

Vibrational Circular Dichroism of a Chiral Triplet Nitrene Investigated under Matrix-Isolation Conditions in para-Hydrogen

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Vibrational circular dichroism (VCD) spectroscopy is an established method for the determination of absolute configurations (AC).¹ It measures the difference in absorbance between left- and right-circularly polarized light by vibrational transitions. The signal intensity of a transition is given by the rotational strength which depends on both the electronic (ETDM) and the magnetic (MTDM) transition dipole moment.

Therefore, VCD spectra of chiral high-spin organic molecules are expected to show a strong intensity enhancement due to the influence of unpaired electrons on the MTDM.² These influences are not assumed to be correctly predicted by the magnetic field perturbation (MFP) theory which was originally developed for closed-shell systems and is implemented in current computational protocols.³

In our study, we isolated chiral triplet nitrene precursor 2-azido-9*H*-fluorenol **1** in para-hydrogen matrices and investigated its properties by matrix-isolation infra-red/vibrational circular dichroism (MI-IR/VCD) spectroscopy. MI-VCD spectra of **1** show satisfactory mirror-image quality and are in agreement with density functional theory (DFT) calculations at B3LYP/6-311++G(2d,p) level of theory. Irradiation at 254 nm formed the triplet nitrene 2-nitreno-9*H*-fluorenol **T-2** whose spectral features are reproduced unexpectedly well by DFT calculations and do not exhibit the anticipated signal intensity enhancement.

Thereby, our experiments demonstrated the general feasibility of MI-IR/VCD spectroscopic studies on chiral high-spin organic molecules and the computational reproducibility of their spectral features.

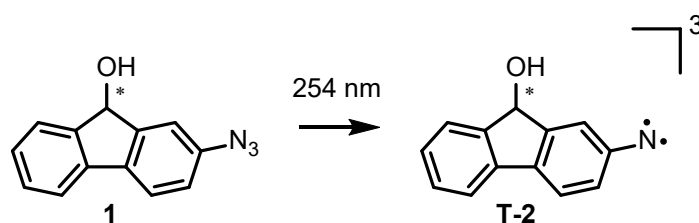


Figure 1: Structure of 2-azido-9*H*-fluorenol **1** and the triplet nitrene **T-2** resulting from photochemical cleavage of N₂.

¹ Merten, C.; Golub, T. P.; Krieborg, N. M. Absolute Configurations of Synthetic Molecular Scaffolds from Vibrational CD Spectroscopy. *J. Org. Chem.* **2019**, *84*, 8797-8814.

² Nafie, L. A. Theory of Vibrational Circular Dichroism and Infrared Absorption: Extension to Molecules with Low-Lying Excited Electronic States. *J. Phys. Chem. A* **2004**, *108*, 7222-7231.

³ Stephens, P. J. Theory of vibrational circular dichroism. *J. Phys. Chem.* **1985**, *89*, 748-752.