

## FEMTOCHEMISTRY

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### Summary

The advances in femtochemistry made in the last decade are considered. Studies of different reaction types, including isomerization, intramolecular proton transfer, photoreaction of a bifunctional compound, electron transfer in donor-acceptor complexes, and two-channel reactions, excited by femtosecond laser pulses, are discussed in details.

### 1. Introduction

Recently, a breakthrough has been made in experimental methods and technologies based on the use of femtosecond light pulses. The novel techniques make it possible to obtain much more detailed information on the structure and dynamics, the two key notions in chemistry and biology. New fields of research called femtochemistry and femtobiology have emerged. This gave an impetus to rapid progress in new lines of investigations based on the use of specific features of femtosecond light pulses.

Operation with femtosecond pulses made it possible to develop investigations in femtosecond time domain with high spatial resolution. Recently, femtochemistry has been progressing very rapidly. This article concerns the advances in femtochemistry made in the last years.

Specific features of femtosecond pulses extend the potential of conventional experiments:

1. Short pulse duration permits real-time monitoring of the dynamics of intramolecular processes on the femtosecond-subpicosecond time scale. This feature of femtosecond pulses predetermined the emergence of a new field of research, which can be called investigations on the mechanisms of physicochemical processes on the femtosecond-subpicosecond time scale.
2. Large spectral width and coherence of light pulses allows a number of vibrational states to be excited coherently. This type of excited states called a coherent vibrational wave packet is new to chemistry and made it possible to develop a new avenue of research, namely, coherent chemistry. It was found that by varying the amplitude and phase characteristics of the excitation pulse one can practically implement the so-called coherent control of the dynamics and yields of reaction products.
3. High intensity (peak power) of femtosecond light pulses enables multiphoton light absorption; generation of short electron pulses, "white light", THz-band X-ray radiation, and creation of light field strengths exceeding the intramolecular field strength. Ultrashort electron and X-ray pulses can be used for the development of two novel avenues of research, namely, optical, electron, and X-ray femtosecond microscopy with basically new capabilities and femtosecond structural dynamics during chemical reactions.

## 2. Experiments Of Physicochemical Processes On Femtosecond-Subpicosecond Time Scale

The most widely used method of experimental research on the reaction dynamics is the "pump-probe" technique (Figure. 1). The first pulse exciting an object under study is followed by the probe pulse, which is applied after the time delay  $\Delta t$  and detects the changes occurred in the molecular system during this time interval. The time delay  $\Delta t$  is varied by varying the optical path length of the probe pulse. The dependence of system's response on the time delay between the excitation and probe femtosecond pulses can be recorded using various methods including fluorescence, absorption, rotation of polarization plane of the probe pulse, as well as nonlinear methods using four-wave mixing, *etc.* Most often, this response is detected from absorption using a "white light" probe pulse generated upon focusing a femtosecond pulse into a cell filled with distilled water. This makes it possible to detect the dynamics of photoinduced absorption spectrum in the spectral region 380—1000 nm. The difference between the optical density of the sample before and after irradiation is detected at different time delays:  $\Delta A(\lambda, t) = A^*(\lambda, t) - A(\lambda)$ , where  $\Delta A(\lambda, t)$  is the differential optical density,  $A(\lambda)$  is the optical density of the sample,  $A^*(\lambda, t)$  is the pulse-induced optical density,  $\lambda$  is the probe pulse wavelength, and  $t$  is the time delay between the excitation and probe pulses.

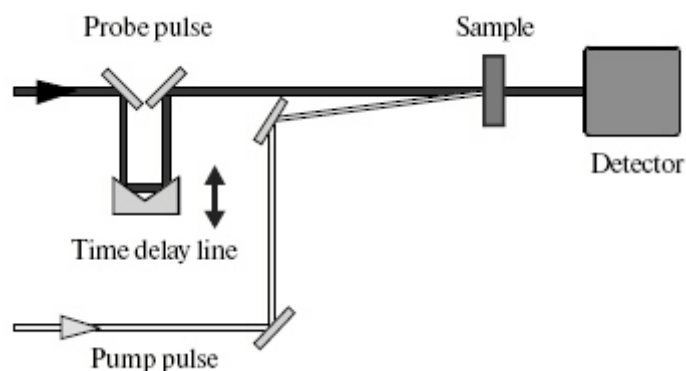


Figure. 1. "Pump-probe" technique: a block scheme.

Figure 2 presents experimental data on the dynamics of intramolecular processes induced by a femtosecond pulse in 8'-(2-hydroxy-1-naphthylmethylenimino)-1, 3-dihydro-1, 3, 3-trimethylspiro[2*H*-indol-2',3'-[3*H*]naphtho[2,1-*b*] oxazine. The cross section parallel to the  $\lambda$  axis gives the photoinduced absorption spectrum at a given time instant, whereas the cross section parallel to the  $\Delta t$  axis gives the temporal evolution of the absorption at a specified wavelength.

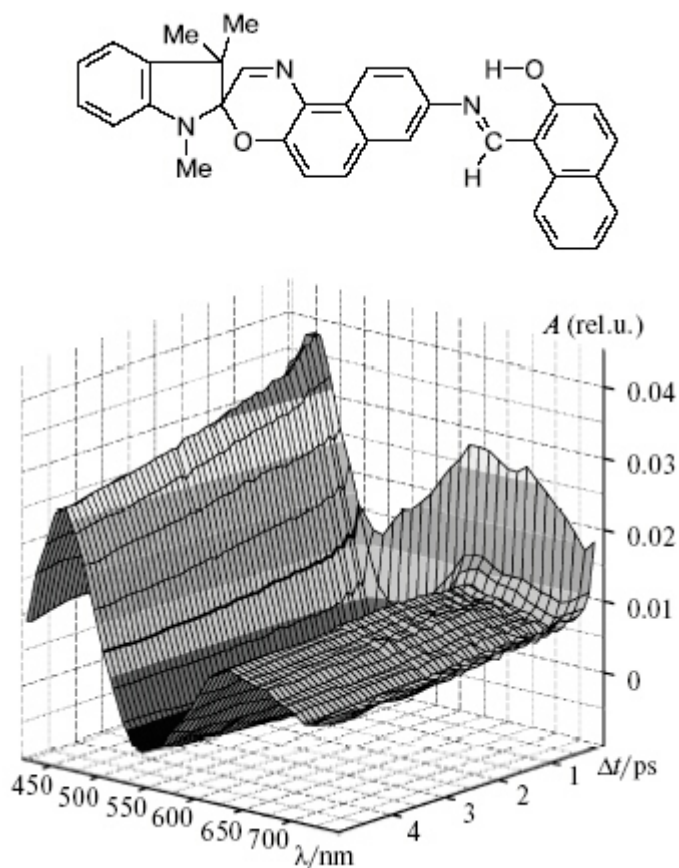


Figure 2. Experimental data on dynamics of photoinduced absorption spectra under the action of femtosecond pulse for 8'-(2-hydroxy-1-naphthylmethylenimino)-1,3-dihydro-

1,3,3-trimethylspiro[2H-indol-2',3'-[3H]naphtho[2,1-*b*][1,4]oxazine (for structural formula, see above). The carrier wavelength of the femtosecond excitation pulse is 400 nm.

Depending on the type of the system under study, the field is divided into femtochemistry of elementary reactions, femtosecond biophotonics, and femtosecond nanophotonics.

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### Biographical Sketch

**Oleg Mikhailovich Sarkisov** currently is the Professor of Chemistry and vice director at the Institute of Chemical Physics of the Russian Academy of Sciences and the Professor at the Faculty of Molecular and Biological Physics of Moscow Institute of Physics and Technology. He received his MS degree from Moscow Institute of Physics and Technology (1967) and his Ph.D. from the Institute of Chemical Physics of the Russian Academy of Sciences (1971). In 1981 he obtained the degree of Doctor of Physical and Mathematical Sciences, in 1984 he obtained the diploma of Full Professor. Since 1983 up to now, he is the head of the Laboratory of Laser Photochemistry and Spectroscopy. Since 1997 up to now, he is vice director of the Institute. The author of more than 200 publications. Oleg M. Sarkisov is the Member of Scientific Council on “Chemical Kinetics and Structure” of the Russian Academy of Sciences; Chairman of chemical dynamics section of Scientific Council on “Chemical dynamics” of Russian Academy of Sciences; the Member of Russian Committee of International Geosphere-Biosphere Programme. He is the supervisor of more than 30 post-graduate students and post-doctoral fellows. O.M.Sarkisov is the coauthor of two monographs and more than 150 scientific articles. His main scientific interests are kinetics and dynamics of elementary reactions, intramolecular and intermolecular energy transfer processes, laser spectroscopy, photochemistry, and atmospheric chemistry.