

INVESTIGATION OF NITRENES & CHIRALITY IN CRYOGENIC MATRICES

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MOTIVATION:

Paramagnetism & Vibrational Circular Dichroism

The theory: VCD spectroscopy measures difference in absorbance of left- and right-circularly polarized light of vibrational transitions → tool for determination of absolute configurations in combination with quantum-chemical calculations^[1]

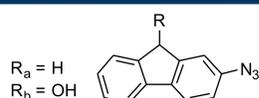
$$\text{VCD} = A_{\text{LCP}} - A_{\text{RCP}}$$

The challenge: open-shell systems (biradicals, carbenes, nitrenes) put theory on VCD implemented in all available computing software to test → approximations of underlying magnetic field perturbation (MFP) theory do not hold for high spin states

The aim: extend scope of VCD structure elucidations beyond closed-shell systems by benchmarking organic molecules with different spin states

The method: combine VCD spectroscopy with matrix isolation

The model system: parent molecule 2-azidofluoren **1a** and its chiral derivative 2-azidofluoren-9-ol **1b**


MATRIX ISOLATION VCD:

Chiral molecules and reactive species in cold solid rare gases

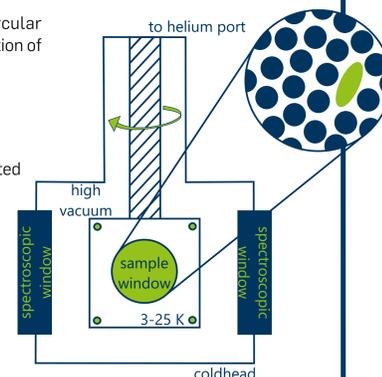
combination of matrix isolation and vibrational circular dichroism spectroscopy (MI-VCD) enables characterization of chiral reactive intermediates

Advantages of MI-VCD

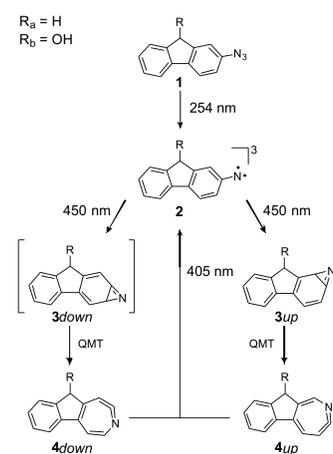
- no solvent interference
- narrow bandwidth
- detailed analysis possible

Challenges of MI-VCD

- optical quality of matrix
- conformational cooling
- analysis often complicated


PHOTOCHEMISTRY:

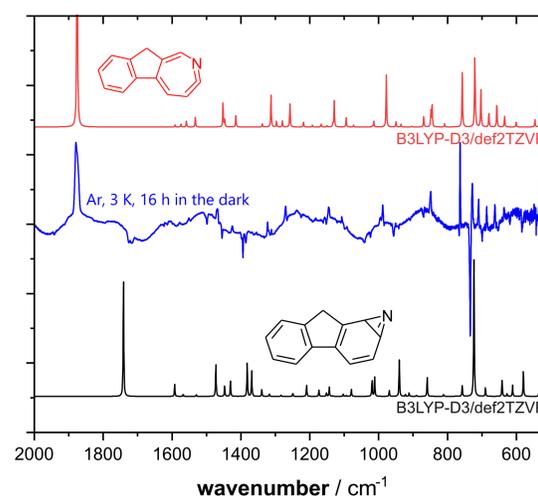
Reversible photo-switching from triplet nitrene to ketenimine



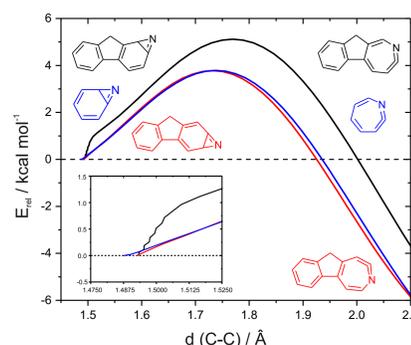
- photolysis of azide **1** at 254 nm generates triplet nitrene **2**
- irradiation at 450 nm triggers rearrangement to ketenimine species **4down** and **4up** via corresponding fluorenylazirine intermediates
- fluorenylazirine **3adown** remains elusive during matrix isolation FTIR experiments → fast quantum mechanical tunnelling (QMT)
- irradiation at 405 nm regenerates triplet nitrene **2**
- photochemical cycle repeatable multiple times
- cf. ultrafast solution experiments by Phillips et al.^{[2],[3]}

ISOMER-SPECIFIC HEAVY-ATOM TUNNELLING:

Ring expansion of fluorenylazirines



- argon matrix containing benzazirine **3aup** left in the dark at 3 K for 16 h, using a cut-off filter to block irradiation $>2000 \text{ cm}^{-1}$
- despite lack of thermal and photochemical energy: experimental difference spectrum (blue) showed ring-opening to ketenimine **4aup**

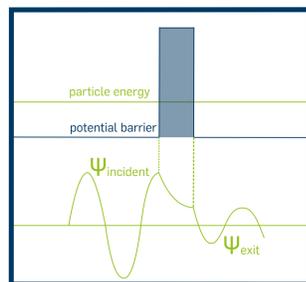
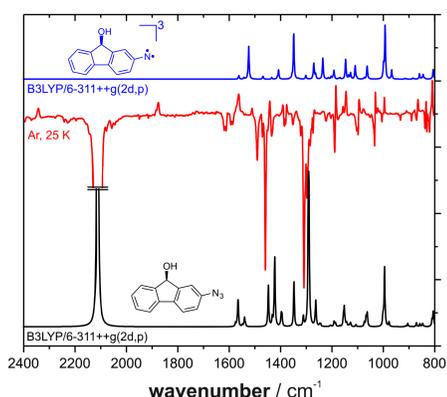


- analysis of kinetic data assuming dispersive behaviour:^[4] rate constants of rearrangement temperature-independent → QMT
- QMT of **3adown** to **4adown** remains undetected → tunnelling rate exceeds time resolution of MI-FTIR experiments?
- estimate of tunnelling probabilities for both isomers by Kozuch's tunnelling approximation^[5]

$$P(E) = \exp[-\pi^2 w \sqrt{2m(V_0 - E)}/h]$$

MI-IR STUDIES:

Matrix effects & preliminary results



- enantiomerically pure 2-azidofluoren-9-ol **1b** isolated in argon at 25 K on CsI window → sublimation at 70°C for 5 h under continuous gas flow
- irradiation at 254 nm generated triplet nitrene **2b**
- no VCD spectrum recorded due to matrix effects of yet unknown nature

ACKNOWLEDGMENTS

J. F. Rowen and F. Beyer gratefully acknowledge their (associative) membership in the GRK 2376 Confinement Controlled Chemistry which is funded by the Deutsche Forschungsgemeinschaft.


REFERENCES

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- [2] S. Y. Ong, P. Zhu, Y. F. Poon, K. H. Leung, W.-H. Fang, D. L. Phillips, *Chem. Eur. J.* 2002, 8, 2163.
- [3] S. Y. Ong, P. Zhu, K. H. Leung, D. L. Phillips, *Chem. Eur. J.* 2003, 9, 1377.
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- [5] S. Kozuch, *PCCP* 2014, 16, 7718.

SUMMARY & OUTLOOK:

Towards MI-VCD studies on chiral reactive intermediates

- isomer-specific heavy-atom tunnelling in ring-expansion of fluorenylazirines **3adown/3aup** observed
- repeatable photochemical cycle of **2a** established
- matrix effects in MI-VCD studies on **1b/2b** detected → optimization of deposition conditions required
- kinetic analysis of rearrangements **3bdown/3bup** to **4bdown/4bup** → further example of heavy-atom tunnelling?

Reactive intermediates not limited to nitrenes → radical **5** and carbene **6** promising targets for MI-VCD studies!

