Spectroscopy and photoisomerization of protonated Schiff-base retinal derivatives *in vacuo*

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The protonated Schiff-base retinal (RPSB) is responsible for many light triggered reactions in nature. Among them is vision in mammals, where upon absorption of a photon the retinal chromophore undergoes isomerization from its native 11-*cis* configuration to the all-*trans* configuration[1], starting a process which eventually sends a signal to the brain. In the rhodopsin protein in the eye the isomerization occurs within 200 fs[2] with a high quantum yield of 67 %, while in gas phase the isomerization from 11-*cis* to all-*trans* occur within 400 fs and the isomerization from all-*trans* to 11-*cis* occur within 3 ps[3].

To further understand this important biochromophore, we examine how the absorption and dynamic of RPSB changes when steric constraint are introduced to the molecule. Three derivatives of RPSB are examined, including C_9=C_{10} *trans*-locked, C_{13}=C_{14} *trans*-locked and a retinal derivative without the β-ionone ring.

The absorption in the visual regime was fairly similar for all three derivatives. The major differences in the absorption spectra was found in the UV. Measurements of the excited-state lifetimes showed that by introducing steric constraints, the potential-energy landscape of the chromophore is changed in a way which is not intuitively clear. Locking a single carbon bond does not only correspond to closing of a specific isomerization path with an increased lifetime as a result. Locking the C_9=C_{10} bond in the *trans* configuration results in a single decay path out of the first excited state with a lifetime of (717 ± 34) fs. Locking the C_{13}=C_{14} bond in the *trans* configuration results in a two-component decay with a short lifetime of (869 ± 98) fs. Note that these lifetimes are both shorter than the 3 ps observed for the unlocked all-*trans* retinal chromophore. Removing the β-ionone ring results in a single exponential decay with a lifetime of (895 ± 59) fs.

Our work shows that by introducing chemical modifications, both the absorption and excited-state dynamics of gas phase protonated Schiff-base retinal may be significantly altered.

References

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