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MOLECULAR PHOTONICS LABORATORY FOR ULTRAFAST SCIENCE AND TECHNOLOGY AT SOFIA UNIVERSITY "ST. KLIMENT OHRIDSKI"

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BASIC CONCEPTS AND MISSION

Molecular Photonics is an emerging field of research located at a strategic crossroad where physics, chemistry, engineering and life science meet. These four closely interacting areas provide a relevant multi-disciplinary background as well as timely motivations for the development of molecular photonics at ultimate time and space scales. Applied and technological as well as exploratory and fundamental issues related to light matter interaction in organic or inorganic-organic hybrid systems at micro and nano-scale are now increasingly at the focus of research in molecular photonics.

The Molecular Photonics Laboratory for Ultrafast Science and Technology (MPLUST) at Sofia University is designed first and foremost to promote contemporary scientific research and education. We implement photon-based methods with femtosecond timing to record molecular dynamics, which fully resolve the primary processes. A focus of the experimental and theoretical work is electron, proton and energy transfer, which have fundamental importance for the building blocks of life profound impact on the development of new photonics technologies. With the laboratory equipment we are able to excite coherently multiple electronic states and to probe the evolution of the resulting electronic wave packet with femtosecond resolution. Additionally, the laboratory tools allow high degree of coherent control over the outcome of chemical reactions.

The MPLUST's mission is to perform multidisciplinary research in the basic science and technological applications of ultrashort laser pulses, to educate students from a wide variety of backgrounds in the field, and to spur the de-

velopment of new technologies. Furthermore, its goal is to advance bio-research and photonics engineering - by focusing its intellectual, scientific, educational and industrial outreach efforts on the rapid and directed development of molecular photonics technology. In doing so, the first strategic roadmap for molecular photonics research in Bulgaria will be formulated. MPLUST will coordinate activities within three Sofia University departments and a number of foreign partners, and will devote efforts in building an extensive network of relationships with other universities, industrial partners, and other molecular photonics research groups abroad. While the majority of MPLUST investigators are distinguished for their substantial individual contributions to organic photochemistry, laser physics, molecular photonics, ultrafast spectroscopy, the establishment of this new research lab is expected to greatly enhance their research potential by placing an emphasis on the vertical integration of knowledge.

IMPORTANCE OF THE LABORATORY RESEARCH FIELD

The speed of the molecular dynamics is given by the speed of elementary chemical processes within the molecules. Dynamics is often classified according to time scale. The focus of the effort described here is on the ultrafast time scale of femtoseconds ($1 \text{ fs} = 10^{-15} \text{ s}$) to picoseconds ($1 \text{ ps} = 10^{-12} \text{ s}$). This is a typical time scale of elementary chemical reactions and of electronic and nuclear motions in molecules. Although there is an assumption that practical chemistry and biology occur on much longer time scales, these longer time scales are often reached by adding statistical probability to the short time scale dynamics of molecules. Furthermore, bio-

logical function results from the unique entanglement of structure and dynamics. By structure we mean the time-independent information about the state of a system in some form of equilibrium or quasi-equilibrium. Structure was the focus of most chemists in the past, and it is the key issue in biology. However nature is not in equilibrium and the ultimate aim in chemistry and biology nowadays is to understand dynamics - how systems move between apparently equilibrated structures, changing their chemical composition and performing biological functions on the way. Thus, the fundamental understanding of chemical and biological dynamics ultimately relies upon a thorough explanation of the ultrafast processes. With the emerging new and highly reliable techniques for femtosecond pulse generation and amplification completely new applications of ultrashort pulses come within reach. The time-resolved spectroscopy is a rapidly advancing field with applications in many areas of science and technology. The significance of the area is even more obvious after the Nobel Prize in Chemistry awarded to Ahmed H. Zewail in 1999 "for his studies of the transition states of chemical reactions using femtosecond spectroscopy".

The multidisciplinary interest in time-resolved measurement techniques is the driving force behind the rapid establishment of University centers all around the world in the recent years. They aim to promote interdisciplinary research using time-resolved spectroscopy, e.g. Physical Biology Ultrafast Laser Science and Technology at Caltech, Center for Time-Resolved Spectroscopy at the University of Durham, etc. One of the research areas in the recently established cluster of excellence Munich Center of Advanced Photonics is studying electron dynamics in atoms, molecules and solids.

HISTORICAL OVERVIEW OF THE THEMATIC RESEARCH IN BULGARIA

The first attempts for experimental studying of fast dynamics with resolution better than 10^{-9} s in Bulgaria are done in the 1980's. After successful measurements of the relaxation kinetics in the nanosecond range [1-2], other experimental studies of ultrafast processes in Bulgaria are not known to us. The reasons for this are: first, the

dynamics of chemical processes is mostly in the sub- ns and fs as it is explained above; second, up to now the fs-lasers were expensive and not available. The lasers used the first time-resolved measurements are home-built laser systems at the Department of physics (Sofia University) with quite poor repeatability of the output parameters, which complicates the experiments tremendously. However, the ultrashort (10-100 fs) laser pulses that now can be generated with today's solid-state laser technologies have several very useful properties, other than the short duration, that may be exploited in experiments and technical applications, e.g. very high peak power, broad spectral band-width (due to the short time duration), very widely tunable wavelength, tunable temporal and phase characteristics. These possibilities have given rise to several new applications of ultrafast pulses, not previously possible (or practically feasible) with earlier technologies. On top of that, today's pulse sources are highly stable and reliable, often computer controlled, which further extends the applications to previously unthinkable environments.

Time resolved methodologies currently available at MPLUST: Femtosecond Broad-band Pump-Probe Spectroscopy

This method is an extension of the traditional steady-state absorption spectroscopy. Here the absorbance at a particular wavelength or range of wavelengths of a sample is measured as a function of time after excitation by a short pulse of light. In this experiment both the light for excitation ('pump') and the light for measuring the absorbance ('probe') are derived by the same pulsed laser source. The sample is photoexcited ("pumped") from the ground-state to the excited state by the strong pump beam and is brought out of thermal equilibrium. The excited state will decay to other states with a characteristic decay time. By measuring the absorption of the weaker probe beam which is delayed relative to the excitation, the time evolution of the state under study (ground state, excited state, radical pair, etc.) can be monitored. Contemporary state-of-the-art femtosecond pump-probe spectrometers use a laser-generated white light for probing. This technique pro-

vides broad probing window, spanning from the UV to the NIR spectral range. The white light (or super-continuum) method is highly advantageous over conventional (single wavelength) pump-probe technique in its capability to capture and resolve reactant, intermediate and product states *simultaneously*. By measuring the pump-probe spectra as a function of time one not only will obtain kinetic traces at multiple wavelengths but also will monitor the complex spectral evolution. Local and interchromophore transitions can be simultaneously detected, and detailed information such as spectral intensities and shifts, line shape and band width changes can be readily detected and analyzed. Induced excited state absorption (ESA) peaks are typical signals appearing in broadband pump-probe spectra; but besides these, other contributions may also be observed depending on the spectral range of interest, such as stimulated emission from excited states and ground state bleaching. On the one hand, the transient signals with varied spectroscopic origins might mix together, complicate the spectra and add difficulties to the component assignments; on the other hand, however, they offer more comprehensive spectral information and thus reveal more detailed dynamic processes.

Figure 1 is a schematic representation of the femtosecond broadband pump-probe experimental setup. The laser source is a commercial

Titanium:Sapphire based pump laser that provides a pulse train of femtosecond pulses (130 fs) with energy of 3.5 mJ at 800 nm, and repetition rate of 1 kHz. The output beam is divided into several fractions by the beam splitters. A portion of laser output (250-300 μ J) feeds a commercial non-collinear optical parametric amplifier (NOPA) to generate the pump pulses while another small fraction of the laser output (5 μ J) is used to generate the white light (WL) for broadband probing. The output of the NOPA is compressed to have pulse durations as short as 30 fs. The typical tuning range of the NOPA is 480-900 nm and its output can be used directly to pump the sample. If pump pulses deeper in the UV range are desired, an optional frequency doubling of the NOPA output is used to produce pump pulses with wavelength in the ~240 - 450 nm range. In the real experiments, the generated pulses (NOPA output and its second harmonic) are optimized by additional prism compressors (not shown in the scheme) to compensate for group velocity dispersion.

The changes in optical density are measured by probing with a femtosecond white-light continuum (WLC) generated by tight focusing of a small fraction of the laser output into a thin Sapphire or CaF₂ monocrystal plate. By this means, a usable probe source that covers the UV-VIS-NIR spectral range (from 300 to 900 nm) is achieved.

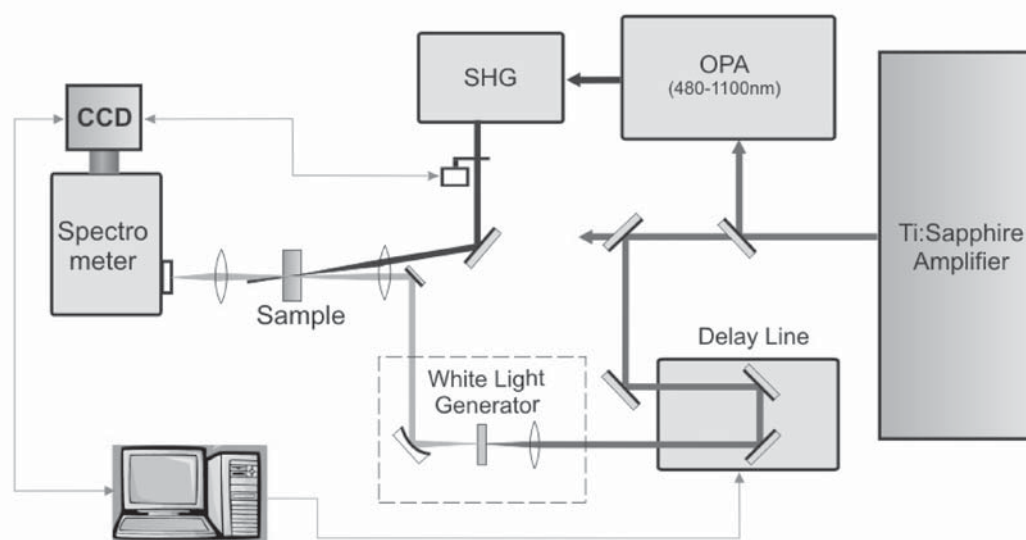


Fig. 1. Schematic representation of the UV-VIS-NIR broadband pump-probe experimental setup

To improve sensitivity of the measurement, transient absorption spectrometer implements dual-beam probe geometry and a digital lock-in technique. The WLC is split into two beams (probe and reference) and focused into the sample using reflective optics. The probe beam passes through excited volume of the sample and the reference passes through the non-excited spot. After passing through the sample, both probe and reference are spectrally dispersed by an imaging polychromator and simultaneously detected on a TEC-cooled CCD. The signals are collected in a two-step measurement cycle. In each step probe and reference signals are recorded at certain conditions determined by the state of the pump shutter (or chopper). The change in optical density is obtained using the standard formalism for pump-probe spectroscopy [3]:

$$OD = -\log_{10} \left(\frac{I_{pr}^{exc}}{I_{ref}^{exc}} \bigg/ \frac{I_{pr}^0}{I_{ref}^0} \right) \quad (1)$$

where the lower index denotes the recorded probe (**pr**) and reference (**ref**) signal, respectively. The upper index characterizes the setting of the shutter which controls the excitation beam: (**ex**): pump shutter is open; (**0**): pump shutter is closed.

The recorded signals at each step are result from integration, typically for several 100 laser pulses. The exact number of acquired laser shots within a single two-step cycle is selectable and will depend on the specific experimental conditions.

The WLC probe pulse passes through several optical elements which introduce a chirp due to the group velocity dispersion (GVD), i.e. its different spectral components accumulate different group delays. As a result, different spectral components of the WLC pulse are interacting with the excited sample molecules at different delay times. Before entering the sample the WLC spreads in time typically from several hundred fs up to ps depending on thickness and the refraction index dispersion of the passed optical material. Independent measurements of the chirp of the WLC will be carried out to correct the pump-probe spectra for time-zero differences.

In this arrangement, the time resolution is around 100 fs, depending on the wavelength of the excitation pulses and sample optical thickness. It is practically measured by the cross-correlation function between pump and probe pulses in a liquid or solid-state transparent media. The spectral resolution of the spectrograph is 3-5 nm in the entire UV-VIS range.

Femtosecond Pump-Repump-Probe Spectroscopy

Many of the photo-induced chemical reactions occur via series of elementary steps including various short-lived intermediate species. The latter can show very similar absorption spectrum hindering the detailed understanding of complex photo-chemical reactions by pump-probe spectroscopy. The problem could be overcome using the recently developed **pump-repump-probe (PREP)** technique [4]. This method is similar to the pump-probe spectroscopy discussed just above, but an additional third pulse is used for excitation of the intermediates involved in the relaxation dynamics. Secondary excitation of the short-lived species could change the reaction pathway yielding novel information on the relaxation dynamics. The method also allows optical manipulation of chemical reactions [4].

The experimental set-up used for the PREP experiments includes an extension of the commercial UV-VIS-NIR femtosecond broadband pump-probe system described above. The necessary modification includes a source for secondary excitation of the sample and an additional optical delay stage for precise control of the relative delay of the secondary pulse, related to the first excitation pulse. In particular, the intermediate species involved in the electron photodetachment of neat water and aqueous electrolytes are expected to show strong absorption on the Ti:Sa laser wavelength of 800 nm. Therefore, in this experiment the secondary excitation pulse is derived directly (typical energy of about 5 uJ) of the regenerative amplifier output.

RESEARCH AREAS AND SCIENTIFIC PROJECTS

The main research areas of the MPLUST are: electron transfer reactions in solutions; photo-induced dynamics in DNA; early-stage resonant

energy transfer in lanthanide-organic complexes as well as ultra fast temperature jumps in hydrogen bonded systems.

Roadmap for the future development of the research laboratory until 2015

The schematic of the main instruments and corresponding expansion in the methods for time resolved analysis available at the Laboratory are shown on Figure 2.

Development of UV-pump-IR-probe and IR-pump-IR-probe spectroscopy will be a powerful approach to elucidate the evolution of molecular structures during ultrafast processes by monitoring vibrational marker modes in real time. This technique can monitor the site-specific interactions in hydrogen bonds and the conversion between excited electronic states by inspection of the fingerprint IR-active vibrations in conjunction with quantum chemical calculations. This spectroscopic technique is a straightforward extension of the pump-probe method developed in the first three years of the project. The fundamental arrangement of the setup, i.e. the temporal sequence of the laser pulses and the detection scheme will remain unchanged. The only components that need to be replaced are the

probe light sources, the spectrograph, the CCD detection array and some of the optical components for steering the IR beams.

Time-resolved fluorescence spectroscopy (Femtosecond Fluorescence Up-Conversion Spectroscopy) provides a powerful technique for investigating electronic properties of solids and liquids. Several different techniques have been used for this purpose over the last four decades. Streak cameras have been used successfully; however, their use is limited to the visible and very near-infrared spectral regions and their usable time resolution in the synchroscan mode at high repetition rate has been limited to about several picoseconds. Optical Kerr cells can provide subpicosecond time resolution, but their low efficiency limits the technique to strong signals. The well-established techniques for growth of high quality nonlinear crystals allow measurement of fluorescence time evolution with subpicosecond time resolution using **fluorescence upconversion technique**. The contemporary state-of-the-art femtosecond upconversion spectrometers can provide time resolution of <100 fs. However, dispersive elements in collection optics prevented measurement of spectra

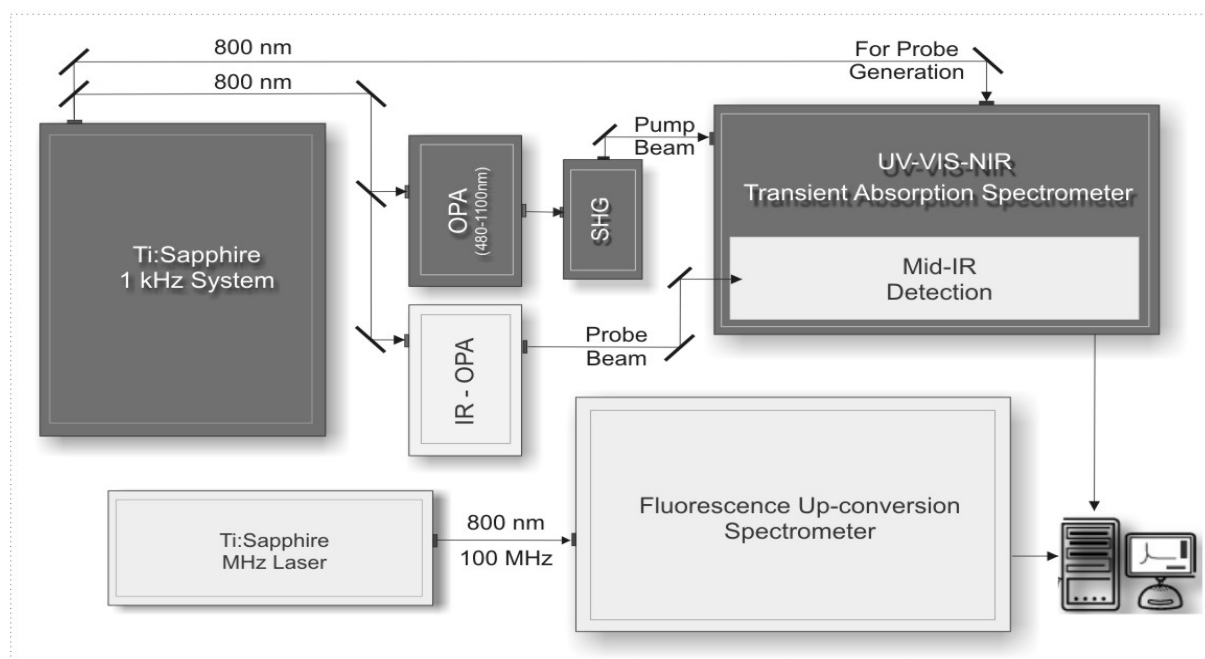


Fig. 2. Layout of the main time-resolved instruments and methodologies, available at MPLUST. The blocks are shaded in order to show the roadmap of the acquired equipments. The dark gray marks the equipment acquired during the establishing of the laboratory, light grey - instruments planned for the future.

and an accurate determination of the zero delay. The required upconversion system for time-resolved fluorescence spectroscopy will have the following desirable attributes: a time resolution of < 100 fs (limited primarily by the laser pulse width), an ability to determine the zero delay precisely, and a wide spectral range (from 430 to 1000 nm with a set of two nonlinear crystals cut at different angles). In addition, this system is extremely sensitive; one can obtain data with a dynamic range exceeding four orders of magnitude from typical chromophores with quantum yield close to unity. This combination of high sensitivity, wide dynamic and spectral ranges, and high temporal resolution is not currently available in any other system. The principle of this technique is phase-matched mixing of the fluorescence excited by an ultrashort laser pulse with a suitably delayed beam from the same laser in a nonlinear crystal.

Acknowledgment

This development was funded by the Bulgarian National Science Fund, through DO 02-167/2008 project and partially it is supported by DRG 02/4-2010 reintegration project.

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