

Photochromic reaction mechanism and dynamics in 3*H*-naphthopyrans studied by time-resolved vibrational and electronic spectroscopy

Photochromism is one of the most spectacular reactions in photochemistry; it is a reversible phototransformation of a chemical compound between its two forms which differ in their electronic absorption spectrum. The colored form is generated from the colorless compound, or vice versa. Under UV light, the colorless 3*H*-naphthopyran molecule is transformed into two colored isomeric forms (video: <http://www.staff.amu.edu.pl/~gotardb/film.mp4>). In such photoreaction, the formation of colored forms takes place in solution in the short time scale of picoseconds, as a result of the photoinduced breaking of the chemical bond between the carbon and oxygen atoms, and consequently the pyran ring opens. The two colored forms generated in solution show similar UV-vis absorption bands but different thermal stabilities. Typically one isomer (transoid-*cis*) is characterized by a relatively short life-time (seconds) and the second one (transoid-*trans*) is substantially a long-lived species (minutes/hours).

The implementation of this project will allow us to explore the mechanism and dynamics of photochromic reactions with innovative application of time-resolved vibrational spectroscopy. This technique will facilitate examination of the course of the reaction in the time window from subpicoseconds to tens of minutes. Analysis of the signals will help a clear identification of transient species generated along the reaction path. In order to determine the kinetics of formation and disappearance of the colored forms, the time-resolved measurements will be performed in the ultra-short time scale (from subpicoseconds to hundreds of picoseconds) as well as in a longer time scale (from seconds to tens of minutes).

The research will be carried out for various derivatives of 3*H*-naphthopyran as well as in media of various properties (viscosity, polarity, polymer matrix *vs.* solution) to test their impact on the dynamics and photochromic reaction mechanism. The transient species emerging along the reaction path will be studied by mid-IR and UV-vis transient absorption spectroscopic methods to record characteristic vibrational and electronic transitions. Experimental results will be supplemented with advanced quantum-chemical calculations to provide the most accurate picture of the processes at the molecular level.

Taking up the proposal will, on the one hand, explain the photochromic reaction mechanism and, on the other hand, establish mid-IR transient absorption as an effective technique for deciphering of photochromic reactions of 3*H*-naphthopyrans at room temperature in both solutions and polymers. So far, the information on the structure of the resulting isomers has been obtained mainly for solutions at low temperature (-45°C) using nuclear magnetic resonance (NMR) spectroscopy. Although the project deals with important issues of photochemistry, the acquired knowledge may be useful to develop new derivatives of 3*H*-naphthopyrans which undergo photoreaction without formation of long-lived colored forms, which is important in many applications such as dynamic holographic materials or fast switchable photochromic lenses.