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PHOTONICS spectra

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APPLICATION NOTE

Temperature Dependent Triplet States of Benzophenone; Spectral and Lifetime Measurements Utilising Transient Absorption Spectroscopy

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Introduction

Triplet excited states in molecules and materials play an important role in many practical applications, from phosphorescent pigments to photodynamic therapy, and even photovoltaic solar cells. New materials that exhibit triplet state photochemistry are constantly under development, and understanding the lifetime and energy transfer processes of their triplet states is a fundamental step in their design and optimisation. In this application note, we demonstrate how transient absorption spectroscopy and temperature-dependent measurements can be employed to investigate and understand the nature of photoexcited triplet states of a molecule.

Triplet states are electronic states with two unpaired electrons with parallel spins in different molecular orbitals. Closed-shell molecules have a singlet state (opposite spin pair) as their ground state, with their triplet being at higher energy. Figure 1 shows a Jablonski diagram representing the different energy levels for a classical molecular structure and the mechanisms for triplet state generation and deactivation. The ground state S_0 has two electrons occupying its bonding orbital (B). Excitation of one electron into the antibonding (AB) orbital takes the molecule into its first excited singlet state S_1. Transitions between states of the same spin multiplicity (singlet - singlet or triplet - triplet) are allowed by selection rules, but singlet - triplet transitions are spin forbidden. In some cases, the molecule can undergo intersystem crossing to a lower lying triplet (T_1): this is favoured by molecules containing heavy atoms and paramagnetic species in solution.

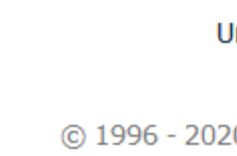

Figure 1. Jablonski diagram of a molecule with singlet (S_n) and triplet (T_n) excited electronic states. Electronic configuration of its bonding (B) and antibonding (AB) orbitals is represented in green

Relaxation of a triplet excited state can proceed via several routes. The molecule may decay to its ground singlet state emitting light, in a process known as phosphorescence. Intermolecular triplet-to-singlet relaxation without the emission of radiation may also take place. A further possibility is the interaction of the molecule with its external environment inducing relaxation to S_0, or quenching, as shown in Figure 1, where oxygen is converted to its singlet state by a molecule in the T_1 state.

Another process, not depicted in Figure 1, is triplet-triplet annihilation (TTA), where two triplet states react with each other to give a single singlet excited state, $T_1 + T_1 \rightarrow S_0 + S_n$. TTA has many possible outcomes: S_n can decay via luminescence or internal conversion, or S_n and S_0 can form a singlet excimer which then dissociates.

The different pathways discussed above make triplet photochemistry a complex subject to study; however, modern optical spectroscopy techniques excel at interrogating these excited state processes. Photoluminescence (PL) spectroscopy is a commonly used technique to probe triplet excited state lifetimes, but it is only effective when there is significant phosphorescence emission from the $T_1 \rightarrow S_0$ transition. At room temperature non-radiative losses often outweigh the radiative phosphorescence decay pathway, so measurements at low temperature or using other techniques are required. An often-used alternative is nanosecond transient absorption (ns-TA) spectroscopy, which probes the triplet ($T_1 \rightarrow T_n$) absorption(s) as a function of time-directly probing the concentration of the triplet as opposed to its luminescence, it is possible to study other decay pathways such as quenching and TTA processes. In addition, measurements in a cryostat may be performed to understand the temperature dependent dynamics of the system.

In this application note we study the photogenerated triplet state of benzophenone by ns-TA and photoluminescence spectroscopy at different temperatures. Benzophenone (Figure 2) is an efficient triplet sensitiser thanks to its high (~100%) intersystem crossing yield. Its S_1 state is generated by promoting an electron from a nonbonding orbital in the n* orbital from the carbonyl group, hence the (n, π^*) label in Figure 2. The higher excited state S_2 arises from the π-orbital to C=O, so it is a (π, π^*) state. Intersystem crossing from S_1 to T_1 is very efficient because transitions between (n, π^*) and (π, π^*) states are highly favoured. This results in a large concentration of triplet states which can evolve via phosphorescence, non-radiative relaxation, or triplet-triplet annihilation (TTA) events.

Temperature Dependent Triplet States of Benzophenone

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