Fifth-order impulsive stimulated Raman spectroscopy for visualizing vibrational coupling in reactive excited states

Kuramochi, Hikaru; Tahara, Tahei

2020

Kuramochi, H., & Tahara, T. (2020). Fifth-order impulsive stimulated Raman spectroscopy for visualizing vibrational coupling in reactive excited states. Proc. Of the 7th Asian Spectroscopy Conference (ASC 2020). doi:10.32655/ASC_8-10_Dec2020.21

<https://hdl.handle.net/10356/144238>

https://doi.org/10.32655/ASC_8-10_Dec2020.21

Fifth-Order Impulsive Stimulated Raman Spectroscopy for Visualizing Vibrational Coupling in Reactive Excited States

Hikaru Kuramochi^{1,2} and Tahei Tahara^{3,4}

¹ Institute for Molecular Science, 38 Nishigo-naka Mjyodaiji, Okazaki 444-8585, Japan

² PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi 332-0012, Japan

³ Molecular Spectroscopy Laboratory, RIKEN, 2-1 Hirosawa, Wako 351-0198, Japan

⁴ Ultrafast Spectroscopy Research Team, RIKEN Center for Advanced Photonics (RAP), 2-1 Hirosawa, Wako 351-0198, Japan

E-mail: hkuramochi@ims.ac.jp

Abstract

Chemical reactions proceed on the complex potential energy surface (PES), which consists of a vast degree of freedom of nuclear coordinates for polyatomic molecular systems. For unraveling (and manipulating) the reaction coordinate and molecular mechanisms that underlie the reaction, it is desirable to map out the PES, which has been a long-lasting central subject in both experimental and theoretical chemistries. In this quest, understanding of the vibrational coupling between normal mode coordinates is essential, since it actually characterizes the complex shape of the PES.

Fig. 1: (A) Schematic illustration of the optical process involved in the present fifth-order impulsive stimulated Raman measurement. (B) Two-dimensional frequency-frequency correlation map obtained by fifth-order impulsive stimulated Raman spectroscopy of PYP.

Here, we report fifth-order time-domain Raman spectroscopy of a bacterial photoreceptor, photoactive yellow protein (PYP), with the aim to visualize vibrational coupling in its reactive excited state. After the ultrashort actinic pump pulse prepared the vibrational coherence as well as population in the excited state, the evolving vibrational structure was tracked by time-resolved impulsive stimulated Raman spectroscopy using sub-7-fs pulses (Fig. 1A) [1,2]. The obtained fifth-order time-domain Raman data were translated to a two-dimensional (2D) frequency-frequency correlation map (Fig. 1B), which visualizes the correlation between low- and high-frequency vibrational modes of the excited state. The 2D map of PYP reveals a cross peak, indicating the coupling between the phenolic C-O stretch mode of the PYP chromophore and the low-frequency modes (~ 160 cm⁻¹) that are assignable to the intermolecular motions involving the surrounding hydrogen-bonded amino acids. The unveiled coupling suggests the importance of the role of the low-frequency vibrational motion in the primary photoreaction process of PYP, highlighting the unique capability of this new spectroscopic approach for studying ultrafast reaction dynamics [3].

Keywords: Ultrafast spectroscopy, Photoreceptor, Impulsive stimulated Raman scattering

References:

- [1] H. Kuramochi, et al., *Rev. Sci. Instrum.*, **2016**, 87, 043107.
- [2] H. Kuramochi, et al., *Nat. Chem.*, **2017**, 9, 660.
- [3] H. Kuramochi, et al., *Sci. Adv.*, **2019**, 5, eaau4490.