

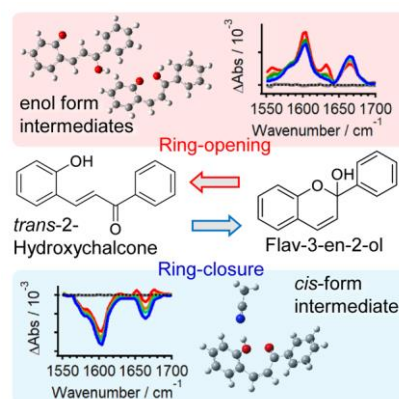
# Accounts of Materials & Surface Research

## Photoinduced ring opening and closure reactions in chalcones monitored by time-resolved IR spectroscopy

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Chalcones are naturally occurring compounds, which are expected as an environmental-friendly photochromic material. In this paper, we review nanosecond time-resolved infrared (TR-IR) study of the photoinduced ring-opening and -closure reactions between *trans*-2-hydroxychalcone (Ct) and flav-3-en-2-ol (F) in acetonitrile, which are crucial to understanding the photochromic reactions in chalcones. TR-IR difference spectra observed after photoexcitation of F showed a positive band at 1632 cm<sup>-1</sup>, which was assignable to the C=O stretching vibration of an enol form 2-hydroxychalcone; an intermediate of the photo-ring-opening reaction. From the time dependence of the TR-IR spectra and vibrational analysis by density functional theory (DFT) calculations, we propose that the photo-ring opening reaction of F proceeds mainly through three different reaction paths. In two of them, two kinds of enol form, single bond *cis*- and *trans*- enol intermediates are generated right after the photoexcitation and then tautomerize into keto forms, *cis*- and *trans*-chalcones (Cc and Ct), respectively, while in the other path, the keto chalcones (Cc, Ct, or both) are produced directly from F without passing through the enol intermediates. In contrast, only one intermediate was detected in TR-IR spectra of the photo-ring closure reaction from Ct to F. On the basis of vibrational analysis by DFT calculations, the intermediate detected in the photo-ring-closure process was assigned to Cc hydrogen-bonding with solvent molecules.



**Keyword:** Time-resolved infrared spectroscopy, Photochromism, 2-hydroxychalcone, flav-3-en-2-ol

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Taka-aki Ishibashi received his B.S., M.S., and Ph.D. in chemistry from the University of Tokyo. After working in research and teaching at Kanagawa Academy of Science and Technology, the University of Tokyo, and Hiroshima University, he has been a full professor at University of Tsukuba since 2012. His current research focuses on the development and applications of molecular spectroscopy for interfacial and solution samples.



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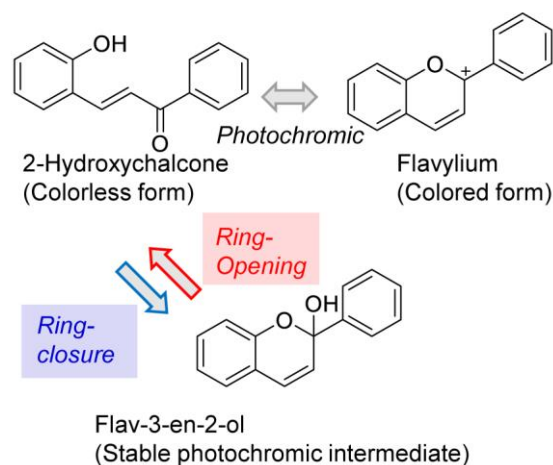
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## 1. Introduction

Certain organic compounds exhibit a reversible transformation between two states with different colors by a photochemical reaction. Such phenomena are called photochromism. Organic photochromic compounds are expected as photofunctional materials that can be applied in photonic devices such as optical sensors and switches. Thus, characterizing molecular mechanisms of photochromic reactions has long been a subject of interest to researchers, especially in material science. To date, photochemical reactions of photochromic molecules have been extensively studied, primarily by time-resolved electronic absorption spectroscopy in the ultraviolet (UV)/visible (Vis) region. This method is powerful to detect transient intermediates of photochemical reactions and investigate their kinetics. However, we often have difficulty in distinguishing co-existing chemical species in electronic absorption spectra because electronic absorption bands are in general broad in the solution phase. Besides, similar chemical species exhibit the electronic bands which are overlapped significantly.

To observe reaction intermediates that are difficult to detect in electronic absorption spectra, we have employed time-resolved infrared (TR-IR) spectroscopy. Vibrational bands usually are narrow and little overlapped as compared with electronic absorption bands. Thus, the positions of vibrational bands are more sensitive to the

molecular structures than those of electronic absorption bands. This review describes our recent application of TR-IR spectroscopy to a photochromic system between 2-hydroxychalcone and flavylum. Outline of this review is summarized in figure 1. Below, we will first briefly introduce the photochromic system and the reaction mechanism proposed by previous UV/Vis studies. Then, we will present our TR-IR results and discuss the mechanism of the photochromic reaction.



- Introduction on the photochromic reaction (Sect. 2, 3)
- Steady-state IR spectra of 2-hydroxychalcone and flav-3-en-2-ol (Sect. 4)
- Photo-ring-opening (Sect. 5) and -closure (Sect. 6) processes monitored by TR-IR spectroscopy

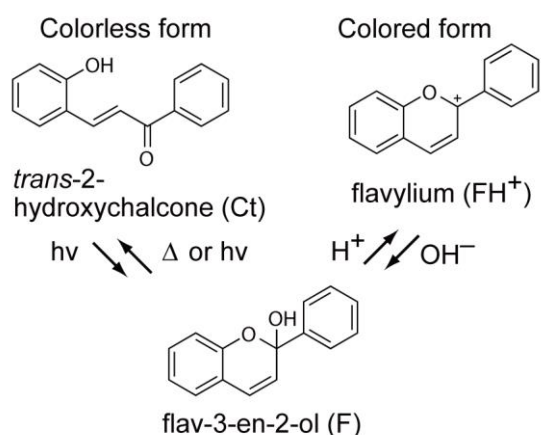
Figure 1. Outline of this review.

## 2. Photochromic reaction between 2-hydroxychalcone and flavylum

Figure 2 shows the proposed mechanism of a photochromic reaction of 2-hydroxychalcone in

solutions.<sup>1-6</sup> In the coloration process, a colorless form, *trans*-2-hydroxychalcone (Ct) is converted to a ring-closed species, flav-3-en-2-ol (F) upon illumination with UV light. F is the photochromic intermediate of this photochromic reaction system, and is then transformed into a colored form, flavylum cation (FH<sup>+</sup>) by a pH-dependent reaction in aqueous solutions. It is worth mentioning that the colored form species, FH<sup>+</sup> is the basic structure of anthocyanins, which are an important family of natural plant pigment widely distributed in flowers, fruits, and vegetables.<sup>7-9</sup> Anthocyanins are widely used as natural coloring agents, and particularly as food additives. Thus, the photochromic systems between Ct and FH<sup>+</sup> are expected to be safe for human health, and have a low environmental impact.<sup>2</sup>

While the coloration process in this photochromic reaction occurs within 1 second, the thermal decoloration proceeds slowly over a few weeks.<sup>1</sup> The rate-determining step of the decoloration is the back reaction from F to Ct. Interestingly, however, F is known to be photochemically converted back to Ct. This



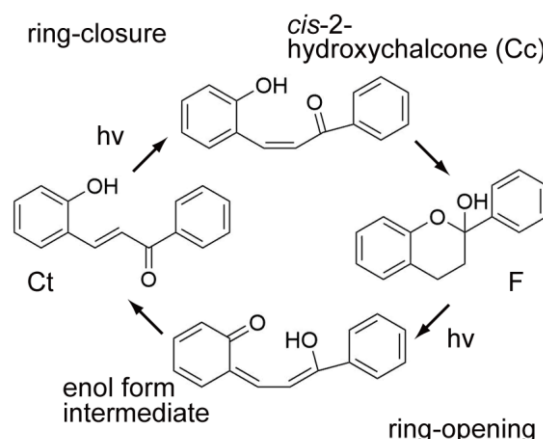
**Figure 2.** Coloration and decoloration schemes in the photochromic reaction between *trans*-2-hydroxychalcone (Ct) and flavylum (FH<sup>+</sup>). Flav-3-en-2-ol (F) is the photochromic intermediate, which can be thermally or photochemically back to Ct.

photoinduced ring-opening reaction from F to Ct is particularly important when we consider applying this photochromic system to optical control devices such as optical switches and memories.

### 3. Photo-ring-opening and -closure reactions monitored by time-resolved UV/Vis spectroscopy

#### 3.1. Photo-ring opening reaction

To date, the photo-ring-opening and -closure reactions between F and Ct in acetonitrile have been studied by time-resolved UV/Vis spectroscopy.<sup>1, 10, 11</sup> Horiuchi et al. has studied the photo-ring-opening reaction by nanosecond flash photolysis.<sup>1</sup> They detected a broad enhanced absorption band due to an intermediate in the 400-680 nm region as well as that due to Ct in the 280-400 nm region in the transient absorption spectra after the photoexcitation of F. The temporal profile of the intermediate band monitored at 530 nm decayed monotonically to the baseline with a time constant of 31  $\mu$ s. Since the intensity of the band due to Ct monitored at 340 nm grew with the same time constant, they attributed the intermediate to



**Figure 3.** Scheme of photoinduced ring-opening and -closure reactions between Ct and F. The ring-closure reaction from Ct proceeds via *cis*-2-hydroxychalcone (Cc), while the ring-opening from F does via the putative enol form intermediate.

the precursor to Ct.

The time constant they obtained was too large to assign the intermediate to the singlet excited state of F. As one possible candidate, they considered the triplet state of F. However, this possibility was excluded by their other experiments showing that oxygen gave no effects on the decay time constant of the intermediate. As another candidate, they considered the ground state enol form of 2-hydroxychalcone because the observed decay time constant was comparable to those of the ground state enol forms of other compounds such as 2-hydroxybenzaldehyde and 3-hydroxyflavone. This possibility was examined by investigating the decay time constants of the intermediate in acetonitrile in the presence of protic molecules such as methanol, ethanol, and water. It is known that protic molecules accelerate enol-keto tautomerization.<sup>12</sup> They observed significant acceleration of the decay time constant by protic molecules. Thus, they suggested that the intermediate was the ground state enol form of 2-hydroxychalcone. The reaction scheme they suggested is shown in the lower part of figure 3.

### 3.2. Photo-ring-closure reaction

In 1960s, Jurd studied the effect of light on the equilibrium between 2-hydroxychalcones and flavylum salts.<sup>3</sup> He proposed that *trans*-form of 2-hydroxychalcones photoisomerizes to *cis*-form, which cyclizes to the ring-closed form as shown in the upper part of figure 3. Since then, many studies have been performed, and now the scheme is established as the general scheme for reactions of 2-hydroxychalcones to flavylum compounds.<sup>4-6, 13</sup>

More recently, Leydet et al. investigated photoreaction of *trans*-pyridinechalcone (Ct'), an analog of Ct, by femto- and nanosecond transient absorption spectroscopy.<sup>11</sup> They monitored the

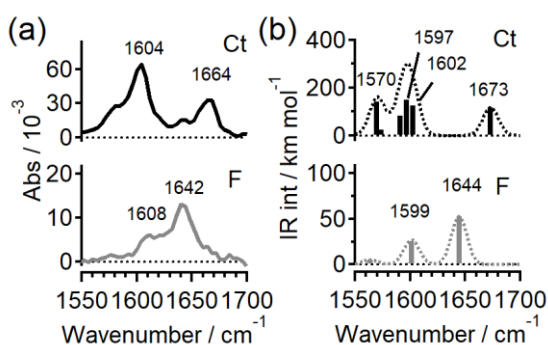
absorbance changes in the 400-750 nm region following the photoexcitation of Ct' in acetonitrile. On a picosecond time range, they observed two distinct signals. The initial signal was assigned to the singlet excited state of Ct', which evolved into the relaxed state with a time constant of 2 ps. The relaxed state was attributed to a twisted excited state, the C-C=C-C dihedral angle of which was about 90°. The photochemical process after the decay of the relaxed state was traced by nanosecond flash photolysis. They confirmed that following the decay of the relaxed state (~16 ns), *cis*-pyridinechalcone (Cc') in the electronically ground state is generated, and then transforms into hemiketal form (F') with a time constant of 10 ms.

Below, we describe our TR-IR results on the photo-ring-opening and closure reactions. We have applied this technique to detect conformational dynamics including the formation of intermediates, which are "silent" in electronic absorption spectra.

### 4. Steady-state IR spectra

Figure 4a depicts steady-state IR spectra of Ct and F in acetonitrile at concentrations of 10 mM obtained in the C=O stretching wavenumber region. The IR spectrum of Ct exhibited vibrational bands at 1604 and 1664 cm<sup>-1</sup>, whereas that of F contained a vibrational band at 1642 cm<sup>-1</sup> and a shoulder at 1608 cm<sup>-1</sup>. The vibrational bands of F were much weaker than those of Ct in the observed wavenumber region. IR spectra of Ct and F predicted by DFT calculations at B3LYP/6-31G(d) level are shown as sticks in figure 4b. Dotted curves in this figure represent the line spectra convoluted with a Gaussian with a full width half-maximum (FWHM) of 10 cm<sup>-1</sup>. The

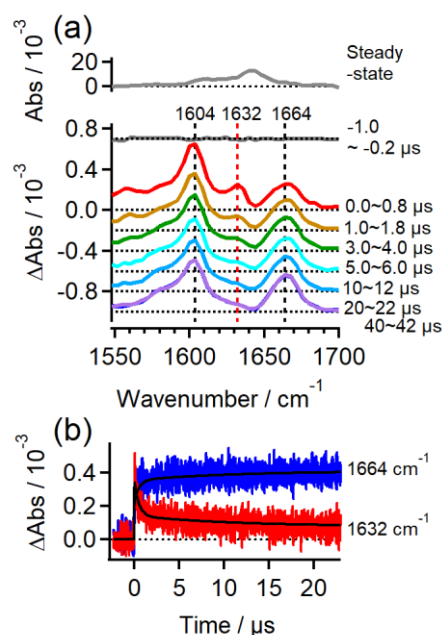
calculated IR spectra well reproduced the wavenumbers and the relative intensities of the bands. Referring to the calculated IR spectra, we assigned the observed vibrational bands as follows. The  $1604\text{ cm}^{-1}$  band was attributed to an overlap of an in-phase stretching mode of C=O and C=C groups, and a ring stretching mode of Ct. The  $1664\text{ cm}^{-1}$  band was due to an out-of-phase one of the C=O and C=C groups (called a C=O stretching mode in the following). The  $1608$  and  $1642\text{ cm}^{-1}$  bands of F are assigned to a benzene ring stretching mode and a stretching mode of the C=C group in the chromene ring, respectively.



**Figure 4.** (a) Steady-state IR spectra of Ct (upper panel) and F (lower panel) in acetonitrile. (b) IR spectra of Ct (upper panel) and F (lower panel) predicted by DFT calculations at the B3LYP/6-31G(d) level (sticks). The spectra convoluted with a Gaussian with a full width half-maximum of  $10\text{ cm}^{-1}$  (dotted curves).

## 5. Photo-ring-opening reaction from flav-3-en-2-ol

We first investigated the photo-ring-opening reaction from F by TR-IR spectroscopy.<sup>14</sup> TR-IR spectra were measured by a home-build apparatus, which was based on a dispersive spectrometer with AC-coupled detection.<sup>15-18</sup> The time resolution of our system was approximately 30 ns and 350 ns for measurements of temporal



**Figure 5.** (a) Steady-state IR spectrum of F (upper panel). TR-IR spectra observed after photoexcitation of F (lower panel). (b) Time profiles of the TR-IR intensities at  $1632$  (red) and  $1664$  (blue)  $\text{cm}^{-1}$ .

profiles and TR-IR spectra, respectively. The spectral resolution was set at  $8\text{ cm}^{-1}$ .

Figure 5a shows TR-IR spectra observed after the photoexcitation of F in acetonitrile at  $266\text{ nm}$ . The top trace is the steady-state IR spectrum of F, while the other traces are TR-IR difference spectra, each of which is the IR spectrum at a given delay time minus that before the photoexcitation. TR-IR difference spectra represent photoinduced IR absorbance changes. Thus, positive bands in the difference spectra represent photo-generated species, including transient intermediates, whereas negative ones do the parent species.

The TR-IR difference spectrum at  $0.0\text{--}0.8\text{ }\mu\text{s}$  after the photoexcitation showed positive vibrational bands at  $1604$ ,  $1632$ , and  $1664\text{ cm}^{-1}$ . In the delay time of a few microseconds, the  $1604$  and  $1632\text{ cm}^{-1}$  bands decreased in intensity, whereas the  $1664\text{ cm}^{-1}$  band increased. The TR-IR spectra showed no further changes at longer delay times ( $>20\text{ }\mu\text{s}$ ). The spectra at the long delay



times only showed positive vibrational bands at 1604 and 1664  $\text{cm}^{-1}$ , where Ct, the final product of the ring-opening reaction, has vibrational bands. This result indicates that the reaction from F to Ct almost finishes within 20  $\mu\text{s}$  after the photoexcitation. The 1632  $\text{cm}^{-1}$  band is notable in the TR-IR difference spectra. This band disappeared at the long delay times. Thus, we assigned this band to an intermediate in the photo-ring opening reaction.

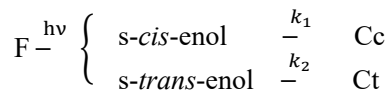
The temporal profiles of the TR-IR band intensities at 1632 (red) and 1664  $\text{cm}^{-1}$  (blue) are shown in figure 5b. The band intensities at both wavenumbers increased rapidly within the time resolution of the apparatus and changed in a few microseconds to tens of microseconds time range. They were fitted by a function of  $A_1\exp(-k_1t)+A_2\exp(-k_2t)+C$  with common time constants of 0.5 and 11  $\mu\text{s}$ ; that is, the decay of the 1632  $\text{cm}^{-1}$  band due to the intermediate species and the rise of the 1664  $\text{cm}^{-1}$  band were fitted with the common two time constants. This observation indicates that the 1632  $\text{cm}^{-1}$  band originates from the precursor of the chemical species that has a vibrational band at 1664  $\text{cm}^{-1}$ . At least, two precursors must be assumed because we observed the kinetics with the two different time constants.

Then, what is the two intermediates? The previous flash photolysis study has reported that following the photoexcitation of F in acetonitrile, an enol form 2-hydroxychalcone intermediate is produced and then transforms into Ct by keto-enol isomerization with a time constant of 31  $\mu\text{s}$ .<sup>1</sup> Judging from the value of the time constant, the kinetics with the time constant of  $k_2^{-1}=11 \mu\text{s}$  detected in the TR-IR seems to correspond to that observed in the previous flash photolysis study. The time constant value obtained by the TR-IR was smaller than that by the flash photolysis study.

One probable cause is water contamination to the sample used in the TR-IR experiment. It is known that the protic additives such as water increase the decay rate of the enol form species.<sup>1</sup> We have performed an TR-IR experiment that examined an influence of adding water to the sample solution, and confirmed that adding a small amount of water (~0.5 volume % of acetonitrile) indeed accelerated the  $k_2$ -kinetics.<sup>14</sup> In contrast, the kinetics with the time constant of  $k_1^{-1}=0.5 \mu\text{s}$  was not clearly detected in the previous flash photolysis study. Therefore, the observed time dependence of the TR-IR spectra was not explained solely by the reaction scheme proposed in the previous flash photolysis study.

We postulate that the two intermediates have similar molecular structures for two reasons. First, the double-exponential kinetics was observed on the 1632  $\text{cm}^{-1}$  band. This observation implies that both intermediates have the vibrational band at this wavenumber. Second, we did not detect any TR-IR bands that are assignable exclusively to one of the two intermediates. A clue to assigning the two intermediates is found in a previous literature on the photochemistry study of hydroxy-4-pyridinechromene (F').<sup>19</sup> F' has a pyridine ring instead of the phenyl ring of F. The study reported that the photoexcitation of F' generates two kinds of enol forms, single bond *cis*- (*s-cis*-) and *trans*- (*s-trans*-) enol forms. The enol forms then undergo keto-enol isomerization to produce *cis*- and *trans*-form chalcones, respectively. Referring to this literature, we suggest that the two intermediates detected in our TR-IR experiments were *s-cis*- and *s-trans*-enol forms of 2-hydroxychalcone. The  $k_1$  and  $k_2$  kinetics are attributed to the tautomerization processes from the *s-cis*-enol to Cc and from the *s-trans*-enol to Ct, respectively. We assign the faster kinetics to the process from *s-cis*-enol to Cc because the distance from the OH

to the C=O groups in *s-cis*-enol is shorter than that in *s-trans*-enol. The reaction scheme that explains the time-evolution of the TR-IR spectra is as follows.

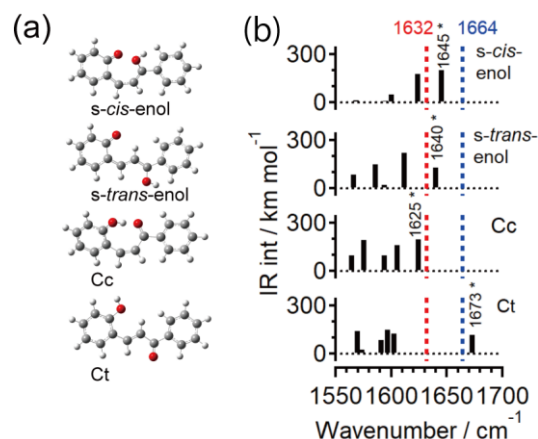


The validity of this reaction scheme was examined by comparing the observed TR-IR spectra with calculated IR spectra obtained by DFT calculations. Figure 6a and 6b show optimized structures and calculated IR spectra of four related species, *s-cis*-enol, *s-trans*-enol, Cc, and Ct, respectively.

The calculated spectra of the *s-cis*- and *s-trans*-enol forms show vibrational bands at 1645 and 1640  $\text{cm}^{-1}$ , respectively. Both bands are due to an out-of-phase stretching mode of C=O and C=C groups. (Hereafter they are called simply a C=O stretching mode.) The calculated wavenumbers are close to 1632  $\text{cm}^{-1}$ , where the TR-IR band of the intermediates was observed. Thus, our assignment of the 1632  $\text{cm}^{-1}$  band to both *s-cis*- and *s-trans*-enol forms is consistent with the calculations.

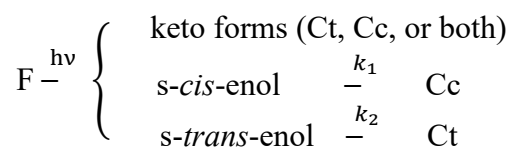
The TR-IR bands at 1604, 1632, and 1664  $\text{cm}^{-1}$  were observed immediately after the photoexcitation (red lines in figure 5a). Considering the reaction scheme proposed above, these TR-IR bands should be due to the enol forms. However, the calculated spectra of neither *s-cis*-enol nor *s-trans*-enol contain vibrational bands at around 1664  $\text{cm}^{-1}$ . This result implies that early photoproducts exist other than the enol forms, and indicates that the reaction scheme above does not sufficiently explain the observed TR-IR spectra.

We modified the reaction scheme to remedy the inconsistency by considering an additional



**Figure 6.** (a) Optimized structures of 2-hydroxychalcone obtained by the DFT calculations. (b) Calculated IR spectra predicted from the corresponding optimized structures are shown in sticks. The number with an asterisk in each panel is the calculated wavenumber of the normal mode mainly due to the C=O stretching coordinate. A scaling factor of 0.9613 was used to calibrate the calculated wavenumbers.

reaction path to the early photoproduct. The early photoproduct should have a vibrational band at 1664  $\text{cm}^{-1}$ . Therefore, one possible assignment of the early photoproduct is Ct. Cc also cannot be excluded as a candidate of the early photoproduct. As discussed immediately below, a DFT calculation predicted that Cc can have the C=O stretching mode at 1683  $\text{cm}^{-1}$  when solvent effect is considered. The keto forms, Ct, Cc, or both, produced through the fast reaction path could contribute to the 1664  $\text{cm}^{-1}$  band observed right after the photoexcitation. The modified reaction scheme is as follows.

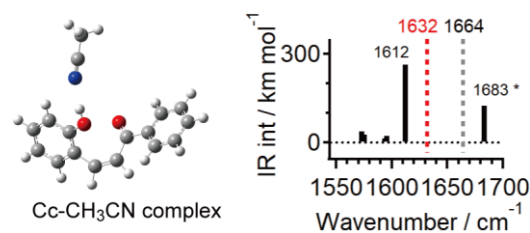


This modified scheme presumes that both Ct and Cc have a vibrational band at around  $1664\text{ cm}^{-1}$  because the three kinetics, fast rise,  $k_1$  decay, and  $k_2$  decay were observed on the kinetic trace at this wavenumber (blue line in figure 5b). However, the calculation does not predict that Cc has IR bands at around  $1664\text{ cm}^{-1}$ . Instead, the C=O stretching mode of Cc is predicted at  $1625\text{ cm}^{-1}$  in the calculated spectrum (figure 6b).

To resolve this inconsistency, we considered the solvent effect. The low calculated wavenumber of the C=O stretching mode of Cc ( $1625\text{ cm}^{-1}$ ) is probably due to an intramolecular hydrogen bond between the OH and C=O groups. However, in acetonitrile, this hydrogen bond could be broken because the OH group can also form a hydrogen bond with acetonitrile. Such a Cc-acetonitrile complex would have the C=O mode at a wavenumber higher than that of the C=O mode of the isolated Cc. We examined this explanation by calculating an IR spectrum of 1:1 complex between Cc and acetonitrile (Cc-CH<sub>3</sub>CN complex).

DFT calculations showed that the most stable structure of the Cc-CH<sub>3</sub>CN complex (not shown) has the intramolecular hydrogen bond (the distance between H and O atoms,  $d_{\text{HO}}$  is  $1.56\text{ \AA}$ ), whereas the second most stable structure does not ( $d_{\text{HO}}$  is  $3.35\text{ \AA}$ ).<sup>14</sup> The complex without the intramolecular hydrogen bond (the second most stable structure) has a larger Gibbs free energy than that with the intramolecular hydrogen bond (the most stable structure) by  $6.7\text{ kJ mol}^{-1}$ . However, the breaking of the intramolecular hydrogen bond is quite possible because conformations without intramolecular hydrogen bonds may be preferable in terms of entropy.

The second most stable structure and the IR spectrum calculated from it are shown in figure 7. The calculated IR spectrum of the Cc-CH<sub>3</sub>CN complex without the intramolecular hydrogen



**Figure 7.** The second most stable structure of the Cc-CH<sub>3</sub>CN complex found in the DFT calculations. The calculated IR spectrum from the structure is shown as stick.

bond has a C=O stretching band at  $1683\text{ cm}^{-1}$ . As we expected, the wavenumber of the C=O stretching mode of Cc becomes close to  $1664\text{ cm}^{-1}$  when the intramolecular hydrogen bond is broken. This result allows us to explain the results of the TR-IR experiment by the modified scheme.

Our observation suggests that the photo-ring-opening reaction process is not so simple as reported in the previous UV/Vis study, demonstrating the usefulness of TR-IR spectroscopy for studying the photochemistry of chalcones and related compound systems. However, we have to mention that the proposed reaction scheme relied on the assumption derived from the DFT calculations: the C=O stretching wavenumber of Ct and that of Cc are similar values when the C=O group of Cc hydrogen-bonds with acetonitrile molecules. One way to validate the assumption is to obtain the IR spectrum of Cc in acetonitrile. However, it could not be separated off from the TR-IR difference spectra obtained in this section because the photo-ring-opening process is a rather complicated reaction involving several paths. In the next section, we discuss the IR spectrum of Cc by studying TR-IR spectra of the photo-ring-closure process from Ct to F.

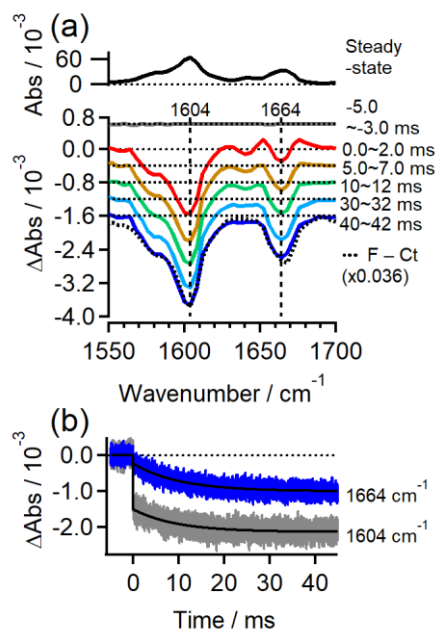
## 6. Photo-ring-closure reaction from *trans*-2-hydrocycalcone



We have investigated the photo-ring-closure reaction from Ct to F by the TR-IR spectroscopy.<sup>18</sup> The investigation was expected to give information on the IR spectrum of Cc because it has been experimentally shown that *cis*-form chalcones are produced during photo-ring-closure reactions from *trans*-form chalcones as shown in the upper part of figure 2.<sup>4,6</sup> The kinetics of the ring-closure process has been studied by transient absorption spectroscopy for a case for *trans*-pyridinechalcone (Ct').<sup>11</sup> As described in section 2.2, *cis*-pyridinechalcone (Cc') is generated after the photoexcitation of Ct', and then decays into hemiketal form, hydroxy-4-pyridinechromene (F') with a time constant of 10 ms. The same reaction scheme is expected to hold for non-substitute *trans*-chalcone (Ct).

Figure 8a shows TR-IR difference spectra obtained after the photoexcitation of Ct in acetonitrile at 355 nm. The top trace is the steady-state IR spectrum of Ct, while the other traces are TR-IR difference spectra at given delay times. The TR-IR difference spectrum at the delay time of 0.0–2.0 ms (red line) showed a large negative signal at 1604 cm<sup>-1</sup> with several small negative and positive signals in 1630–1680 cm<sup>-1</sup>. The negative signals appeared at 1604 and 1664 cm<sup>-1</sup>, which agreed well with the wavenumbers of the vibrational bands of Ct observed in the steady-state spectrum (top trace). Therefore, the negative signals are mainly contributed from the vibrational bands of Ct. The positive signals observed at apparent wavenumbers of 1652 and 1676 cm<sup>-1</sup> are due to a chemical species generated by the photoexcitation of Ct.

Amplitudes of the negative signals at 1604 and 1664 cm<sup>-1</sup> grew more negative with time and reached almost a constant value at 40 ms after the photoexcitation. In figure 7a, the TR-IR difference spectrum at 40–42 ms (blue line) is compared with



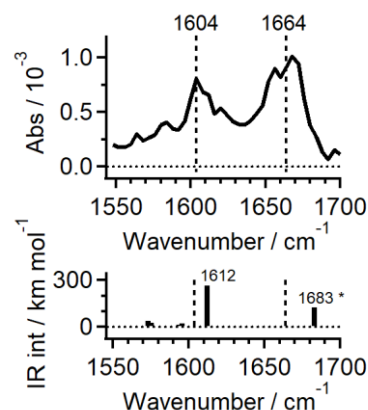
**Figure 8.** (a) Steady-state IR spectrum of Ct (upper panel). TR-IR spectra obtained after photoexcitation of Ct at each delay time (lower panel). The black dotted curve in the lower panel is the IR difference spectrum between F and Ct. (b) Time profiles of the TR-IR band intensities at 1604 (gray) and 1664 (blue) cm<sup>-1</sup>.

the Ct minus F spectrum (dotted line), which was obtained from the steady-state IR spectra of Ct and F shown in figure 4. These spectra were quite similar in shape, indicating that the photo-ring-closure reaction of Ct to F almost finished at this long delay time.

The TR-IR band intensities at 1604 and 1664 cm<sup>-1</sup>, where the negative signals due to the bleaching of Ct was observed, are plotted against the delay time in figure 8b as gray and blue lines, respectively. At both wavenumbers, the negative signals immediately appeared, reflecting the depletion of Ct upon the photoexcitation. Notably, the amplitudes of the negative signals at both wavenumbers became more negative during the period from 1 to 40 ms. These temporal profiles

were fitted by mono-exponential functions with a common time constant of 10 ms. The observed growth of the negative signals cannot be understood by the negative contribution due to Ct alone. If the negative signals were solely due to Ct, their growth would mean that the reactant, Ct, continued to decrease even when the excitation light pulse is no longer present, but it is unlikely. Instead, this behavior can be explained adequately if we assume a positive contribution from the photo-generated intermediate as follows. The intermediate should be produced immediately after the photoexcitation and have vibrational bands at 1604 and 1664  $\text{cm}^{-1}$ . The positive contribution from the intermediate at these wavenumbers decayed with the depletion of the intermediate. In contrast, the negative contribution from Ct remained after the decay of the positive contribution, resulting in the growth of the negative signals. The TR-IR spectra after the growth showed no further changes. Therefore, the intermediate should be the precursor of the final product, F. From the reaction scheme shown in figure 3, the precursor was assigned to Cc. The time constant obtained in our TR-IR measurement was in good agreement with that of Cc' reported in the previous study,<sup>11</sup> supporting the interpretation that the observed intermediate is Cc.

The IR spectrum of Cc was estimated from the TR-IR difference spectra and the steady-state IR spectrum of Ct (Ct-spectrum). In the estimation, Ct-spectrum was multiplied by an appropriate constant, C, and added to the TR-IR difference spectrum at 0.0-2.0 ms. C was determined so that the sum of the constant multiplied spectrum (C×Ct-spectrum) and the TR-IR spectrum at 40–42 ms becomes similar to the steady-state spectrum of F. The estimated spectrum is shown in the upper panel in figure 9, together with the calculated IR spectrum of the Cc-CH<sub>3</sub>CN complex



**Figure 9.** The reconstructed IR spectrum of the intermediate species produced just after photoexcitation of Ct (upper panel). The IR spectrum of the Cc-CH<sub>3</sub>CN complex obtained by the DFT calculation (the same spectrum as that shown in figure 6) (lower panel).

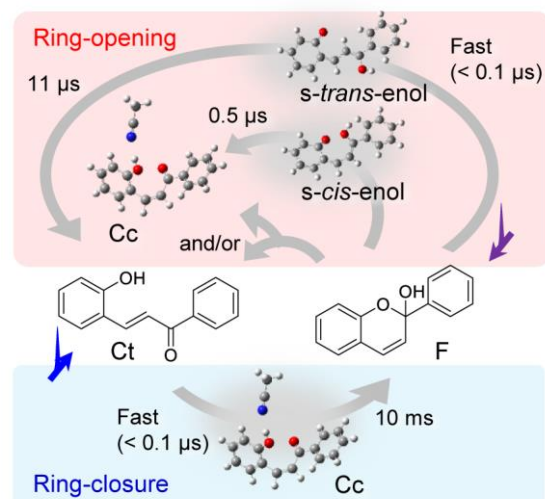
obtained by the DFT calculation (the same spectrum in figure 7) in the lower panel. The estimated spectrum showed two major bands at 1590–1620  $\text{cm}^{-1}$  and 1650–1680  $\text{cm}^{-1}$ . The observed band positions are close to 1612 and 1683  $\text{cm}^{-1}$ , respectively, where the calculation of the Cc-CH<sub>3</sub>CN complex predicts relatively strong vibrational bands. This result is consistent with the assignment of the intermediate to Cc interacting with solvent molecules.

In section 5, we suggested the reaction scheme where Cc as well as Ct is produced after the photoexcitation of F. This scheme, however, presumed that Cc has a vibrational band at around 1664  $\text{cm}^{-1}$ . The validity of the assumption was experimentally supported by the results presented in this section as we obtained experimental evidence that the intermediate produced during the photoreaction of Ct has an IR absorption band at around 1664  $\text{cm}^{-1}$ . Therefore, the TR-IR results on the photoreactions from F to Ct and from Ct to F are consistent and support to each other.

## 7. Summary and future prospective

This paper has reviewed our recent TR-IR studies on the photo-ring-opening and -closure reactions between Ct and F, which are important to understand the photochromic reactions in chalcones. In the photo-ring-opening reaction, we detected the TR-IR band at  $1632\text{ cm}^{-1}$ , which was assigned to the C=O stretching modes of the intermediates, *s-cis*- and *s-trans*-enol forms of 2-hydroxychalcone. The results of the TR-IR measurements and the DFT calculations indicated that the photo-ring-opening proceeds through three different paths: the keto forms of 2-hydroxychalcone are produced not only through the *s-cis*- and *s-trans*-enol intermediates but also directly from F in the sub-microsecond time range. This reaction scheme, however, had the assumption that Cc has a vibrational band at around  $1664\text{ cm}^{-1}$  as a result of the interaction with solvent. The assumption was experimentally validated by monitoring the TR-IR spectra of the photo-ring-closure process from Ct to F, during which Cc is suggested to be produced as a precursor to F. The overall reaction scheme proposed based on our TR-IR studies are summarized in figure 10.

To gain further evidence for the proposed scheme, we are now planning some additional experiments and calculations in the future. First, TR-IR experiments for the ring-opening process at long time delay are planned. From figure 10, we can notice again that the same species, Cc hydrogen-bonding to the solvent, is produced both in the photo-ring-opening (upper part) and -closure (lower part) processes. Considering the TR-IR results of the ring-closure process, Cc produced in the ring-opening process would be back to F with the time constant of 10 ms. This back reaction can be detected in TR-IR



**Figure 10.** The overall reaction scheme for photo-ring-opening (upper) and -closure (lower) processes between F and Ct.

experiments of the ring-opening process in the millisecond time range. Second, experiments with other solvents should be examined. Such experiments can be effective to support our conclusion, especially, concerning the formation of Cc hydrogen bonding to the solvent. It might be also important to examine solvent effects on the *s-cis* and *s-trans* enol form intermediates by the DFT calculations for the full understanding of the photoreactions of this system in solution. Third, it is attractive to investigate the ring-opening process in the short time range (<0.1 μs) by ultrafast TR-IR spectroscopy. Such investigation would provide information on the detailed kinetics of the direct path to the keto chalcones from F, which probably takes place on a potential energy surface in the electronic excited state.

There are many photoresponsive molecules that can alter their optical properties by photoreactions. Understanding the reaction mechanisms of such molecules is important for their applications as photofunctional materials. We believe that time-resolved observation of photochemical reactions through vibrational spectra is useful to investigate the reaction

mechanisms, because it is possible to detect intermediates and reaction paths, which are “silent” in electronic absorption spectra. We are currently trying to apply this technique to other photoreaction systems such as photoinduced proton transfers and redox reactions.

We also note that our method that probes conformational dynamics longer than ~0.1 μs is complementary to ultrafast TR-IR spectroscopy. The method can be suitable to monitor photoreactions of large molecules such as proteins, where conformational changes distant from a photosensor domain would be important for their functions. Such changes are often “silent” in electronic spectra and occur on long time scales, microseconds to seconds. We expect that our method will be useful for such studies.

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