

Vibrational coherence spectroscopy applied to biomimetic molecular switches.

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Ultrafast C=C double bond photoisomerization converts light energy in mechanical energy at the molecular scale and may therefore be exploited in molecular devices for functional switching or rotary motion.[1] In the rhodopsin protein (Rh), the sensor for vision, the ultrafast photoisomerization of the protonated Schiff base of retinal (PSBR) triggers the protein activity. This photoreaction has outstanding speed and quantum yield and it appears to be vibrationally coherent, meaning that the energy of the absorbed photon is efficiently funneled into the isomerization coordinate on a time scale faster than energy dissipation to the environment. This unique property is the promise for an optimum photomechanical energy conversion. Following a biomimetic approach, the N-alkylated indanylidene-pyrrolinium (NAIP) molecular framework (see Figure 1A) was designed and synthesized such that its π -electron system would mimic that of PSBR in Rh. Consequently, its photoreaction dynamics in solution was shown to be very similar to that of Rh [2], including signatures of low-frequency vibrational coherence in the photoproduct ground state[3].

Here we apply a recently built experimental set-up utilizing sub-8fs pulses to perform vibrational coherence spectroscopy [4] on the NAIP compounds. While performing transient absorption spectroscopy with such short, spectrally broad pulses, one may resolve the signatures of the electronic population kinetics as well as vibrational dynamics along the photoreaction, in the form of overlapping oscillatory signals (see Figure 1). Comparing experimental results obtained with on- and off-resonance excitation allows us to discriminate ground state from excited state vibrational activity.

Importantly, the vibrational activity and photoreaction dynamics are critically influenced by the methyl substitution on carbon C5. In fact, the C5-non-methylated compound displayed in Figure 1A does not display any of the signatures of the vibrationally coherent photoreaction observed in the C5-methylated compounds [3]. In particular, the observed vibrational activity does not survive the excited state decay in the former compound. The molecular origin of the influence of the C5 methylation on the onset of a vibrationally coherent photoreaction is under computational investigation.

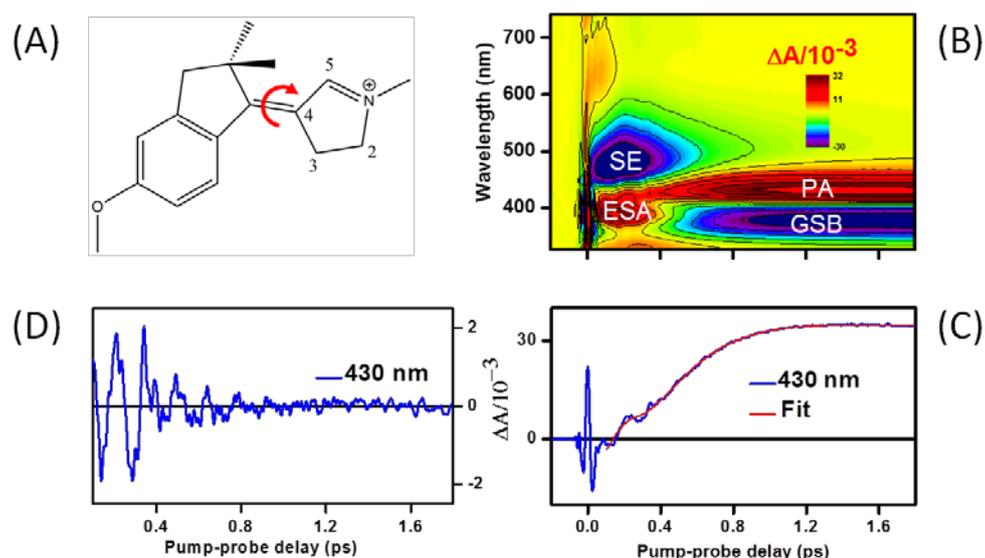


Figure 1: (A) The NAIP compound of interest here carries a hydrogen atom on carbon C5. (B) 2D map representation of the transient absorption data recorded on this compound with a resonant 8-fs pump pulse centered at 400nm. (C) Illustration of the multiexponential global fitting of the electronic population decay kinetics, at the specific wavelength of 430nm. (D) The oscillatory residuals of the fit reveal the vibrational dynamics accompanying the photoreaction. The Fourier transform of this trace is dominated by a 232 cm^{-1} mode attributed to excited state vibrational activity.

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