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Parallel Relaxation Pathways of Malachite Green Revealed by Ultrafast Pump-Dump-Probe Spectroscopy

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【Introduction】

Malachite green (MG) is one of triphenylmethane dyes that are well-known to undergo ultrafast relaxation upon photoexcitation. The relaxation dynamics of this prototypical molecule has been intensively studied by a variety of spectroscopic methods, and it was found that the relaxation dynamics can be characterized by three typical time constants of τ_1=150 fs, τ_2=0.6 ps and τ_3=3 ps (solvent dependent).[1,2] As shown by a simple relaxation scheme in Figure 1, it is generally believed that the relaxation is accompanied by cooperative rotational motions of the phenyl groups, which leads to a ground-state intermediate (S_x state). However, owing to spectral overlaps of these relevant states, the relaxation scheme of MG is still in dispute. To clarify its relaxation pathways, we studied the ultrafast relaxation dynamics using pump-dump-probe spectroscopy.
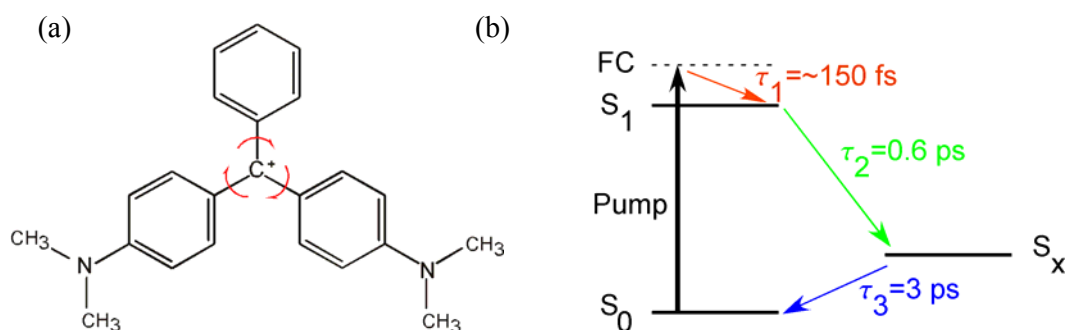

Figure 1 (a) Molecular structure of MG; (b) Energy level of MG and its well-known relaxation scheme.

【Results and discussion】

The MG molecule was photoexcited by a short laser pulse (15 fs, 610 nm) through the S_0-S_1 transition, and an induced transient absorbance change was monitored by another short pulse with the same wavelength. As shown by blue curves in Figure 2, a strong negative signal due to the ground-state bleaching is observed at 1 ps. The bleaching signal decreased with the pump-probe delay time, reflecting that the excited state molecule returns to the ground state on the picosecond time scale. At 4 ps, a positive signal appeared around 650 nm, which is assignable to the absorption of the S_x state. To clarify the relaxation scheme of MG, we introduced a dump pulse at 760 nm, which spectrally

overlaps with the stimulated emission band of the S_1 state. When we applied the dump pulse 0.6 ps after photoexcitation, the bleaching signal was substantially reduced as shown by red curves in Figure 2, reflecting that the S_1 state population is driven back to the ground state by the dump pulse. Interestingly, we found that the signal due to the S_x state remained unchanged, although the S_1 population is drastically changed by the dump pulse. This observation does not accord with the relaxation scheme in Figure 1 (b) and implies that the S_1 state does not serve as a precursor of the S_x state as it is, and the formation of the S_x state is much faster than expected. To further examine the formation time of the S_x state, we also performed the pump-dump-probe experiment with different pump-dump delay times. We found that the signal due to the S_x state decreased only when it is dumped at very early times. This result suggests that the S_x state is produced in the early stage of the S_1 state (the Franck-Condon region).
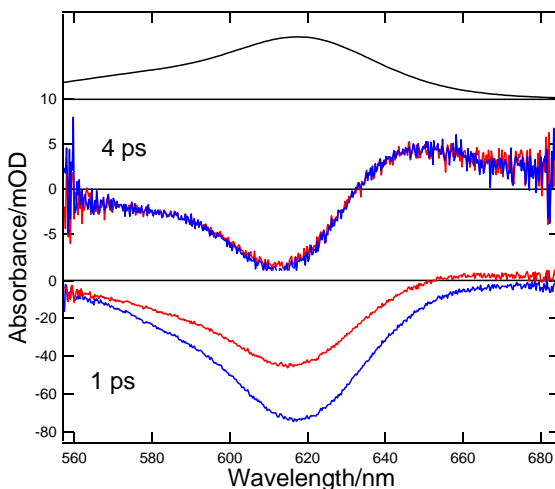

Figure 2 Transient absorption spectra of MG in water with (red curve) and without (blue curve) the dump pulse. (black curve: steady-state absorption spectrum of MG)

Based on these experimental results, a new relaxation scheme of MG is proposed to fully account for the experimental observations as shown in Figure 3. In the new scheme that we propose, there is a branch in the Franck-Condon region, which generates the S_1 state and S_x state with τ_1=150 fs time constant, and then these two states evolve independently. The S_1 state
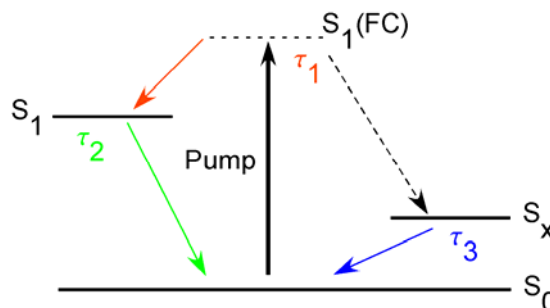

Figure 3 New relaxation scheme of MG.

molecule and S_x state molecule return to the ground state with time constants of τ_2=0.6 ps and τ_3=3 ps, respectively. Comparing with the old relaxation scheme, the new scheme shows that the relaxation of MG occurs through parallel pathways rather than the sequential single pathway. We note that with ordinary time-resolved experiments, it is difficult to distinguish the new relaxation scheme from the previous one. The present study demonstrates that the pump-dump-probe spectroscopy has a high capability for study of complicated molecular dynamics.

【References】

[1] A. Mokhtari, A. Chebira, J. Chesnoy, J. Opt. Soc. Am. B **7**, 1551 (1990).
[2] A. Mokhtari, L. Fini, J. Chesnoy, J. Chem. Phys. **87**, 3429 (1987).