フェムト秒誘導ラマン分光によるジフェニルシクロプロペノンの光解離反応の研究

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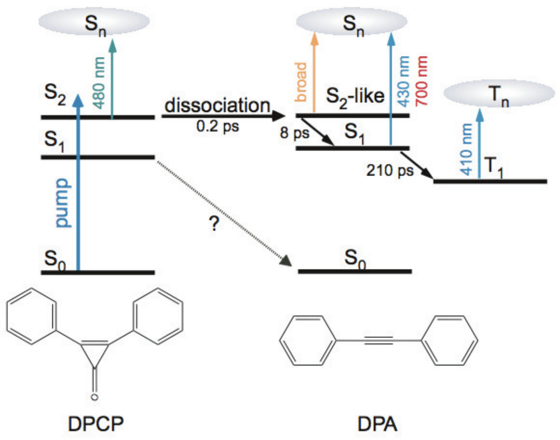

Figure 1: Reaction scheme of the photo- dissociation of diphenylcyclopropenone in cyclohexane solution.

Diphenylcyclopropenone (DPCP) possesses an unsaturated three membered ring structure which is connected to a carbonyl group. Upon irradiation with ultraviolet laser light, DPCP photo-dissociates into carbon monoxide and diphenylacetylene (DPA). As shown in the lower part of Figure 1, the three membered ring is then transformed into a CC-triple bond. This photodissociation process was recently studied by our group using femtosecond transient absorption spectroscopy [1]. Due to the ultrafast time resolution, it could be proved, that the dissociation from the initially excited S_2 state of DPCP to the S_2 state of the photoproduct DPA takes place in only 200 fs. Following this fast reaction, the product DPA molecule relaxes to the S_1 state within 8 ps to finally reach the triplet state T_1 after another 210 ps. These two lifetimes of DPA formed from DPCP agree well with the lifetimes of the S_2 and S_1 obtained by directly exciting DPA to the S_2 state. However, it is not before 30 ps that the spectral shape of the transient absorption of directly excited DPA and DPA obtained from DPCP become identical. From this significant difference at early delay times, it was claimed that the S_2 conformation of DPA obtained by photodissociating DPCP differs from that of ordinary DPA in the S_2 state. However, the actual structure of the S_2 state of the photoproduct is still unknown.

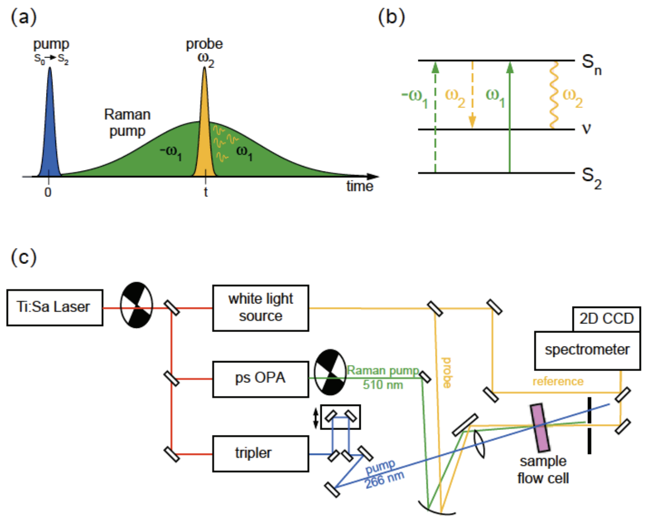

Figure 2: Femtosecond stimulated Raman spectroscopy. (a) Pulse sequence in time domain, (b) Energy level scheme of the Raman process, (c) Experimental setup

To get structural details of the excited states, time-resolved Raman spectroscopy has been widely employed, since the intensity and frequency of the Raman bands sensitively reflect the moleculer conformation as well as chemical bond strength. Using picosecond nonlinear Raman spectroscopy (CARS) for DPA with a time resolution of 20 ps, Ishibashi et al [2] reported that the S_2 DPA has a planar structure with C≡C triple bond character, while the S_1 state has a bent structure with C=C double bond character.

In this study, to investigate the ultrafast structural dynamics in the photodissociation, we carried out femtosecond stimulated Raman scattering (FSRS) spectroscopy [3,4] both for DPCP and DPA. This three pulse technique allows us to measure the excited state Raman spectra with high frequency resolution on the femtosecond time scale. The principle of this technique is illustrated in Figure 2(a) and (b): At time zero an ultrashort pump pulse transfers population to the excited state. The strong picosecond Raman pump pulse (frequency ω_1) and the weak fs probe pulse (frequency ω_2) interact with the excited molecule at time t and generate a vibrational coherence. This vibrationally coherent state can interact with the Raman pump once again within the vibrational coherence time, giving rise to a stimulated Raman gain signal.

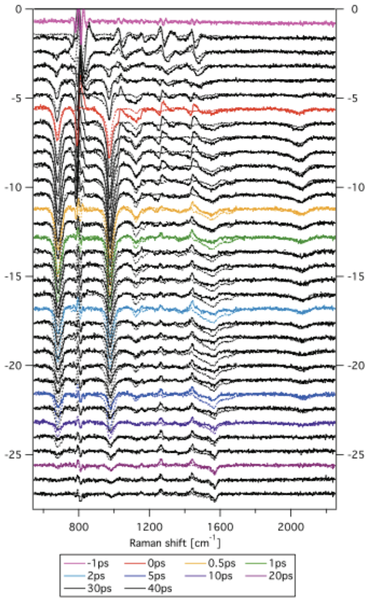

Figure 3: FSRS spectra of DPCP (solid lines) and DPA (dashed lines) at different delay times.

Our newly developed experimental setup is depicted in Figure 2(c): The third harmonic of the fundamental laser beam is used as pump pulse and compressed whitelight serves as probe pulse. A tunable OPA allows to adjust the wavelength of the picosecond Raman pump pulse in the visible spectral region to obtain optimal resonance conditions. Using this setup, we could measure the excited state Raman spectra at different delays after initiating the DPCP photodissociation with a time resolution better than 300 fs. For direct comparison, the corresponding DPA spectra were also acquired under identical experimental conditions (Figure 3). Based on this data, we discussed differences and similarities in the excited-state structural dynamics of the photoproduct and DPA.

References

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