Time-resolved vibrational spectroscopy of coumarin cages which can trigger fast bio/chemical reactions

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The uncaging mechanism of the coumarin cage DEACM has been investigated and uncaging was resolved on a picosecond time scale, putting DEACM among the fastest known photocages. The influence of the solvent environment is investigated for two different attached leaving groups (LGs), i.e. azide and thiocyanate.

To be able to address biological and chemical processes by light enables steering them in time and space. One successful approach uses photocages, consisting of molecules that contain a shielded reactive LG which is released after light absorption and consequently activated. The release of the thiocyanate and azide LGs from the DEACM coumarin cage ([7-(diethylamino)coumarin-4-yl]methyl-LG) is probed by ultrafast visible pump - infrared probe spectroscopy from 100 fs to 3 ns. The ultrafast spectroscopy results are compared to light-induced steady-state FTIR and UV/Vis difference spectra. The used LGs are selected for their vibrational stretch modes which appear in a spectral region that is free from solvent or cage absorption, providing a convenient window for their detection. A previous study based on fluorescence measurements proposed that the cleavage kinetics to take place on a <ns time scale, but the actual release of the LG was not observed.[1] We resolve the release process of azide and thiocyanate by fs-infrared spectroscopy, evident by the disappearance of the bound LG and appearance of the free LG in its anionic form. DEACM is found to be one of the fastest known photocages. Adding water to the solvent acetonitrile mimics a biological environment and is found to decelerate the appearance of the anion. Understanding the full mechanism may assist in the design of photocages that improve the yield of desired reaction products and suppress that of side products.

[1] B. Schade, V. Hagen, R. Schmidt, R. Herbrich, E. Krause, T. Eckardt, J. Bendig, J. Org. Chem. **64**, 9109 (1999).