

Species-selective photochemistry of coumarin-cages by VIPER 2D-IR

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We demonstrate the species-selective spectroscopy of a mixture of isotopomers of a photocage. In order to select an isotopomer and monitor its photochemistry, the VIPER 2D-IR pulse sequence is used, employing resonant vibrational pre-excitation followed by an off-resonant visible-pump pulse.

A common approach to trigger biological and chemical reactions uses caged compounds. These cages carry a leaving group (LG) whose release can be induced by light, rendering the uncaging controllable with high spatiotemporal resolution. The achievable temporal resolution does not only depend on the duration of the applied light pulse but also on the uncaging kinetics. In the present work we use the 7-[(diethylamino)coumarin-4-yl]methyl (DEACM) cage, which is one of the fastest cages known [1].

In samples comprising different photocages which have similar absorption spectra the individual species cannot be selectively addressed, because they will all release their cargo upon light irradiation. To circumvent this problem, we used the VIPER 2D-IR pulse sequence [2, 3] on a mixture of two DEACM-N₃ isotopomers which differ only in the position of a ¹³C atom. Their visible absorption spectra are near identical, but by applying the VIPER pulse sequence one isotopomer can be selected for uncaging via vibrational pre-excitation by the IR-pump pulse. The wavelength of the following visible-pump pulse is tuned to be resonant with the electronic transition of the pre-selected molecules. Hence, only the chosen isotopomer is observed to undergo photochemistry and to release its cargo. We compare the experimental results to DFT computations using the FCclasses approach [4] which predict the changes in the UV/Vis spectrum generated by pre-excitation of different vibrational modes.

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