

# Infrared pre-excitation grants isotopomer-specific photochemistry

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**Abstract.** Species-selective photochemistry is often hampered by overlapping UV-Vis spectra. We overcome this long-standing problem by combined vibrational and electronic excitation as demonstrated by isotopomer selection. The influence of various factors on selectivity is discussed.

## 1 Introduction

In solution and at room temperature, UV-Vis spectra of similar molecules are generally broad and superimposed. Many applications are conceivable where the individual addressing of one of such species within the ensemble would be beneficial. One example is orthogonal uncaging, where one specific photocage can be chosen to release its cargo upon the absorption of light, even in presence of a similar but not identical second cage.

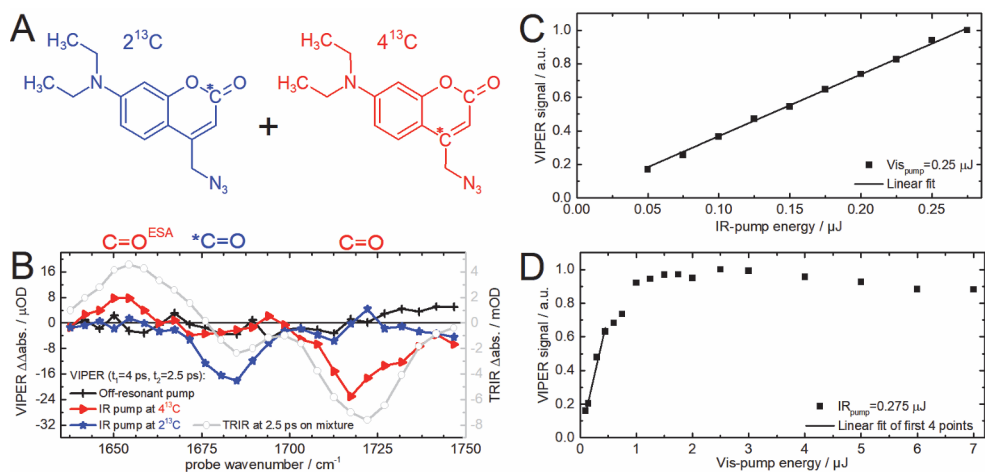
Here we present a extreme test case for such a scenario, by choosing a photocage mixture of two isotopomers (see Figure 1A). In order to induce and monitor species-selective photochemistry, the ultrafast VIPER (Vibrationally Promoted Electronic Resonance) pulse sequence is employed. [1,2] This method utilizes the high degree of molecular specificity in the infrared (IR) spectrum, which is in contrast to the generally occurring broad overlapping features in the UV-Vis spectrum. A narrow band species-specific vibrational pre-excitation is followed here by a non-resonant UV-Vis pulse. The IR pre-excitation shifts the molecules into resonance with the UV-Vis pulse, leading to electronic excitation and thus uncaging. The vibrational mode dependency of this effect is modelled by computations. [3] The experimental parameters on which the used two-photon process relies, such as the Vis and IR pulse energies, are also explored.

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## 2 Optimization and modelling of species-specific VIPER

The system on which the VIPER effect is applied here, is the coumarin-based DEACM photocage. [4,5] Our cage (see Figure 1A) has an attached azide as a release group which splits off after electronic excitation. [5] Isotope labeling this cage on the coumarin ring system (at the carbonyl:  $2^{13}\text{C}$ , or near the leaving group:  $4^{13}\text{C}$ ) does not affect the uncaging mechanism nor the UV-Vis spectral properties. [6] Both the ring modes as well as the carbonyl mode are shifted by introducing  $^{13}\text{C}$ . The uncaging process can be followed by monitoring the isotopomer's carbonyl mode, which allows for clear distinction of the isotopomers. Resonant Vis excitation (via Vis-pump IR-probe, or Time Resolved InfraRed -TRIR- in short) of a mixture of both isotopomers in solution leads to superimposed uncaging features of both species (see Figure 1B, grey open spheres, collected at 2.5 ps delay). In contrast, applying the mode-specific VIPER pulse sequence to the same mixture, isotopomer-specific features appear, depending on which IR mode of which molecular species has been excited (red and blue curves). If the IR pulse is off-resonant with either species, no signal is observed (black curve). [6] Thus, the VIPER data only reports on the electronic excitation of the vibrationally pre-excited species, even in co-existence with a second near identical molecule.



**Fig. 1.** A Chemical structures of the two DEACM isotopomers, with  $^{13}\text{C}$  at position 2 ( $2^{13}\text{C}$ ; blue molecule) and at position 4 ( $4^{13}\text{C}$ ; red). The isotopomer is marked with a star. B Comparison of the VIPER and TRIR data on a 40/60 mixture of  $2^{13}\text{C}/4^{13}\text{C}$ . Above the graph the mode assignments are given, with ESA denoting the electronically excited state. The TRIR data are obtained with resonant Vis excitation at 400 nm. For the VIPER experiment, the delays represent the timings of the  $\text{IR}_{\text{pump}}$  ( $t_1$ ) and the off-resonant  $\text{VIS}_{\text{pump}}$  ( $t_2$ ; centered at 437 nm) pulses with respect to the  $\text{IR}_{\text{probe}}$  pulse. C-D Optimization study of coumarin 6, depicted together with linear fits to the data (black lines). C The normalized VIPER signal scales linearly with the  $\text{IR}_{\text{pump}}$  pulse energy. D The normalized VIPER signal grows only linearly for low  $\text{VIS}_{\text{pump}}$  powers.

We also find that the size of the VIPER signal is currently limited by the IR pulse energy available to us, and not by the available Vis pump power (see Figure 1C-D for data on coumarin 6). The latter shows a clear saturation effect. It is interesting to note that the VIPER effect of both coumarin 6 [1] and that of the DEACM photocage (Figure 1B) is more pronounced when the IR pump pulse is resonant with the lower wavenumber one of

the two most intense ring modes in the range around  $1580\text{ cm}^{-1}$ - $1610\text{ cm}^{-1}$ . That is found for both isotopomers as well as the unlabelled compound.

Quantum chemical computations reveal that the shift of the UV-Vis spectrum is mode-dependent. The electronic spectrum shifts more if the electronic transition involves the same structural region of the molecule as the pre-excited normal mode, consequently resulting in a strong vibronic coupling. The electronic spectrum shift is most pronounced for IR excitation of modes which are significantly displaced during the vibrational transition. [3] In essence, the computations show the same mode-dependency as found experimentally.

### 3 Conclusion and Outlook

Our demonstration of triggering and tracking of isotope-selective photochemistry in solution paves the way for the VIPER pulse sequence to follow and control other, more complex chemical and biological systems.

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