

Exploring vibrational dynamics of Anabaena Sensory Rhodopsin by Pump Impulsive Vibrational Spectroscopy

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Cis-trans isomerization of retinal chromophore is one of the most important photo-chemical reactions in nature. It plays a major role in many fundamental physiological processes like photo-synthesis, vision etc. Anabaena Sensory Rhodopsin (ASR) is one of the microbial retinal proteins (MRP) which is believed to play a vital role in gene expression of eubacteria.^[1] It is a unique MRP which can bind both 13-cis (13C) and all-trans (AT) isomers in ground state.^[2] 13C isomer shows faster kinetics but smaller quantum yield (QY) compared to AT isomer.^[3,4] On the contrary, it has been observed for bovine rhodopsin faster kinetics lead to higher QY of the reaction.^[5] This raises the long standing question on how kinetics and quantum yield are related. Vibrational coherent Raman technique like pump-impulsive vibrational spectroscopy (pump-IVS) (fig.1) has been found to be useful to shed new light on this issue. This is advantageous

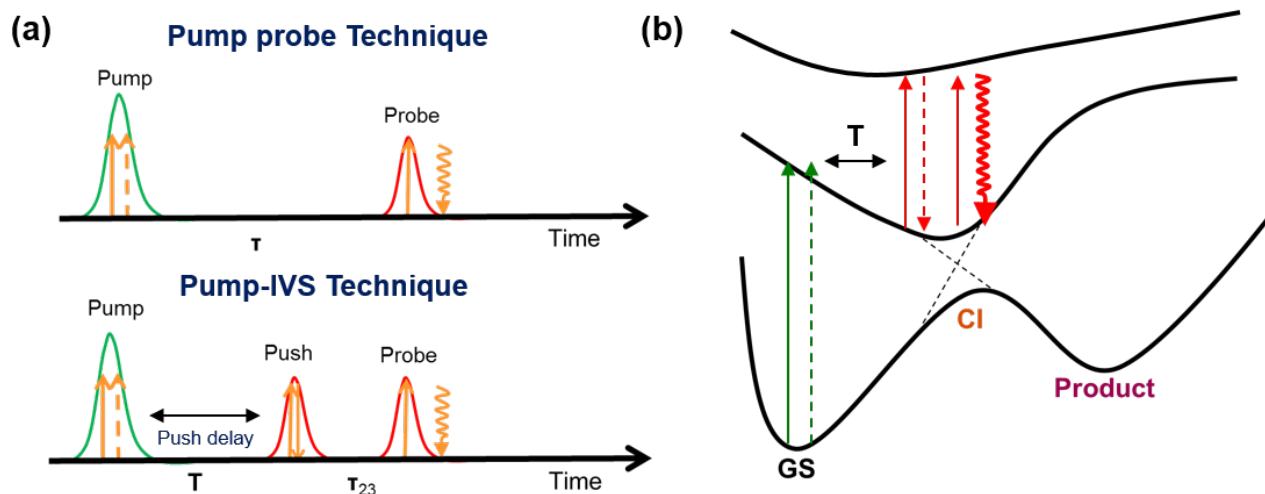


Figure 1: Pump- impulsive vibrational spectroscopic technique: (a) higher order analogue of Pump-probe spectroscopy where 'Push'-pulse re-induces the vibrational coherences in excited state (b) excited state dynamics can be tracked by varying the push delay (T).

because it is capable of tracking population as well as vibrational dynamics which opens a new dimension to follow the reaction. Information about the change in vibrational modes, due to structural change, can act as a bridge between the kinetics and QY.

Our study addresses: which vibrational modes are active at different part of the potential energy surface (PES) and how the modes evolve when it passes through conical intersection (CI). In this work, pump-IVS with time resolution $<20\text{fs}$ is used to capture the vibrational dynamics in ground state (GS) as well as excited state (ES) and disentangle them. Excitation pulse (sub-13 fs), resonant with the GS absorption of the chromophore, is used for this experiment. The push and probe pulse (15 fs) were made resonant to photo-induced absorption of the molecule. This study captures the change in vibrational signature in low frequency as well as in fingerprint region up to 2000 cm^{-1} as the reaction proceeds. Strong GS vibrational mode around 810, 1010 and 1540 cm^{-1} were observed, which matches the spontaneous Raman spectrum of the molecule. Strong increase of vibrational modes around 180 and 1340 cm^{-1} at certain push delays (fig.2)

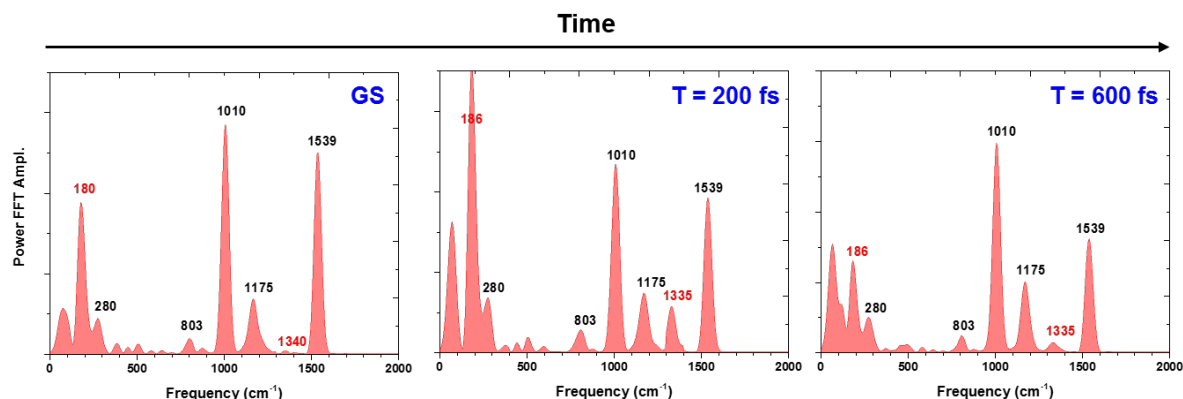


Figure 2: Change in vibrational mode of as the reaction proceeds at different time: Ground state, $T=200\text{ fs}$, $T=600\text{ fs}$ for light adapted ASR which contains mixture of AT and ^{13}C -isomer. Same feature is also observed for dark adapted ASR which contains almost pure AT-isomer.

confirms their activity in the ES PES. The pure contributions of each of the species AT, ^{13}C GS isomer and their corresponding photo-products (K_{AT} and $\text{K}_{^{13}\text{C}}$) were extracted and compared. This enables us to assign the $\text{C}_{14}\text{-C}_{15}\text{-H}$ in-plane-rock to be responsible for 1340 cm^{-1} mode. Furthermore, correlation between population and vibrational dynamics was derived: this enables to disentangle the contribution of species appeared at different part of PES. In summary, our study shows the evolution of vibrational dynamics from the Franck-Condon to photoproduct region through CI.

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References:

- [1] S. Y. Kim, S. R. Yoon, S. Han, Y. Yun, K-H. Jung *Mol. Microb.*, **2014**, 93, 403
- [2] A. Kawanabe, Y. Furutani, K-H. Jung, H. Kandori *J. Am. Chem. Soc.*, **2007**, 129, 8644
- [3] A. Wand, R. Rozin, T. Eliash, K-H. Jung, M. Sheves, S. Ruhman *J. Am. Chem. Soc.*, **2011**, 133, 20922
- [4] A. Cheminal, J. Leonard, S. Y. Kim, K-H. Jung, H. Kandori, S. Haacke *Phys. Chem. Chem. Phys.*, **2015**, 17, 25429
- [5] D. Polli, P. Altoe, O. Weingart, K. M. Spillane, C. Manzoni, D. Brida, G. Tomasello, G. Orlandi, P. Kukura, R. A. Mathies, M. Garavelli, G. Cerullo *Nature*, **2010**, 440, 467