

Seminar über Ultrafast Science and Technology

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Titel: Anti-Kasha behavior in Metal Complexes

A central assumption to interpret the photophysics of any molecular systems and rationalize excited state spectroscopy is the so-called Kasha principle. This is an empirical law stating that, regardless the photo-excited state of a given multiplicity, any detectable photophysical or photochemical outcome stems always from the lowest excited state of the same multiplicity. Accordingly, the photophysical or photochemical outcomes are expected to be independent on the excitation wavelength.

The violation of Kasha's principle is uncommon and a physical system showing an anti-Kasha behavior offers the unique possibility to study dynamics in higher excited states and to conceive multi-response molecular devices.

In the last year we have extensively investigated metal-dithiolene complexes with d^8 -square planar structure. This is a class of metal-containing molecular complexes whose valence electrons show exceptionally mobility giving origin to outstanding redox, linear and non-linear optical properties. Their high hyperpolarizability and non-linear optical behavior make them interesting for photovoltaics, visual and sensing technologies, and molecular electronics.

Recently we focused our attention on a novel family of metal-dithiolene complexes that shows a systematic violation of the Kasha principle, which seems in addition to be proton-switchable. To study such a unique behavior and the specific conditions to observe it we investigated with ultrafast transient absorption spectroscopy the photo-induced excited states dynamics of two representative complexes.

We found that in both the complexes the lifetime of photoexcited higher excited states is 2 to 3 orders of magnitude longer than conventional metal-complexes. This allows physicochemical processes from these states and ultimately the observed anti-Kasha behavior. We rationalize it as the consequence of a neat spatial separation between the molecular orbitals of higher excited states, which gives a charge-transfer character to the internal conversion, slowing down the process. We observed anti-Kasha chemi-luminescence and we provide important information to model their photocatalytic activity.

Zeit: Do, 17.10.2019 14:00 Uhr

Ort: Hörsaal B78, Gebäude Exakte Wissenschaften, Sidlerstrasse 5, Bern, Schweiz