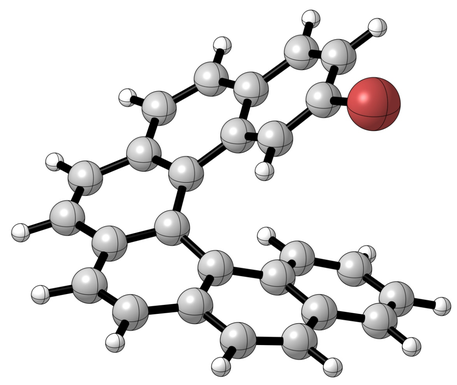
Assumptions:

- Specific stacking
- Different trapping cavities/sites[d]

[d] C. Crépin, P. de Pujo, B. Bouvier, V. Brenner, Ph. Millié, *Chem. Phys.* **272** (2001) 243-258







(M)-2-bromo-hexahelicene

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