1-5-5. Application of Multiphoton Absorption and Multiple Excitation

Overview

With advances in laser technology, various photochemical responses utilizing multiple excitation and multiphoton absorption have been reported not only for reactions at the molecular level but also for responses in aggregates. In addition, specific processes in artificial systems using multiple photons, such as the Z-scheme type reaction in natural photosynthesis, are being studied. These research results and their characteristics are briefly described in the following.

Current Status and Frontiers

Multiphoton absorption processes are generally categorized into simultaneous and sequential processes. In simultaneous processes, multiple photons are absorbed at once, even when the incident light is off-resonant to the one-photon absorption. The absorption cross-section for the simultaneous multiphoton absorption is usually very small. On the other hand, an intermediate state generated by a first one-photon resonant absorption undergoes further resonant absorption of photons in sequential processes. Consequently, this process has a higher probability than the simultaneous process. Furthermore, in sequential processes, another intermediate state generated from the initial excited states can undergo further light absorption. Such sequential processes are often termed multiple excitation to distinguish them from simultaneous multiphoton absorption processes.

From a viewpoint of photochemistry, these multiphoton processes offer several advantages. While molecules have various electronic excited states, the states accessible by optical transitions are limited by selection rules. Multiphoton absorption obeys selection rules different from that of one-photon absorption, potentially enabling transitions to one-photon forbidden states. Furthermore, because additional photons are absorbed by the actual intermediate species in the sequential process, we can select the species for the subsequent photon absorption by changing the time interval between the first and subsequent light exposures. As examples of these processes, it was reported that cycloreversion reactions of diarylethenes and fulgides take place with significantly higher efficiency via simultaneous or sequential two-photon absorption compared to single-photon excitation of equivalent energy (Fig. 1(a)).

Furthermore, multiphoton absorption generally allows the use of long-wavelength light to select molecules and generate highly excited states and/or intermediates. Using this advantage, we can induce multiphoton sensitized reactions. As an example, the bond cleavage reaction by visible two-photon process was reported for hexabisimidazole derivatives (HABI), which usually undergoes the biradical formation only by UV light irradiation. For a system where porphyrin (Por) is connected to HABI, it was found that the rapid electron transfer to HABI occurring only from higher excited states of Por produced by the visible sequential two-photon absorption. Anion radical of HABI thus produced undergoes the bond cleavage, followed by the charge recombination resulting in the biradical formation (Fig. 1 (b)). Similarly, in systems semiconductor nanoparticles

combined with organic molecules, selective electron transfer from a highly excited electronic state via multiple excitation has been reported.

For electron transfer systems, other results utilizing two-photon processes have also been reported. Examples include consecutive photoinduced electron transfer, where a radical anion generated by a conventional photoinduced electron transfer by one-photon absorption is excited by another light to enhance its reducing power and used for subsequent reactions. In addition, Z-scheme-type inorganic photocatalytic systems utilizing two-photon processes, similar to the Z-scheme in plants, have also developed.

Furthermore, multiphoton absorption enables spatially selective excitation even along the optical axis due to its nonlinear dependence on light intensity (quadratic in the case of two-photon absorption). A recent example demonstrates the controllability of motion direction in photomechanical materials by varying the focusing position. Furthermore, for a diarylethene solid system, one-color reaction switching via off-resonant simultaneous two-photon cycloreversion and three-photon cyclization as well as the formation of spatial patterns of coloration and discoloration dependent on the spatial intensity profile of the laser beam have been demonstrated.

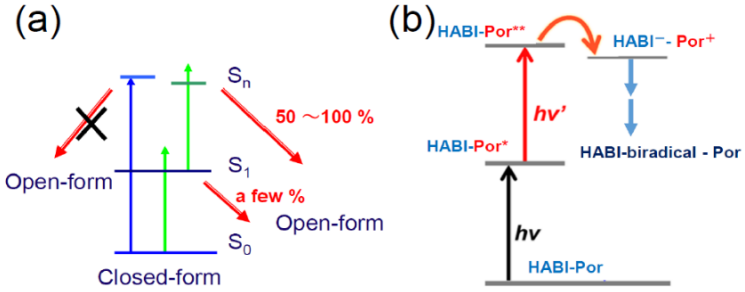

Figure 1. Photochemical reactions induced by two-photon absorption. (a) Highly effective cycloreversion reaction and (b) charge separation followed by biradical formation.

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Future Perspectives and Directions

Challenges to be resolved or realized within the next 10 years: Multiphoton induced responses that transcend conventional limitations. Development into socially implementable devices such as efficient solar cells utilizing multiphoton absorption and multiple excitation, Z-scheme photocatalysts, and artificial photosynthesis systems.

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