1-1-1. Transient Absorption Measurements

Overview

Since the development of the flash photolysis method by Norrish and Porter (1949), transient absorption measurements have been widely used as a central technique in the investigation in photochemistry. Over these 75 years, advances in pulsed lasers have dramatically improved the temporal resolution of the measurement. Today, it is possible to track temporal changes with femtosecond (fs) and, depending on the measurement technique, even attosecond (as) resolution. Concurrently, the scope of study has expanded from intermediates with relatively long lifetimes, such as radicals, ion radicals, and excited triplet molecules, to include shorter-lived intermediates and their dynamics, such as excited singlet molecules, vibrationally unrelaxed molecules, higher electronic states and their dynamics.

Current Status and Frontiers

In transient absorption measurements, the pulsed flash excitation light serves as the temporal origin. Intermediate species are identified from time-resolved spectra at various delays. Information derived from the time evolution of transient absorbance of the intermediate state provides insights into photochemical reaction mechanisms. Monitoring light often utilizes the UV-visible or near-IR regions. Accordingly, the transient absorption signal primarily corresponds to the electronic spectrum of the intermediate. Because all chemical species such as electronic ground-state molecules, excited singlet and triplet states, ions, ion radicals, and neutral radicals exhibit unique electronic spectra, transient absorption measurement can, in principle, detect all such species. Therefore, transient absorption measurements have been used as a central technique for measuring and identifying photochemical reaction intermediates and elucidating reaction dynamics, often in combination with other methods such as time-resolved fluorescence measurements and vibrational spectroscopy.

In Japan, research using flash photolysis began in the 1950s. After the development of Q-switched and mode-locked lasers in the 1960s, time resolution has improved dramatically. At the present, even the attosecond resolution is achieved, depending on the measurement method. In the case where a pulsed laser with a time duration shorter than the molecular vibration period is used as a pump pulse, beat signal corresponding to molecular vibrations can be observed in the time evolution of the transient absorbance, as shown in Figure 1. Analysis of these signals can sometimes provide insights into the molecular vibrations and geometrical change involved in the reaction.

To identify the electronic spectra of intermediates observed as transient absorption signals, reference spectra of intermediates produced by specific methods, such as chemical or electrochemical techniques, and several reference data are also required. However, in recent years, advances in computational science can provide the electronic spectra of these intermediates with a certain degree of reliability.

Measurements of dichroism of transient absorption have been applied to the acquisition of information on rotational relaxation in non-luminescent molecules, intramolecular energy transfer, and electron transport. Furthermore, beyond merely creating and monitoring intermediates with excitation light, active control of photochemical reactions is achieved by intentionally irradiating a second (excitation) pulse to induce multiphoton absorption or dumping (forced deactivation) to the ground state.

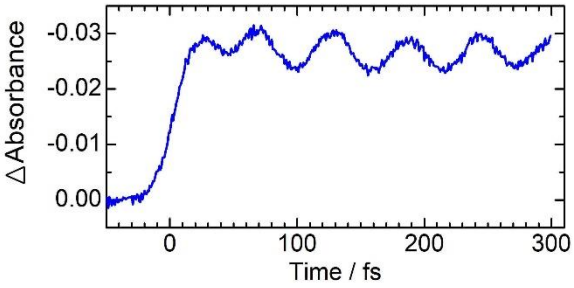

Figure 1. Transient absorbance of oxazine 4 in methanol solution irradiated with a femtosecond laser (pulse duration: 20 fs). The excitation and monitoring wavelengths were 650 nm.

References

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Future Perspectives and Directions

Challenges to be resolved or realized within the next 10 years: In recent years, significant improvements have been made in the precision and temporal resolution of measurements of more direct detection methods of transient chemical species, such as time-resolved measurements of the molecular structure of transient species using X-ray diffraction, and measurements of surface dynamics using time-resolved probe microscopy. We anticipate improvements in both spatial and temporal resolution through detection methods combining these direct techniques with versatile measurement methods like transient absorption.

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