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2-Nitreno-9-fluorenylidene – a Quintet Ground State Carbenonitrene

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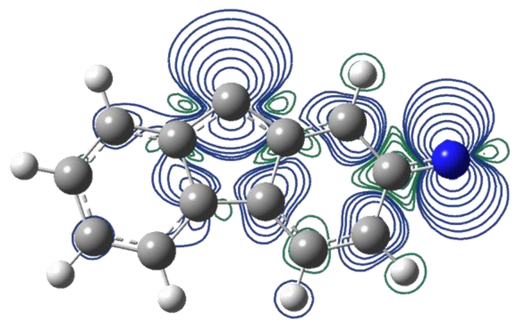

Introduction

Reactive intermediates, such as carbenes and nitrenes, have been the subject of many studies in physical organic chemistry during the past years. Due to their unpaired electrons in the triplet state, these molecules might serve as promising candidates for the development of organic magnets. In order to increase the magnetic properties, molecules consisting of more than one spin center, like ferromagnetically coupled polycarbenes or polynitrenes, have been investigated.[1] However, few research has been conducted on molecules where both, a carbene and a nitrene, are present. In this work, 2-azido-9-diazofluorene and its photochemistry was investigated, which yielded a molecule exhibiting a carbene and a nitrene center with an overall quintet ground state.

Quintet Generation

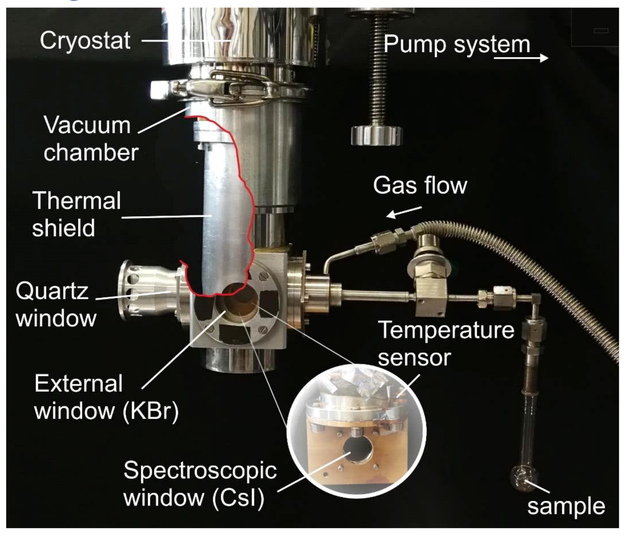

Figure 1. Matrix Isolation setup used for the IR measurements.

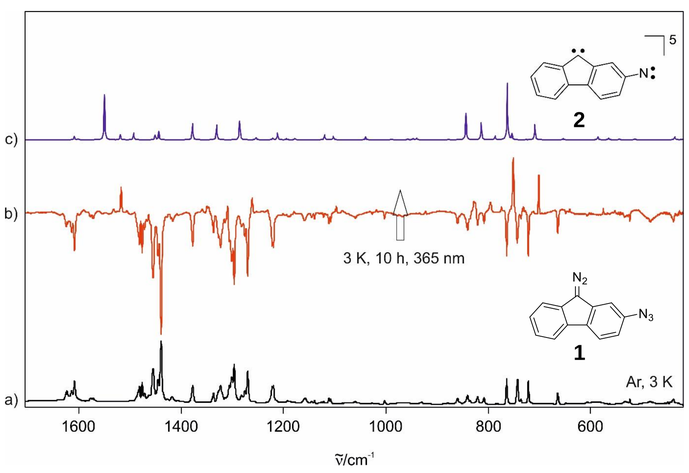

Figure 2. IR spectra showing the formation of the quintet species **2**. (a) Deposition spectrum of **1** in an argon matrix at 3 K. (b) Difference spectrum showing the changes after irradiation with 365 nm for 10 h. (c) Calculated IR spectrum for the quintet species **2** at the B3LYP-D3/def2-TZVP level of theory.

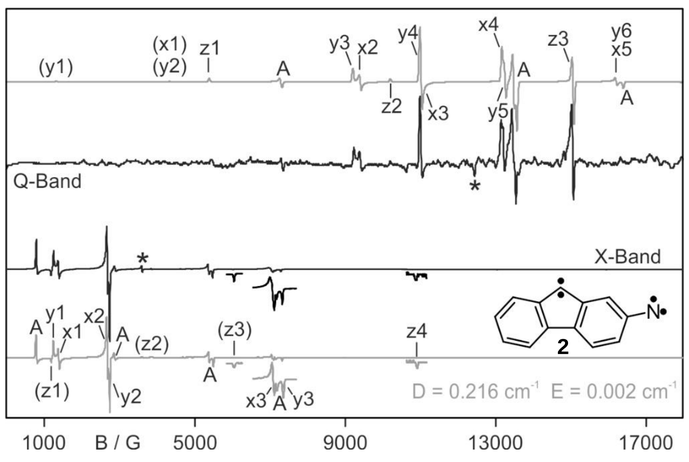

Figure 3. X- and Q-band EPR spectra of the quintet **2** isolated in an argon matrix in comparison to simulated spectra showing the obtained D and E values (D = 0.216 $cm^{-1}$and E = 0.002 cm^{-1}).

Further Photochemistry

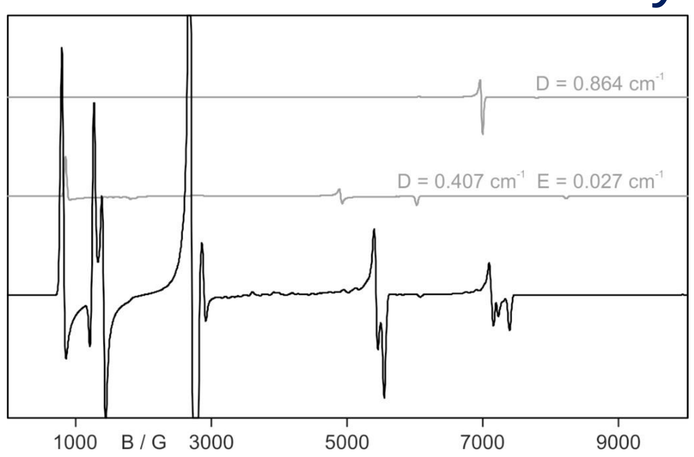

Figure 4. Comparison of the EPR spectrum of the photoproduct of precursor **1** with simulated EPR spectra for triplet 9-fluorenylidene **^{3}Fl** (D = 0.407 cm^{-1} and E = 0.027 cm^{-1}) and triplet 2-nitrenofluorenone (D = 0.864 cm^{-1}).

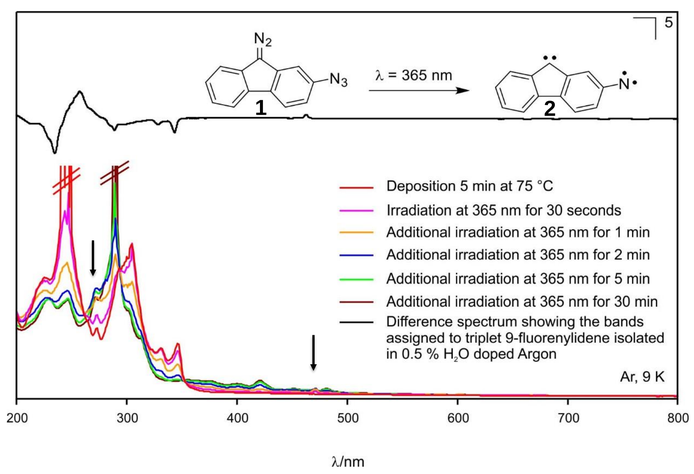

Figure 5. UV/Vis spectra showing the photochemistry of **1** in an argon matrix at 9 K. The red spectrum shows the UV/Vis spectrum obtained after deposition of the precursor. The other colored spectra show the UV/Vis spectra gained after the respective irradiation with a 365 nm LED. The black spectrum shows the UV/Vis spectrum of triplet 9-fluorenylidene **^{3}Fl**.

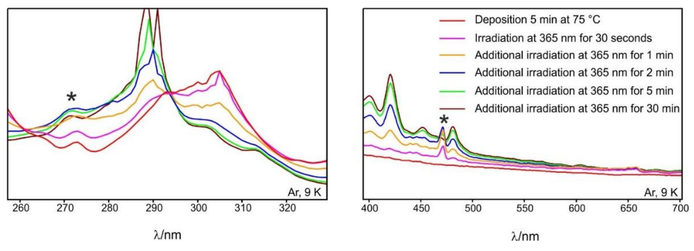

Figure 6. Different wavelength regions of the UV/Vis spectrum shown in **Figure 5** enlarged to show changes during the irradiation of **1**. Notable changes are highlighted with an asterisk.

⇒ Successful generation of the quintet species

⇒ Photochemical side products indicate a stepwise quintet formation

⇒ Investigation of the kinetics of the quintet formation

TA Measurement

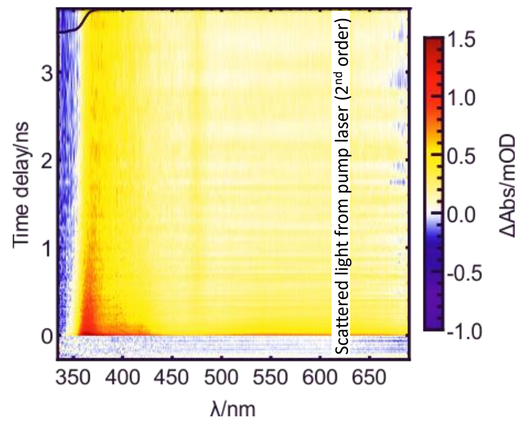

Figure 7. UV/Vis transient absorption (TA) map. The difference in absorbance is plotted against the time delay τ after excitation and the wavelength λ. The colors refer to the intensity of the signals that were observed. The steady-state absorption spectrum is shown in black with a negative sign to compare the measured absorbance difference with it.

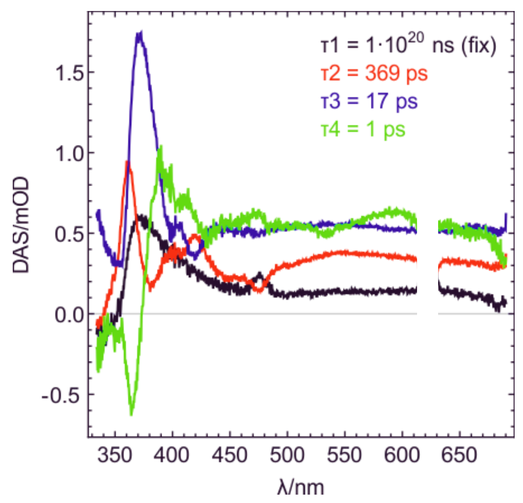

Figure 8. Decay-associated difference spectra of the UV/Vis TA measurement showing the spectral components linked with the lifetimes they were assigned to.

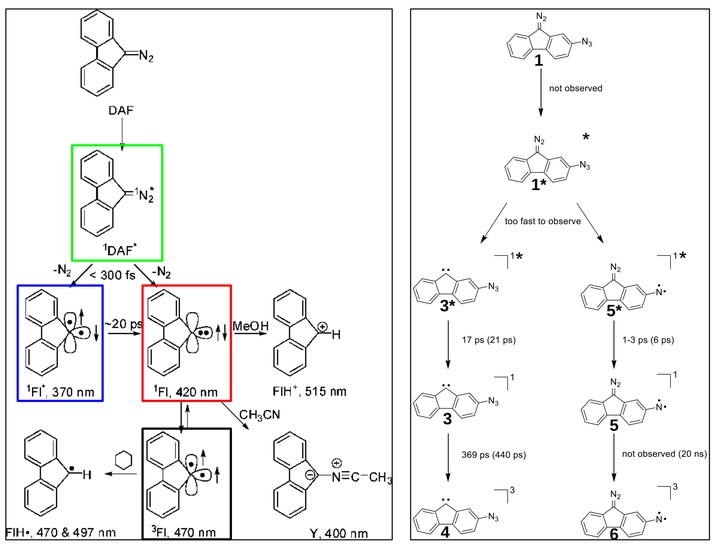

Figure 9. Comparison of the results obtained by Platz et al.[2,3] (left) with the measured data (right). Lifetimes in brackets were taken from measurements of Platz et al. for 9-fluorenylidene **^{3}Fl** as well as 2-nitrenofluorene.[2,3]

Conclusion and Outlook

- Successful generation of the quintet carbenonitrene in an argon matrix
- Matrix UV/Vis spectra indicate a stepwise photolysis of the precursor
- UV/Vis TA measurement shows formation of a carbene and a nitrene
- Data agree with literature, however no quintet species was observed
- Selective photolysis of the diazo or azide functionality
- Isolation in reactive environments such as LDA water ice
- IR TA measurements to verify obtained results
- Study of carbenonitrene formation in nanocrystalline suspensions

References

[1] E. Mendez-Vega, J. Mieres-Perez, S. V. Chapyshev, W. Sander, *Angew. Chem. Int. Ed.* 58, 1-6 (2019).

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Acknowledgement

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