論文題目：Development of Highly-sensitive and High-speed Nanosecond Time-resolved Mid-/Near-infrared Spectrometer and Its Application to Photochemistry of Aromatic Carbonyl Compounds

(高感度・高速ナノ秒時間分解近・中赤外分光装置の開発と
芳香族カルボニル化合物の光化学反応機構解明への応用)

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The photochemical reaction of aromatic carbonyl compounds shows significant varieties in their paths and kinetics depending on their substituents and solvents. The reaction paths and kinetics are determined by the nature of the excited states involved. Therefore, for understanding the mechanism and dynamics of photochemical reactions, it is important to know the nature of the excited electronic sates, including their electronic configurations and energy level ordering. Particularly, the low-lying excited triplet states are of great importance because most the photochemical reaction of aromatic carbonyl compounds proceeds via the low-lying excited triplet states.

In order to observe the low-lying excited triplet states, time-resolved infrared spectroscopy, in which T–T transitions are observed, has been found to be useful. Because T–T transitions are spin-allowed, they are comparable in intensity with S–S transitions. Furthermore, time-resolved infrared spectroscopy is applicable to a room-temperature solution sample. Thus, time-resolved infrared spectroscopy is a powerful tool for observing the low-lying excited triplet states.

In spite of high sensitivity and versatility, the existing time-resolved infrared spectrometer has significant deficiency to be improved: a limited spectral range below 4000 cm^{-1}, a long measurement time and a low spectral resolution. In addition, the data processing using a separated digitizer is considerably inefficient. Utilizing a high-throughput monochromator covering wide spectral range and a-state-of-the-art data processor, the performance of the apparatus would be significantly improved.

In the present study, the author intends to:

1. Improve the performance of the time-resolved infrared spectrometer.

2. Establish the methodology for observing close-lying excited states directly by spectroscopy.

3. Elucidate the mechanism of the substituent and solvent dependence of photoreduction of aromatic carbonyl compounds.

This thesis is composed of the following seven chapters: Chapter 1 gives the general introduction.

In chapter 2, the time-resolved infrared spectrometer developed in this study is described. **Figure 1** shows the block diagram of the present apparatus. Utilizing the high-throughput monochromator, whose f-number is 4.3 and whose focal length is 500 mm, the throughput of the present spectrometer becomes four times as high as that of the previous one. As a result, the minimum limit of detection less than 5×10^{-6} with the spectral resolution of 8 cm^{-1} is achieved (**figure 2**). In addition, the high-speed digitizer mounted in the PC raises the upper limit of the repetition rate five times higher than and makes the number of the data elements that can be dealt with at a time twice more than those of the previous one.

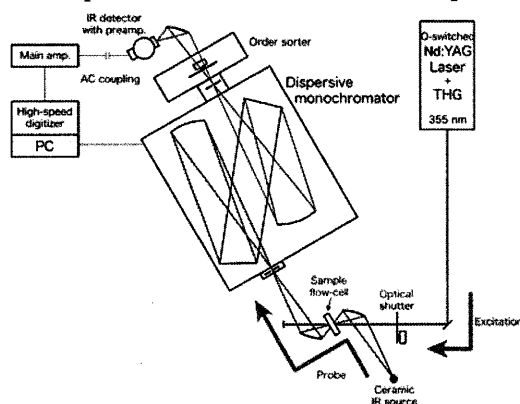Some tips for the noise reduction techniques and the sample cell system are also described here.

Figure 1. Block diagram of time-resolved infrared spectrometer constructed in this study.
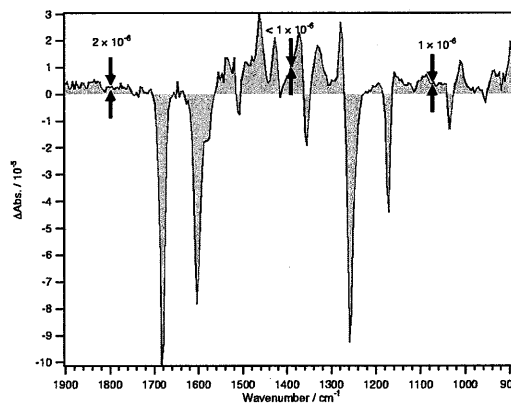

Figure 2. An example of the time-resolved infrared spectrum with best S/N.

In section 3, the photoreduction reaction of benzophenone (**scheme 1**) is studied by the nanosecond time-resolved infrared spectroscopy. Making good use of it, the author successfully observed the whole reaction of the photoreduction of benzophenone, from the laser excitation to the formation of the products, except for the formation and the depletion of benzophenone in the S_1 state in real time. This kind of pursuit of reaction cannot be achieved by any other spectroscopy and was achieved for the first time.

The time region from ~ -1 to 4 μs of the time-resolved spectra were analyzed by singular value decomposition technique. As a result, it was found that the time-resolved spectra could be reproduced by two components whose time constants were infinity and 1.9×10^{6} s^{-1}. Consequently, the rate of the hydrogen atom abstraction k_A is revealed as 1.9×10^{7} s^{-1} mol^{-1} dm^{3} for benzophenone.

The individual spectra of the transient species and the product species, namely benzophenone in the T1 state, benzophenone ketyl radical, and benzopinacol, are extracted from the time-resolved spectra (**figure 3**). Especially, the infrared spectrum of benzophenone ketyl radical is the first vibrational spectrum reported,

because the Raman spectrum is hindered by strong emission from the ketyl radical itself.
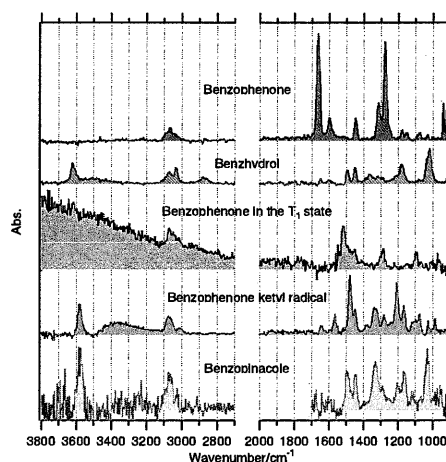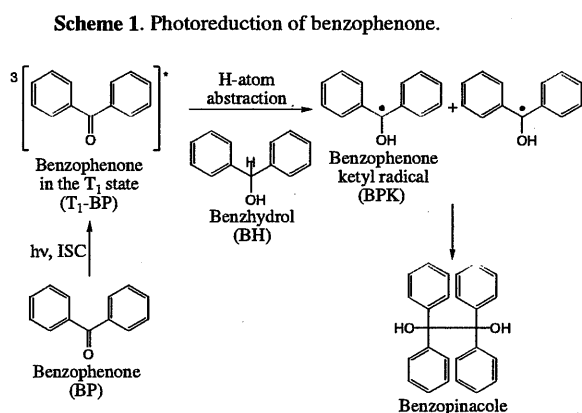
Scheme 1. Photoreduction of benzophenone.

Figure 3. Individual infrared spectra of species extracted from the time-resolved infrared spectra.

In chapter 4, the infrared spectra of benzophenone in the lowest excited triplet state are reviewed in detail. The decay rate of the transient species heavily dependent on the concentration of O_2 gas confirmed the assignment for the transient species to the lowest excited triplet state.

Within the vibrational spectrum, the CO stretch band was not observed, which is rather strange in terms of the polarity in the carbonyl group in the ground state.

The T–T electronic transition between the low-lying excited triplet states were discovered in the middle infrared region. It was suggested that, from this T–T transition observed in the infrared region, the energy of the low-lying excited triplet states, such as the T_2 and T_3 states, can be determined.

In chapter 5, time-resolved infrared spectra of photoexcited acetophenone and its derivatives, namely 4'-CF3-, 4'-CH3-, and 4'-CH3O-acetophenone and 2'-acetonaphthone (**figure 4**), were measured (**figure 5**). It was found that the higher-wavenumber and the lower-wavenumber bands did not shift with the substituents while the intensity ratio between them varied significantly. From this

Figure 4. Compounds examined in this study. R: CF_3-, H-, CH_3-, and CH_3O-.

substituent dependence of the spectra, it was suggested that the thermal equilibrium between the lowest $n\pi^*$ and the lowest $\pi\pi^*$ states is established for the compounds examined here. Also, the higher-wavenumber and the lower-wavenumber bands were assigned to the $n\pi^*$ –$n\pi^*$ and $\pi\pi^*$–$\pi\pi^*$ transitions, respectively (**figure 6**).
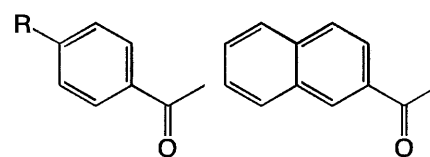
From this point of view, the mechanism of the substituent dependence of the photoreduction reaction rate was also explained. It was suggested that the partial reactivity of the $\pi\pi^*$ states, which have been previously ascribed to the state mixing with the $n\pi^*$ state, was ascribable to a partial population of the $n\pi^*$ state that was involved in the thermal equilibrium.

The solvent dependence and the temperature dependence of the transient infrared spectra of photoexcited 4'-CH3O-acetophenone were also examined. The relative intensity of the $\pi\pi^*$–$\pi\pi^*$ band increased as the polarity of the solvent increased, which was also explained by the thermal equilibrium. Finally, the possibility of the equilibrium between the lowest $n\pi^*$ and the lowest $\pi\pi^*$ states was confirmed by the temperature

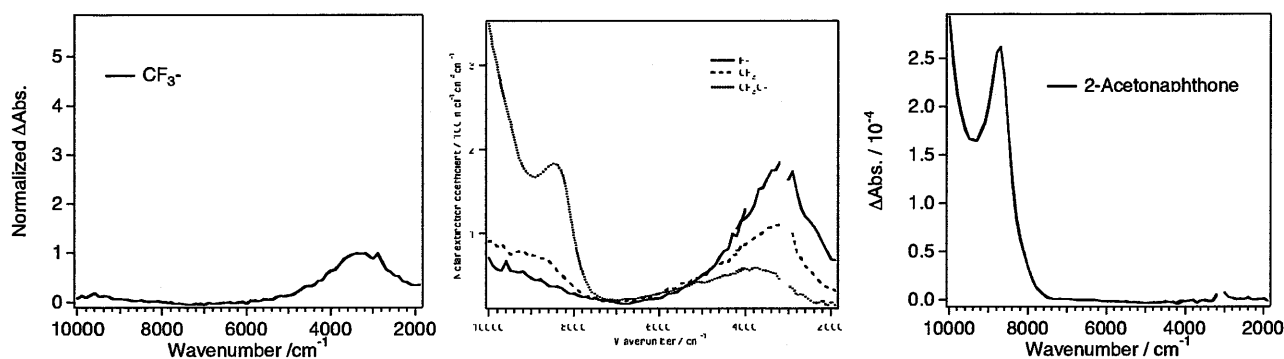dependence of the relative intensity of the band.

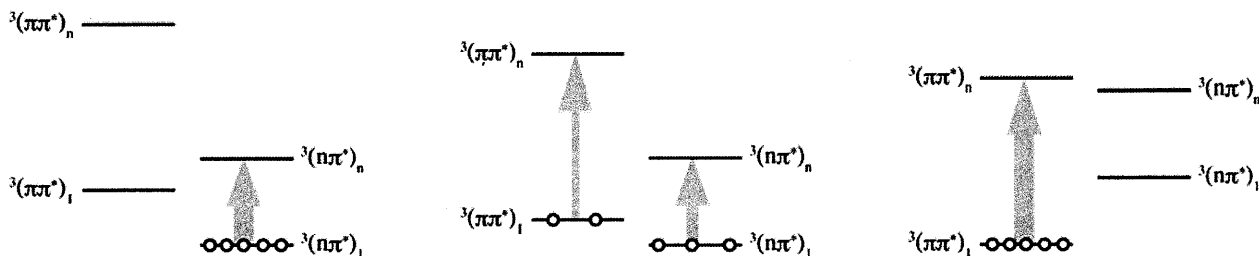Figure 5. Transient infrared spectra of 4'-substituted acetophenones and 2'-acetonaphthone.


Figure 6. Model diagram of the low-lying excited triplet states. The establishment of the thermal equilibrium between the

lowest $n\pi^*$ and the lowest $\pi\pi^*$ states were supposed (center).)

In chapter 6, the vibrational bands in the transient infrared spectra of photoexcited acetophenones were studied. It was found that the vibrational bands disappear for the compounds the lowest $n\pi^*$ and the lowest $\pi\pi^*$ states of which is supposed to be isoenergetic or significantly close to each other, namely acetophenone and 4'-CH$_3$-acetophenone. This fact supports the idea that the lowest $n\pi^*$ and the lowest $\pi\pi^*$ states is close to each other enough to come to thermal equilibrium
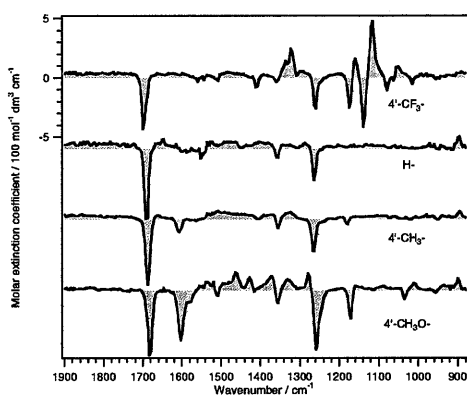
Finally, the conclusion of the present study is given in chapter 7.