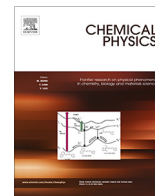




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# Ultrafast photodissociation dynamics of diphenylcyclopropanone studied by time-resolved impulsive stimulated Raman spectroscopy

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## ABSTRACT

We studied ultrafast photodissociation reaction of diphenylcyclopropanone (DPCP) in solution by time-resolved impulsive stimulated Raman spectroscopy (TR-ISRS) using sub-6-fs pulses. The obtained femtosecond time-resolved Raman data of excited-state DPCP did not show any noticeable spectral change during its lifetime of 180 fs. This indicates that photoexcited DPCP is trapped at the excited-state potential energy minimum before undergoing the photodissociation, which is consistent with the predissociation picture of ultrafast photodissociation reaction of DPCP. The present study demonstrates the high capability of TR-ISRS for structural characterization of short-lived reactive transients that decay within only a few hundreds of femtoseconds.

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## 1. Introduction

Chemical reactions consist of the formation and dissociation of chemical bonds, which involve various skeletal deformations in each elementary step. Revealing such nuclear rearrangements during chemical reactions is one of the most essential issues in fundamental studies of chemical reactions. Toward this goal, it is highly desirable to record a series of snapshot structures of a reacting molecule from the reactant, all the way down to the product with high time resolution. Nevertheless, this is impractical for thermally activated chemical reactions because it is generally difficult to start them by an external trigger with high temporal accuracy. On the other hand, in ultrafast photochemical reactions, the reactant molecules are instantaneously excited to an unstable region on the excited-state potential energy surface (PES), and they simultaneously start structural changes immediately. Therefore, we have a chance to observe continuous structural evolution of reacting molecules towards the photoproduct formation in this case. Observation of such a continuous structural change provides essential information about the nuclear motion responsible for facilitating the reaction (i.e., reaction coordinates), and thus enables us to clarify the relevant reactive PESs. Even for photochemical reactions, however, such observation has been limited so far to a few extre-

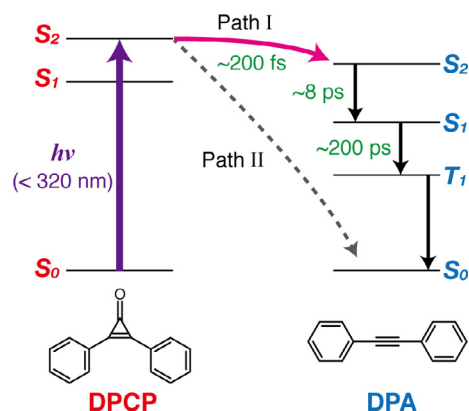
mely fast reaction systems like photoisomerization of the retinal chromophore in visual pigment rhodopsin and cis-stilbene [1,2].

Photodissociation reaction of diphenylcyclopropanone (DPCP) is one of the fastest photochemical reactions to date, and it involves a drastic structural change from the reactant to the product. Upon irradiation of the ultraviolet light, DPCP undergoes a photodissociation reaction, producing diphenylacetylene (DPA) and carbon monoxide [3], with a high quantum yield ( $1.00 \pm 0.03$  [4]). Previously, we investigated the excited-state dynamics of DPCP by femtosecond time-resolved absorption spectroscopy [5], and proposed a reaction scheme that is schematically illustrated as path I in Scheme 1. In this scheme, following photoexcitation to the optically allowed  $S_2$  state, excited-state DPCP undergoes a 200-fs decay and produces the  $S_2$  state of DPA and carbon monoxide. This scheme is based on the observation of the excited-state absorption (ESA) in the visible region upon the photoexcitation of DPCP, which is assignable to  $S_2$  DPA having a characteristic several-picosecond lifetime. Similar spectroscopic signatures have also been observed in the transient absorption studies of DPCP carried out by other groups [6,7]. In addition to this path I, another reaction scheme has been proposed, in which  $S_2$  DPCP directly generates DPA in the  $S_0$  state (path II) [8]. Therefore, further study is necessary to clarify the dynamics and mechanism of this, one of the fastest of all chemical reactions.

As demonstrated in the above-mentioned transient absorption studies, the photodissociation reaction of DPCP is completed within only  $\sim 500$  fs. Because significant nuclear rearrangements take place on such a very short time scale, one would expect

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**Scheme 1.** Reaction scheme representing the ultrafast photodissociation of diphenylcyclopropenone (DPCP), which yields diphenylacetylene (DPA) and carbon monoxide as the products.

drastic structural dynamics on the reactant- or product-state PES. Thus, it is intriguing to examine how the molecular structure evolves in the initially prepared  $S_2$  state of DPCP (or in photoproduct DPA), which is expected to provide not only a deeper understanding of the photodissociation of DPCP itself but also a wealth of fundamental knowledge about the reactive PESs in general.

In this paper, we report on the ultrafast photodissociation dynamics of DPCP studied by time-resolved impulsive stimulated Raman spectroscopy (TR-ISRS) using sub-6-fs pulses [2,9–13]. This time-domain Raman approach allows us to track the change in the vibrational structure of the transient species with femtosecond temporal accuracy and a very wide frequency window ranging from the terahertz to  $>3000$   $\text{cm}^{-1}$  region. Using TR-ISRS, we previously reported an attempt to track continuous structural evolution of cis-stilbene during its ultrafast photoisomerization [2]. More recently, we used TR-ISRS to investigate ultrafast photoreaction dynamics of several photo-responsive proteins [14,15], clarifying key structural events that drive their functions. These studies demonstrated the exquisite capability of TR-ISRS to study the structural dynamics occurring on the femto-to-picosecond time scale. In this study, we examined the structural dynamics of DPCP in the excited state, aiming at obtaining new insights into the mechanism of its ultrafast photodissociation reaction.

## 2. Experimental

### 2.1. Materials

Diphenylcyclopropenone (98%) was purchased from Sigma Aldrich. It was used after the separation by column chromatography and subsequent recrystallization from cyclohexane. Spectroscopic-grade cyclohexane was purchased from Wako Pure Chemicals and used without further purification. To avoid the accumulation of product DPA during the measurement, a large amount of the sample solution ( $\sim 500$  mL) was prepared and circulated. We estimated that  $\sim 2\%$  of DPCP was converted to DPA after the TR-ISRS measurement. Considering the much lower molar extinction coefficient of DPA at the actinic pump wavelength ( $\epsilon = \sim 430$   $\text{M}^{-1} \text{cm}^{-1}$  at 315 nm) compared to DPCP ( $\epsilon = \sim 15300$   $\text{M}^{-1} \text{cm}^{-1}$  at 315 nm), contribution of the accumulated DPA to the TR-ISRS data was estimated to be negligible.

### 2.2. Time-resolved impulsive stimulated Raman spectroscopy

Details of the TR-ISRS setup have been described elsewhere [13]. Briefly, a Ti:sapphire regenerative amplifier (780 nm, 80 fs,

1 mJ, 1 kHz) pumped two noncollinear optical parametric amplifiers (NOPAs). The output of the first NOPA at 528 nm was sum-frequency mixed with the fundamental in a type-II BBO ( $\beta$ -barium borate) crystal, generating the actinic pump pulse ( $P_1$ , 315 nm, 45 fs). The output of the second NOPA (460–640 nm, 5.8 fs) was divided into two, and they were used as the impulsive Raman pump pulse ( $P_2$ ) and the probe pulse ( $P_3$ ) to monitor the transient absorbance change. The pulse durations were evaluated at the sample position by self-diffraction frequency-resolved optical gating (SD-FROG [16]). The  $P_1$ ,  $P_2$  and  $P_3$  pulses were focused into a 300- $\mu\text{m}$ -thick flow cell of the sample solution. The sample was flowed at a rate sufficient to replenish the sample between consecutive pulses. All the data were obtained with the  $P_1$  polarization parallel to the others. At the sample position, the energies of the  $P_1$ ,  $P_2$ , and  $P_3$  pulses were typically 120, 95, and 4 nJ, with 160, 100, and 90  $\mu\text{m}$  beam diameters, respectively. The TR-ISRS data were obtained by mechanically chopping every other  $P_2$  pulse, while the  $P_2$  pulse was physically blocked and the  $P_1$  pulse was chopped for the conventional pump-probe measurement.

### 2.3. Theoretical calculations

Geometry optimizations of the ground state and  $S_2$  state of DPCP were carried out by the density functional theory (DFT) and time-dependent DFT methods, respectively, using the B3LYP functional and the 6-311 + G\*\* basis set. All the theoretical calculations were performed with the Gaussian 09 suite program [17].

## 3. Results and discussion

We first discuss the pump-probe data of DPCP. Fig. 1A shows the steady-state and transient absorption spectra of DPCP in cyclohexane, as well as the spectra of the optical pulses used for the measurements. The actinic pump pulse (315 nm, 45 fs) was tuned to the red edge of the  $S_2 \leftarrow S_0$  absorption band of DPCP, and the broadband probe pulse (460–640 nm, 5.8 fs) monitored the  $S_n \leftarrow S_2$  ESA of DPCP. (Note that the  $S_n \leftarrow S_2$  ESA band of product DPA is also within this probe spectral range, so that  $S_2$  DPA can be detected once it is generated by the photodissociation reaction [5].) The obtained pump-probe signal of DPCP is shown in Fig. 1B. The data show a rapid decay of the ESA signal with a time constant of 180 fs, which is in a good agreement with our previous pump-probe measurements of DPCP [5]. Nevertheless, the present data only exhibits the complete decay of the ESA of DPCP, and we did not observe any noticeable residual transient absorption signal assignable to  $S_2$  DPA that is formed through the photodissociation reaction (path I). It is in sharp contrast to the result of the previous study in which the ESA of  $S_2$  DPA was clearly observed. The absence of the residual transient absorption signal implies that the formation of  $S_2$  DPA is negligible and that DPA is directly formed in its ground state under the present experimental condition (path II). We tentatively attribute this discrepancy with the previous pump-probe study to the difference in the actinic pump wavelength: 315 nm in the present study and 267/295 nm in the previous study. We discuss this point more in detail later.

Next, ultrafast structural dynamics of  $S_2$  DPCP was investigated by TR-ISRS. In Fig. 2A, a schematic of TR-ISRS is shown. In TR-ISRS measurements, firstly, the actinic pump pulse ( $P_1$ ) prepares the excited-state population of the molecule, initiating its photoreaction. After the variable delay time  $\Delta T$ , the ultrashort Raman pump pulse ( $P_2$ ) is introduced to induce coherent nuclear wavepacket motion in the excited state through the impulsive stimulated Raman scattering process. The ultrashort probe pulse ( $P_3$ ) records the induced coherent nuclear wavepacket motion as an oscillatory component of the  $P_2$ -induced differential absorption signal by

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