

How studies of the photochemical interaction of UV radiation with RNA can be optimized

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UV light triggers chemical reactions in DNA and RNA that can lead to deleterious genetic mutations. Quantum control simulations by LMU researchers led by Regina de Vivie-Riedle promise to facilitate future studies of the underlying mechanisms. Credit: psdesign1 / Fotolia.com

A theoretical study of the UV light induced reaction of the RNA-nucleobase uracil, carried out by LMU researchers, suggests that carefully shaped laser pulses can be used to trap the crucial intermediate state for detailed characterization.

LMU researchers led by Regina de Vivie-Riedle, Professor of Theoretical Chemistry at LMU Munich, have developed a concept which suggests how studies of the photochemical interaction of UV radiation with ribonucleic acid (RNA) can be optimized. The energetic photons of

which UV radiation is composed trigger chemical transformations in the nucleotide bases that form the subunits of both DNA and RNA, which may result in deleterious genetic mutations. In order to obtain a better understanding of the molecular mechanism that leads to such photodamage, the dynamics of purified samples of RNA and DNA bases are extensively investigated with [ultrashort laser pulses](#) with a view to characterizing transient intermediates that arise in the course of the photochemical reaction. The problem with this approach is that the excited molecules very rapidly release the energy injected by the short laser pulse. "This phenomenon of photorelaxation is regarded to be an inbuilt protective response that minimizes the risk of photodamage, but it also makes it very difficult to learn much about the [excited state](#) itself," as Daniel Keefer, a member of de Vivie-Riedle's group explains.

Together with Spiridoula Matsika, a former Humboldt Fellow at LMU from Temple University in Philadelphia, Regina de Vivie-Riedle and her co-workers demonstrate how the ultrafast relaxation process in the compound uracil, one of the RNA bases, can be controlled with tailored light fields. This study also shows how the excited state can be effectively 'trapped' to facilitate its characterization. The basic idea is to shape the laser pulse in such a way that the molecule remains in the excited state for longer (over 50 picoseconds instead of 190 femtoseconds) – rather as if the process of relaxation into the ground state was temporarily interrupted by pressing the Pause button. The results and their implications are described in the *Journal of the American Chemical Society*.

Earlier experiments that employed femtosecond laser pulses to excite uracil served as the starting point for the new study. The LMU researchers optimized the exciting [laser pulses](#) with respect to various control aims, achieving both an acceleration and a significant extension of the excited state lifetime by almost 30-fold. Especially this trapping in the crucial state opens the path for follow-up spectroscopic studies of the

reaction which leads to photodamage. Moreover, these results should be applicable to the other bases found in nucleic acids. "We are confident that our model will facilitate future studies of the reaction mechanisms that lead to photodamage of nucleotides," says de Vivie-Riedle.

More information: Daniel Keefer et al. Controlling Photorelaxation in Uracil with Shaped Laser Pulses: A Theoretical Assessment, *Journal of the American Chemical Society* (2017). [DOI: 10.1021/jacs.6b12033](https://doi.org/10.1021/jacs.6b12033)

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