

# Identification of the transition states by real-time vibrational spectroscopy

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The experimental visualization of the transition states (TSs) during chemical reactions is desirable to fully understand the reaction mechanisms. The technology to generate ultrashort pulses has developed from the late 1980s. In 2002, Kobayahi group generated the stable visible-near infrared sub-5-fs laser pulses. Utilizing such short pulses, it is now possible to identify the TSs with a pump-probe measurement. Typical molecular vibrations, such as carbonyl stretching modes or C=C stretching modes, have vibration periods in the 20 fs range. Therefore, molecular vibration can be real-time observed using the sub-5-fs pulses, and the molecular structural changes during chemical reactions including the TSs can be traced as the instantaneous frequencies of molecular vibrations.

In this work, I tried to clarify the reaction mechanisms using the sub-5-fs laser pulses, supported by theoretical calculations. I found interesting results of proton transfer (PT) in the photo-reaction and Claisen rearrangement in the thermal-reaction.

At first, the structural change during ultrafast PT in the electronic excited state was observed. As a result, photo-excitation PT takes place in indigo carmine by the stepwise mechanism (Figure 1). Moreover, the result gives the answer to why indigo is photo-stable over extremely long period. The photo-decoloration of indigo carmine, which is caused by photo-isomerization, was suppressed by a single PT after photo-excitation. However, the unstable mono-enol intermediate generated by the single PT then reverted to the reactant indigo compound.

As a next step, I examined the reaction mechanism of Claisen rearrangement. The excited vibrational states were produced by the broadband visible sub-5-fs pulses by the Stimulated Raman process and a “non-thermal” Claisen rearrangement in the electronic ground state were observed. The Claisen rearrangement was found to follow a three-step pathway (Figure 2). In the first step, the C<sup>4</sup>-O<sup>3</sup> bond is weakened to generate a bis-allyl-like intermediate. Next, the formation of a weak C<sup>1</sup>-C<sup>6</sup> bond results in the generation of a six-membered intermediate. Finally, C<sup>4</sup>-O<sup>3</sup> breaking and C<sup>1</sup>-C<sup>6</sup> formation occur simultaneously (i.e., in a concerted process) to generate the product.

In this way time-resolved spectroscopy with few-fs-time resolution allows to observe real-time vibrational amplitudes of molecules and opens up a new way to clarify the reaction mechanisms or develop new chemical reactions.

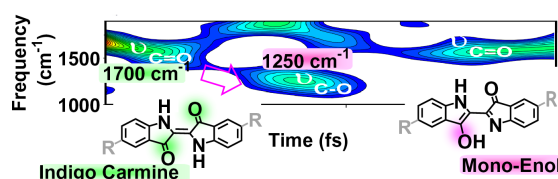


Figure 1. Spectrogram of proton transfer

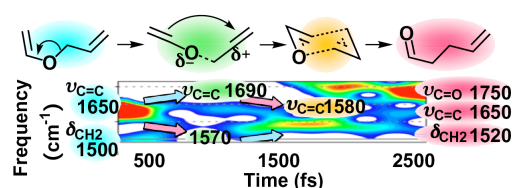


Figure 2. Spectrogram of Claisen rearrangement