

STUDY OF CONFORMATIONAL RELAXATION IN THE EXCITED ELECTRONIC STATES OF BENZIL BY FEMTOSECOND TRANSIENT ABSORPTION SPECTROSCOPY

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Introduction

The photophysics of benzil (diphenylethanedione) has been a subject of several investigations with regard to the conformations about the central C-C bond in the excited S_1 and T_1 states [1-5]. While the structure of the S_0 state has been reported to be a skewed one, the labile bi-molecule benzil, after excitation to its singlet state, emits from a relaxed trans planar configuration. Very weak fluorescence from the unrelaxed skewed configuration has also been reported. A time resolved study of the phosphorescence emission from benzil in semi solid glasses has also provided a convincing proof of geometrical relaxation occurring in the triplet excited states of benzil. Our present time resolved absorption spectroscopic study in the ultrafast time scale has been able to show for the first time the conformational changes in the S_1 state of benzil in solution.

Experimental

The ultrafast transient absorption spectrometer has been indigenously designed and built in Chemistry Division, BARC. Briefly, the 100 pJ pulses of 70 fs duration at 620 nm generated in an Argon ion pumped Colliding Pulse Modelocked (CPM) dye laser, have been amplified to about 300 mJ pulses of 100 fs duration in a Nd:YAG laser pumped five stage dye amplifier. Pump pulses at 310 nm has been generated by doubling the 620 nm output from the amplifier in a 0.5 mm BBO crystal and the residual fundamental has been used to generate the white light continuum (400-950 nm) in a flowing water medium of 1 cm path length. The transient absorption spectra are recorded using a dual diode array optical multichannel analyser and the decay dynamics at a particular wavelength region (10 nm width) are monitored using two photodiodes coupled with the boxcar integrators. The overall time resolution of the absorption spectrometer is measured to be 400 fs by measuring the growth of the bleaching signal for malachite green in ethylene glycol. It has also been seen that the transient spectra recorded at 0.5 ps after the laser pulse is free from the group velocity dispersion effect due to the optical materials used in the spectrometer.

Results and Discussion

Fig. 1A shows the time resolved absorption spectra of the transients produced due to excitation by 310 nm laser pulses in cyclohexane, isopropanol and dimethylsulfoxide (DMSO) solutions. In cyclohexane the spectra recorded at 50 and 400 ps after the laser pulse is very similar to the $S_1 \rightarrow S_n$ absorption spectra as reported by Ikeda *et al* [6]. But the spectra recorded at 0.5 and 2 ps are more broad and the positions of the peaks and shoulders are also different. In isopropanol and DMSO, which are more polar and viscous solvents the characteristics of the