ABSTRACT

Intra- and intermolecular charge transfer as well as internal conversion processes are studied in various molecular systems. The dynamics of these fundamental photoinduced processes are investigated by pump-probe femtosecond spectroscopy and steady-state fluorescence. Transient spectra are obtained using white light continuum as probe, while time resolved measurements are performed by probing at specific wavelengths with non dispersive detection. Noncollinearly phase matched optical parametric amplifiers (NOPAs) are used as tunable pump and probe pulse sources. This technique enables to study ultrafast phenomena with an unprecedented time resolution of 60 fs for UV-C excitation pulses at 270 nm. Upon excitation of their structural subunits, triphenylmethane lactones (phenolphthalein and malachite green lactone) undergo ultrafast photoinduced electron transfer (ET) with the formation of a radical ion pair of their structural subunits. The phenol radical cation is formed by ET with a time constant of 50 fs and 80 fs after excitation to the S₁ state of phenolphthalein in acetonitrile and ethyl acetate, respectively. In malachite green lactone both S₂ → S₁ electronic relaxation and ET are completed within 150 fs in aprotic (acetonitrile and ethyl acetate) as well as in protic environment (methanol). Subsequently, in methanol the opening of the lactone ring is detected directly by observing the appearance of the malachite green cation absorption band on a 2 - 4 ps time scale. The results demonstrate that the ET in these molecules occurs faster than the time scale of inertial solvation dynamics, while the lactone ring opening occurs on the time scale of longitudinal dielectric relaxation. It is assumed that on one side an intramolecular vibrational mode promotes the charge transfer and on the other side diffusive solvation dynamics is responsible for the breakage of the C-O bond in the lactone ring.

The controversial behavior of the excited biochromophore indole in water, which fluoresces on a nanosecond time scale and undergoes photoionization within 60 fs, is explained with an ultrafast branching occurring immediately after excitation. The excited indole population is divided by the ultrafast branching into a fraction (62%) which exhibits a 1Lₐ/1Lₜ state reversal and a fraction (38%) that undergoes photoionization generating indole radicals and solvated electrons. The electron solvation dynamics is resolved to occur with a time constant of 350 fs. From the comparisons with the photoionization dynamics in neat water and in 1-methylindole the origin of the solvated electron has been found to be the intermolecular electron transfer to the solvent and not an H-transfer to the solvent.

Internal conversion (IC), an important nonradiative process occurring in organic compounds upon the UV radiation, is explored in o-hydroxybenzaldehyde (OHBA), a molecule that exhibits excited state intramolecular proton transfer (ESIPT). It is shown that the IC of OHBA proceeds as a thermally activated process over an energy barrier of about 200 meV caused by an avoided crossing between the ππ* and πσ* state. The IC shows pure statistical behavior depending on the total excitation photon energy although the preceding ESIPT is a ballistic motion of a well-defined wavepacket. Thus, the coordinates involved in the ESIPT and in the IC are found to be orthogonal.