Femtosecond Spectroscopic Studies of Barrierless
Excited-State Decay of Triphenylmethane Dye Molecules
in Alcohol Solutions

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Abstract. We observed solvent-dependent non-monotonic decays in the ground state
recovery of triphenylmethane dyes. The nature of the decay is discussed.

Many chemical and biological reactions proceed on potential surfaces having zero or
a low barrier [1,2] and are influenced by the surrounding medium and by vibrational
relaxation during the course of the reaction. In this work, we chose triphenylmethane
dye molecules, malachite green (MG) and crystal violet (CV), in alcohol solutions
as model systems to investigate the time dependence of barrierless reactions.

Three experimental arrangements were used in this work: fluorescence up-
conversion (FL), transient absorption (TA), and transient dichroism (TD) and
birefringence (TB). FL and TA data were taken with 60fs pulses while TD and TB
data were taken with ~30 fs pulses. The FL data could be well fit as sum of
exponentials by a nonlinear least square fitting program. Attempts to fit TA, TD and
TB data to a sum of exponentials were unsuccessful. A linear prediction singular
value decomposition (LPSVD) program was used instead. The parameters for the
exponentially damped cosinusoidal terms were determined for each data set.

TD and TB spectroscopy with heterodyne detection enhance and linearize the
small amplitude signal and improve the signal-to-noise ratio. Providing there is no
depolarization in the time window we study, a TD experiment gives the same
information as a TA experiment. Both MG and CV are good saturable absorber
dyes. The excited state absorption should be negligible in our experimental
wavelength region. Thus the ground state recovery (GSR) is expected to be the major
contribution to our TA and TD signals.

Fig.1 shows FL and GSR data for MG in water. The FL decay is highly non-
exponential, while the GSR rises, then reaches a plateau before the signal decays.
This lag in GSR is similar to two other examples of barrierless reaction:
bacteriorhodopsin [3,4] and 1144-cyanine [5]. We note the difference in FL and GSR
measurements: FL measures the population change within a narrow window along
the potential surface while GSR should be more representation of total population
change in the excited state. The TA data with the probe polarization parallel and
perpendicular to pump polarization, respectively, yield no obvious difference. This
result excludes the possibility that a transition dipole direction change is responsible
for the "lag" observed.

Fig.2 displays the TD data of MG in alcohols. The "lag" is strongly dependent
on solvent. One way to fit these peculiar curves is with a low frequency oscillatory
component (in addition to the high frequency quantum beats, and exponential decays)
for MG in water, methanol and ethanol. No low frequency component is required to fit the data of MG in propanol (an exponential rise time fits the data well). Fig. 3 displays the normalized low frequency components of MG in different solvents from TD and the rise time of MG in propanol. The results here indicate two trends: one is that the "lag" is strongly dependent on solvent. The other is that the low frequency oscillation becomes lower in frequency as viscosity increases. This is interpreted as the frequency is determined by the effective moment of inertia when solvent molecules adiabatically follow the phenyl ring rotation. The TB data for MG show similar phenomena. CV in water and methanol gives a similar low frequency component but CV in ethanol does not require a low frequency component to fit the data.

References