VCD spectroscopy under cryogenic conditions: Of matrix effects and photochemistry of chiral molecules

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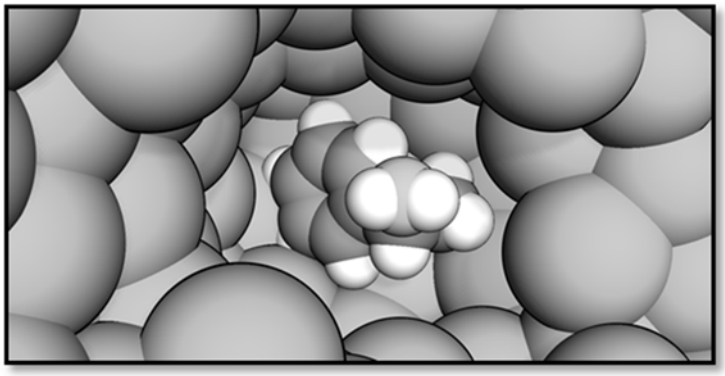
Vibrational Circular Dichroism (VCD) spectroscopy measures the small difference in the absorption of left- and right circular polarized infrared light by a chiral sample. It allows the unambiguous assignment of absolute configurations by comparison of experimental and computationally predicted spectra,[1] but it is also highly sensitive to even very subtle differences in structures, such as conformational changes induced by solute-solvent interactions.[2-3] In our work, we take advantage of this conformational sensitivity and use VCD spectroscopy to probe intermolecular interactions of interest in catalysis[4] and supramolecular chemistry.[5-6]

In this talk I will focus on our activities to combine VCD spectroscopy with the matrix-isolation technique as sample preparation method for the isolation of small molecules and reactive intermediates. Highlighting some recent results, we show that trapping chiral molecules in solid rare gas matrices can help us understand problems faced in the interpretation of solution phase spectra. These challenges in the analysis are, for instance, flat potential energy surfaces[7] or rapidly rearranging photoisomerization products.[8] As matrix effects were found to occasionally make the interpretation of MI-VCD spectra quite challenging, we also implemented an experimental setup to record VCD spectra in liquid rare gases. The first experiments using this cryosolutions-VCD setup helped us to reveal matrix-effects in MI-VCD spectra and to benchmark computational approaches for the prediction of anharmonic VCD intensities.[9]



[1)] Merten, C.; Golub, T. P.; Kreienborg, N. M., Absolute Configurations of Synthetic Molecular Scaffolds from Vibrational CD Spectroscopy. *J. Org. Chem.* **2019,** *84*, 8797. [2)] Scholten, K.; Merten, C., Solvation of the Boc–Val–Phe–nPr peptide characterized by VCD spectroscopy and DFT calculations. *PCCP*. **2022,** *24*, 3611. [3)] Weirich, L.; Merten, C., Solvation and self-aggregation of chiral alcohols: how hydrogen bonding affects their VCD spectral signatures. *PCCP*. **2019,** *21*, 13494. [4)] Merten, C., Recent Advances in the Application of Vibrational Circular Dichroism Spectroscopy for the Characterization of Asymmetric Catalysts. *Eur. J. Org. Chem.* **2020,** *2020*, 5892. [5)] Kemper, M.; Engelage, E.; Merten, C., Chiral Molecular Propellers of Triarylborane Ammonia Adducts. *Angew. Chem. Int. Ed.* **2021,** *60*, 2958. [6)] Weirich, L.; Merten, C., Induced VCD and conformational chirality in host–guest complexes of a chiral ammonium salt with crown ethers. *PCCP*. **2021,** *23*, 18300. [7)] Pollok, C. H.; Merten, C., Conformational distortion of α-phenylethyl amine in cryogenic matrices - a matrix isolation VCD study. *PCCP*. **2016,** *18*, 13496. [8)] Pollok, C. H.; Riesebeck, T.; Merten, C., Photoisomerization of a Chiral Imine Molecular Switch Followed by Matrix-Isolation VCD Spectroscopy. *Angew. Chem. Int. Ed.* **2017,** *56*, 1925. [9)] Kreienborg, N. M.; Bloino, J.; Osowski, T.; Pollok, C. H.; Merten, C., The vibrational CD spectra of propylene oxide in liquid xenon: a proof-of-principle CryoVCD study that challenges theory. *PCCP*. **2019,** *21*, 6582.