FEMTOPROCESSES

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Contents

Summary

A review of ultrashort laser pulses use in various scientific areas is presented. Physical principles of the generation of ultrashort pulses of light and superhigh light fields, methods for measuring their duration, uses of femtosecond laser pulses in chemistry and optical spectroscopy, control of the amplitude and phase of molecular pulses with the help of femtosecond laser pulses are considered. Some applications of femtosecond lasers in physics and chemistry, as well as in technology, biology and medicine are discussed.

1. Introduction

From the outset of lasers it was aspiration to receive their radiation in the form of pulses with minimum possible duration. This aspiration was based by the following circumstances.

First, radiation with rather small energy, being, concentrated in a short time interval, allows to receive considerable peak power, and intensity of light at focusing of a laser bunch. This is all-important for researches of interaction of radiation with matter. Such new areas of physics as nonlinear optics and studying of superdense high-temperature plasma had the development in many respects thanks to successes in the field of generation of powerful intensive pulses of laser radiation.

Secondly, decreasing of duration of light pulses raises the time resolution of methods

of research of the fast phenomena. Many phenomena concerning a microcosm of atoms and molecules include the processes with characteristic times of picosecond and femtosecond duration range. Generation of laser radiation in the form of pulses of such duration gives basic possibility "to freeze" picture of evolution of ultrafast process, otherwise, to receive "an instant photo" at a given time. The technique "pump-probe" used is stroboscopic, inherently. As a result of impact by the short pulse the investigated object is excited, and then by means of delayed for a certain time-interval pulse the information on changes, occurring in this interval, turns out. Changing sequentially the delay time, it is possible to track changes of the object in time after the excitation moment. Obviously, the shorter the pulse, the more fine changes in time can be investigated.

During development of quantum electronics tremendous successes in the field of generation of ultrashort pulses of laser radiation have been reached. Some indicator of this progress is that fact that into use of researchers began to enter successively nanoseconds (10^{-9}s), picoseconds (10^{-12}s), femtoseconds (10^{-15}s), and recently began to use attoseconds (10^{-18}s). Precisely the same has occurred with laser, which power may run into megawatts (10^{6} W), Gigawatts (10^{9} W), Terawatts (10^{12} W) and, now, pettawatts (10^{15} W).

By 1998 the long way of reduction of time scales light pulses has been passed practically up to the end: pulses with duration $\tau_{\text{p}} = 4.5\,\text{fs}$ in a visible range (only two periods light pulses) and $\tau_{\text{p}} = 40$ fs on length of wave of the CO_2 laser (10 microns) – light pulse with one period of pulses – are received! One period of optical oscillation is a limiting duration of a light pulse, but simultaneously and limiting "speed" of optical response of the matter. That is why, not without reason, development of femtosecond lasers is compared with the invention of a microscope.

On the other hand, transition to femtosecond pulses is also next jump on a scale of intensity of light. At duration of a pulse $\tau = 100$ fs rather small energy $W = 0.1$ J corresponds to a power P=10^{12} W. Thus, in rather modest systems on scales it is possible to pass to the power levels, which else more recently it was possible to receive only in multi-kilo-joule installations, devoted for controlled thermonuclear synthesis.

Thus, absolutely new experimental possibilities were appeared in nonlinear optics. In the field of focused femtosecond pulses the intensity of light of 10^{21} W/cm^2 is received and, as a consequence, intensity of a light field reaches 5•10^{11} V/cm. So, we reach the fields exceeding intra-atomic ($E_{\text{a}} = 5\times10^{9}\,\text{V/cm}$ for hydrogen atom). In so high light fields new problems of nonlinear electronic physics can be investigated and become a reality for direct experiments in which it is possible to observe the effects predicted by nonlinear quantum electrodynamics (nonlinear scattering of light on relativistic electrons, scattering of light on light in vacuum, *etc*.)

With the help of femtolasers a large body of researches is now performed in physics, chemistry, biology, technology, modern electronics *etc*. The substantial repertoire of laser radiation – its coherence, range of intensity and frequency, controllability of focal area and of beam length – has been comprehensively explored in the contexts of micro-

and macro-diagnostics of cells, biochemical kinetics, therapy and surgery.

2. Generation of Ultrashort Light Pulses

To obtain extremely short light pulses one uses a phasing principle of spectral components of light. Phasing of spectral components allows to truncate simultaneously a light pulse and sharply to increase its peak power. The limit of duration of a pulse is established by spectral width of light $\Delta t_{\min} = 2\pi / \Delta\omega$. Apparently, from this formula, to receive extremely short light pulses (with only a few periods of light pulses), it is necessary to have the radiation which spectral width is of about carrying frequency.

Though basically it is possible to offer ways of phasing of components in the spectrum of non-laser light source, such approach appears rather difficult and energetically unprofitable. Therefore initial broadband radiation, phasing of which components leads to generation of short pulses, is usually obtained at self-interactions of laser pulses in nonlinear medium. In this case it is a question of a regular broadband light packet in which it is necessary to change phase relations.

Figure 1 illustrates one of the most effective version of this technique — a compression of the phase-modulated pulse. The fast phase modulation that expands the spectrum turns out here due to the self-influence of the initial pulse in the substance with cubic nonlinearity. Phasing of spectral components and consequently also pulse compression is carried out in dispersed delay lines (pair of diffraction lattices).

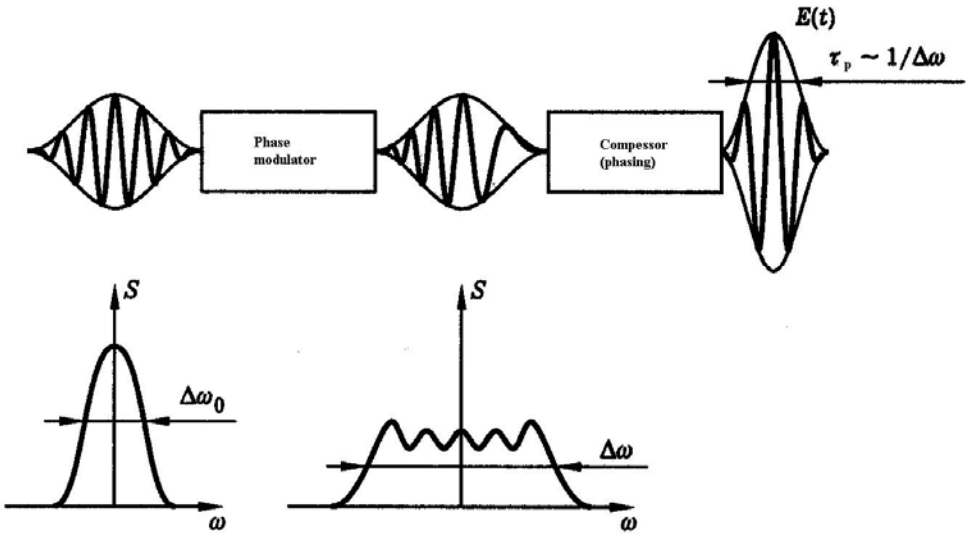

Figure 1. The principle of generation of extremely short light pulses: fast phase modulation and compression.

A principle of operation of the scheme shown on Figure 1 is possible to explain on the basis of spectral representations (phasing of spectral components, synchronization of modes), as well as directly considering transformation of the envelope of a pulse, i.e. on time language. The compression in this scheme should be treated as a result of

"catch up" in dispersion lines of the delay of low-frequency spectral components, settling down at the front of pulse, by high-frequency components, originally grouped on its tail. It is necessary to notice that discussed principles have deep analogies in classical optics of wave bunches. So, the problem of generation of a train of short pulses due to superposition of the synchronized discrete modes analogously to a classical problem of diffraction of a plane wave on an amplitude lattice. Compression of the phase-modulated signal by a dispersive element (by optical compressor) is a temporal analogue of spatial focusing of a bunch by means of a lens.

In all these situations the main point — control of the phase of light wave. The control of a phase in space the optics has mastered, in essence, in the XIX century. Fast control of a phase in time, that is necessary for generation of extremely short pulses, was the achievement in last decades of XX century. For its realization it is necessary to have, obviously, systems with quickly changed in time parameters. In the limit, it is a question of changes in a time of an order of the period of light pulses, the most perspective way of the decision of the problem is the control of light wave itself based on use of fast optical nonlinearity.

Let consider the elementary theory of the optical compressor. Action of compressor is based on use of nonlinearity of the refraction index of an optical fiber. The light pulse of kind

$$E = \cos(\omega t - kz), \quad k = \omega n / c, \tag{1}$$

propagated in the medium with a nonlinear refraction index

$$n = n_0 + n_2 I, \tag{2}$$

and undergoes phase self-modulation. Really, total phase gain got by a pulse on a distance *z*,

$$\varphi = kz = \omega n_0 z / c + \omega n_2 I z / c. \tag{3}$$

As intensity of light depends on time, i.e. $I = I(t)$, there is a time-dependent nonlinear additive to a phase

$$\Phi(t) = \omega n_2 I z / c \tag{4}$$

and also consequently the time-dependent additive to frequency

$$\Delta\omega(t) = \frac{\partial \Phi}{\partial t} = \frac{\omega}{c} n_2 z \frac{\partial I}{\partial t}. \tag{5}$$

Expansion of a frequency spectrum of the pulse, arising owing to self-modulation, it is possible to estimate as

$$\Delta\omega = \frac{\omega}{c} n_2 z \frac{I_0}{\tau_0}, \tag{6}$$

where τ_0 — duration of a pulse, I_0 — peak intensity. So, the frequency spectrum of a pulse strongly extends. Sending the self-modulated pulse into dispersive substance, it is possible to compress a pulse up to duration

$$\Delta t_{\min} = \frac{2\pi}{\Delta\omega} = \tau_0 \frac{\lambda}{n_2 I_0 z}, \tag{7}$$

where λ — wavelength of a light .

To obtain pulse width, comparable with the period of optical oscillations, a range of scanning of frequency $\Delta\omega$ should be comparable with bearing frequency ω. Real way of obtaining necessary frequency modulation is phase self-modulation of light in the substance with almost no inertial nonlinearity (electron Kerr-effect). Non-inertia of nonlinear response, as a rule, is connected with smallness of the nonlinear additive to a refraction index n_2, therefore the large lengths z of interaction are necessary. As a suitable substance for producing phase self-modulation an optical fiber-guide have been appeared.

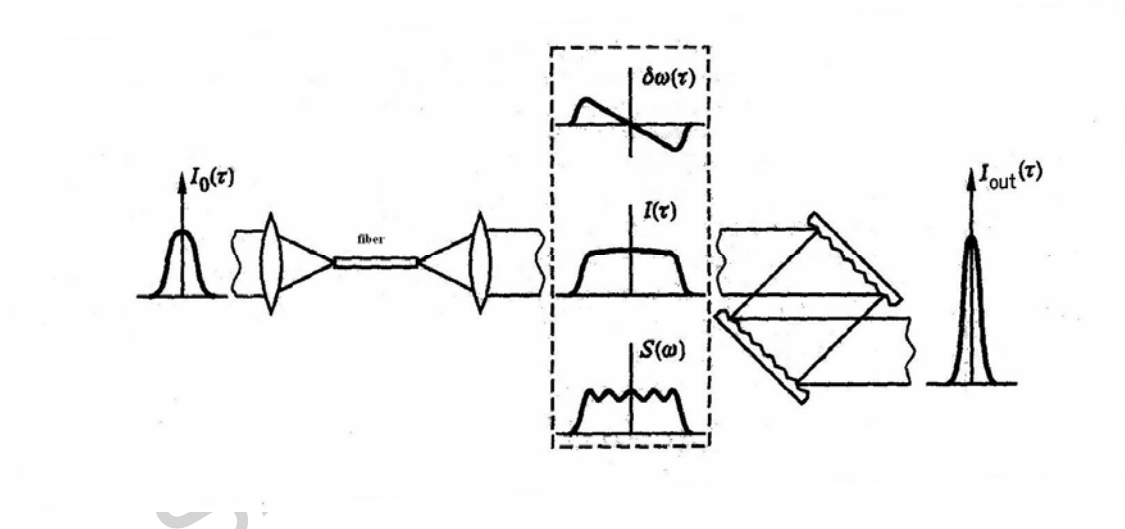

Figure 2. The scheme of the compressor of light pulses on the basis of an optical fiber.

The practical scheme of a compression of light pulses in which phase self-modulation of light in an optical fiber-guide is used, is shown on Figure 2. In the fiber-optical compressor a useful role play dispersive properties of an optical fiber. The dispersion of a group velocity of light in an optical fiber leads to that various spectral components of light are separated in time, namely, carrying frequency is increased from the beginning to the its end (a fiber dispersion is supposed normal). On other words, the pulse gets linear frequency modulation (see Figure 3). If now to pass it through the device, which high-frequency components of a field pass faster than low-frequency

(analogue of a medium with an abnormal dispersion), it is possible to combine all spectral components in time and to receive very short pulse of light.

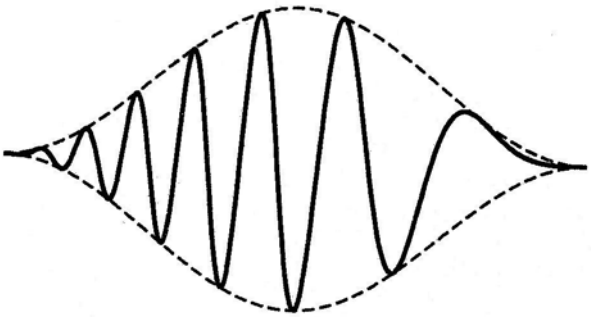

Figure 3. Frequency-modulated pulse.

The necessary element, possessing an abnormal dispersion, is based on dispersive prisms or diffraction lattices. From the equation of diffraction lattice $d \sin\theta = m\lambda$ is seen that light with long wavelengths are deflected by the lattice on large angles, rather than the small. It gives the chance to construct by means of two lattices the scheme in which long light waves take place longer ways than short and, hence, get a demanded time delay.

Notice that in presented on Figure 2 pair of lattices the unwanted effect occurs — spatial (transverse) shift of high-frequency and low-frequency field components. The specified lack it is possible to eliminate by use of the mirror returning radiation back to lattice pair (see Figure 4). After double pass spatial displacement of frequency components is compensated. The phase plate (transparent) serves for additional correction of delays of spectral components. Will notice that strongly dispersive systems – combination of diffraction lattices or prisms – allow to expend a frequency spectrum of light in space and to operate amplitudes and phases of frequency components of the spectrum, and it is absolutely similar to, how it was done by Abbe with Fourier-components of an angular spectrum.

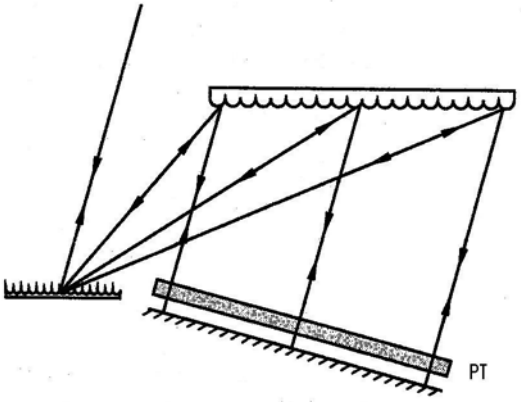

Figure 4. The scheme of the two-through passage optical compressor on diffraction lattice: *PT* — the transparent phase-shifter.

It is necessary to note that in middle 90th there was a break in technique of generation of ultrashort light pulses. The new crystals, capable to generate laser radiation with very wide amplification band, have been created: titan-sapphire (with amplification bandwidth 3500 cm^{-1}), chrome-forsterit and others. The phenomenon of self-synchronization of modes has been discovered. It became possible in titan-sapphire laser to realize intra-resonant compression: phase self-modulation of the pulse is carried out directly in the active element of the laser (for the account Kerr nonlinearity), but compression with the help of pair of glass prisms or the multilayered dielectric mirror possessing negative dispersion of a group delay (depth of penetration of light in such mirror depends on the wavelength). Lasers of this kind are pumped up by continuous radiation of the argon laser or the second harmonic of the laser on neodymium garnet. The titan-sapphire laser is very compact (the length of a crystal of an order of millimeter), is easily transferred into regime self-synchronization of modes and it generates pulses with duration 10 fs and energy of an order of nano-joules on wavelength 800 nanometers. Methods of amplification and transformation of frequency of such pulses are well developed.

The quest for faster and faster time-resolved measurements has reached recently (2007) a new level. A.L. Cavalieri with colleagues reported that they have measured a delay of 100 attoseconds in the emission of electrons ejected from a surface irradiated by light. This is not just the experiment with the best time resolution yet: it is also the first time that attosecond metrology has been applied to a solid, rather than a gaseous, system. Attosecond pulses are created when intense laser pulses of femtosecond duration are focused into a gas sample. A process known as high-harmonic generation then kicks in to produce light at a range of frequencies that are precisely phased together, creating a train of very short, coherent pulses.

A.L. Cavalieri *et al.* focused their 90-electronvolt extreme ultraviolet pulse at an angle on a tungsten metal surface. The lower-frequency optical pulse that created the attosecond pulse follows along the same path, but its passage can be delayed in steps of 300 attoseconds. Electrons liberated through the photoelectric effect by the first pulse are detected by a spectrometer that measures their kinetic energy. The optical laser field pushes these photoelectrons' energy up or down, depending on the precise position of both the attosecond pulse and the photoelectron in the laser field's cycle. By varying the time delay between the pulse and the optical field, and measuring the shift in the up and down motion of the energy spectrum, the authors could precisely measure the emission time of the photoelectrons. They were able to distinguish electrons coming from different energy states in the surface, observing that electrons from the more deeply bound core states in the surface were emitted around 100 attoseconds after those from the conducting band.

3. Measurement of Ultrashort Pulse Duration

One of the main tasks on a way of wide use of ultrashort light pulses is development of essentially new methods of measurement of duration with picosecond, femtosecond and attosecond resolution. The standard techniques of measurement, that use photo-detectors and oscillographs, has appeared suitable only for nanosecond pulses, and to the aid of experiments nonlinear optical phenomena have come, which run depends on

intensity of a wave. To them, in particular, concern generation of the second harmonic and a two-photon luminescence at crossing of two light bunches. From the size of crossing area of bunches and a velocity of light, the duration of a pulse of radiation is obtained.

In the two-photon method the light bunch is divided by a glass plate into two bunches of equal intensities (see Figure 5). These bunches after reflection from mirrors, go from the different sides of a ditch with organic dye. And such a dye is selected whose molecules are excited by two quanta of light (two-photon resonance). Excited molecules give up the stored energy, radiating visible light. Brightness of a luminescence is proportional to intensity of light pulses. As a result, in a ditch luminous tracks are observed which is possible to photo.

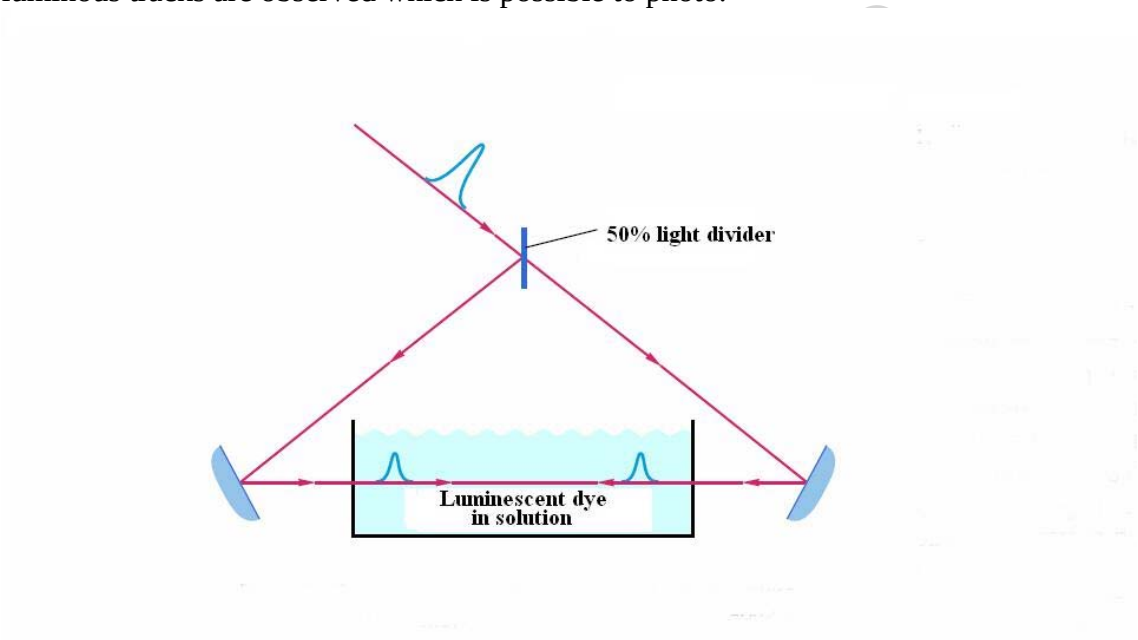

Figure 5. The scheme of measurement of duration of ultrashort optical pulse by luminescence method in two-photon luminescence.

In crossing place of two pulses, propagated in a ditch towards each other, the intensity of light two times as large than the light from a single pulse, and, hence, study of brightness distribution along the track allows to determine duration of a light pulse. At registration of picosecond's pulse a bright luminous central part has a length of an order of a few fractions of millimeter.

For measurement femtosecond duration of pulses the correlation methods, well developed earlier in radio engineering, are also used. For measurement of autocorrelation function $G(t)$ a signal $I(t)$ is delayed, then this delayed signal is multiplied with the original signal in the nonlinear device and then integrated. It is widespread the scheme of the nonlinear-optical correlator where as the delay block the prism of total internal reflection is placed on the movable table. Multiplication of an optical signal occurs in the nonlinear crystal focused for non-collinear generation of the second harmonic. As this takes place an integrating signal of a photo-detector measures the autocorrelation function of intensity of the second order

$$G(t) = \int_{-\infty}^{\infty} I(t)I(t+\tau)dt. \qquad (8)$$

As an example Figure 6 illustrates interferential autocorrelation function and spectrum of the 270 fs laser pulse.

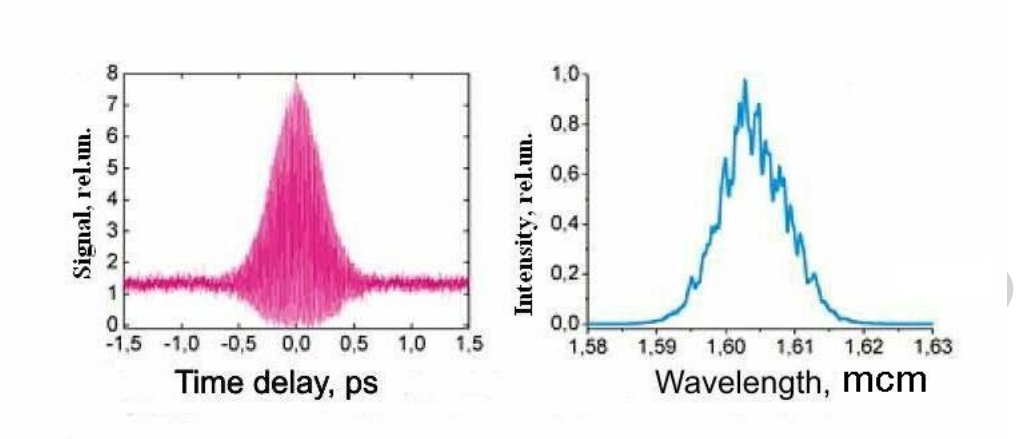

Figure 6. The interferential autocorrelation function (left) and the spectrum of 270 fs laser pulses (right).

4. Femtosecond Technologies

Now we will consider some applications of femtosecond light pulses. On a basis of femtosecond lasers high-precision technologies are successfully developed, such as cutting and processing of materials, and also systems of three-dimensional optical memory. Thus it used that circumstance that influence of femtosecond light pulse on substance can be strong, but simultaneously local, i.e. concentrated in very small volume. The specified possibility is caused, on the one hand, by smallness of the energy of the pulse, and, on the other hand, by high intensity of light. It is directly visible from the formula

$$I = W / S\tau \ , \qquad (9)$$

connecting among themselves energy W and pulse duration τ, cross-section area of bunch S and intensity of light I. For example, for W = 10 μJ, τ = 10 fs, S = 10^{-7} cm^2 it is received I = 10^{16} W/cm^2. In a light field of such intensity nonlinear-optical processes effectively occur, such as two-photon absorption of light, optical breakdown, *etc*. However space area in which these processes are exhibited in the appreciable scale is rather small. Let estimate, for example, the size of area of condensed matter in which the femtosecond light pulse is capable to cause ionization of atoms. Energy of ionization of atom makes nearby 10 eV, or 1.6x10^{-18} J. The light pulse with energy 10 μJ is capable to ionize, hence, nearby 5 x 10^{12} atoms. Considering that one atom has the volume 3x10^{-23} cm^3 (such a volume the water molecule in a liquid phase occupies), we will receive volume of area of ionization $V = 150\,\mu m^3$ that corresponds to a volume of a cube with length of an edge 5 microns. So, the size of area in which the focused

femtosecond light pulse strongly influences substance, changing its properties, actually can be extremely small.

Experiments confirm this conclusion. Studying optical breakdown of transparent dielectrics in the field of focused femtosecond laser pulses shows that the linear size of breakdown area can be only some microns. With the same spatial resolution it is possible to influence on molecules in polymeric matrices, causing two-photon absorption of light and structural change of molecules. Last effect is taken as a principle in systems of three-dimensional optical memory developed now. The data recording density in such systems can reach 10^{12} bits/cm^2. There are also rather perspective technological applications of femtosecond lasers, connected with cutting of materials and processing of surfaces, as we mentioned above.

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Bibliography

Books and Reviews

D'Alessandro Domenico (2004). Introduction to Quantum Control and Dynamics. *Chapman & Hall/CRC Applied Mathematics & Nonlinear Science,* pp.360. [This book presents the mathematical concepts and fundamental physics behind the analysis and control of quantum dynamics, emphasizing the application of Lie algebra and Lie group theory. After introducing the basics of quantum mechanics, the book derives a class of models for quantum control systems from fundamental physics. It examines the controllability and observability of quantum systems and the related problem of quantum state determination and measurement. The author also uses Lie group decompositions as tools to analyze dynamics and to design control algorithms. In addition, he describes various other control methods and discusses topics in quantum information theory that include entanglement and entanglement dynamics. The final chapter covers the implementation of quantum control and dynamics in several fields. Armed with the basics of quantum control and dynamics, readers will invariably use this interdisciplinary knowledge in their mathematical, physics, and engineering work.]

Flytzanis C. (1984). Bistability, Instability and Chaos in Passive Nonlinear Optical Systems. *Nonlinear Phenomena in Solids.* Ed. M.Borisov – Singapoure, World Scientific Publ.

Gladkov S.M., Koroteev N.I. (1990). Quasi-resonance nonlinear optical processes with excited and ionized atoms. *Physics-Uspekhi*, **160**, pp.105-143. [Review of nonlinear optical interactions of excited gaseous substances with radiation of powerful subpicosecond laser systems.]

Ivanov A.A., Alfimov M.V., Zheltikov A.M. (2004). Femtosecond pulses in nanophotonics. *Physics-Uspekhi*. **47**, 687-696. [The authors give an overview of the physical fundamentals of femtosecond nanophotonics — the basic physical phenomena behind the interaction of ultrashort laser pulses with nanoscale objects, nanocomposite materials, supramolecular structures, and molecular aggregates.]

Kryukov P.G. Ultrashort-pulse lasers. *Quantum Electronics***, 31**, No.2, pp.95-119. [The author considers physical principles of femtosecond lasers, measurement methods of ultrashort pulses duration, generation systems and amplification. There are also in this review many examples of uses of femtosecond lasers in physics, chemistry, technology and medicine.]

Martin M.M. and, Hynes J.T. (eds.) (2004). Femtochemistry and Femtobiology, *Elsevier B.V.* , p.800. [This book contains important contributions from top international scientists on the-state-of-the-art of femtochemistry and femtobiology at the beginning of the new millennium. It consists of reviews and papers on ultrafast dynamics in molecular science. The coverage of topics highlights several important features of molecular science from the viewpoint of structure (space domain) and dynamics (time domain). First of all, the book presents the latest developments, such as experimental techniques for understanding ultrafast processes in gas, condensed and complex systems, including biological molecules, surfaces and nanostructures. At the same time it stresses the different ways to control the rates and pathways of reactive events in chemistry and biology. Particular emphasis is given to biological processes as an area where femtodynamics is becoming very useful for resolving the structural dynamics from techniques such as electron diffraction, and X-ray and IR spectroscopy. Finally, the latest developments in quantum control (in both theory and experiment) and the experimental pulse-shaping techniques are described.]

Prasad Paras N. (2004). Nanophotonics. *Hoboken, New-York: Wiley*, p.415. [The book provides an excellent introduction to the field of nanophotonics, and covers a wide range of topics. It is not particularly math heavy, nor does it assume knowledge of much jargon, so is suitable for a fairly wide audience (advanced undergraduate or graduate level). Excellent reference book for the contemporary research and development work.]

Shapiro M. and Brumer P. (2003). Principles of the Quantum Control of Molecular Processes. *Wiley. New York*, p.354 [A detail discussion of quantum control approach.]

Zewail A.H. (2000). Femtochemistry. Past, present and future. *Pure Appl. Chem*., **72**, No.12, 2219-2231. [This review highlights, with historical perspective, the development of the field, with focus on the evolution since the its birth in 1987, the scope of applications and some future development in femtochemistry and the sibling field, femtobiology.]

Zheludev N.I. (1989). Polarization instability, multistability and chaos in optics. *Physics-Uspekhi*, **157**, 881. [Temporal polarization instability is seen as an oscillatory or random variation in time of the polarization parameters of light interacting with a nonlinear system. Spatial polarization instability is the formation of "frozen" complex quasiperiodic or pseudochaotic distributions of the polarization parameters of a wave along the direction of propagation. The problem of polarization instability or multistability is intimately related to the polarization of eigenwaves in the nonlinear problem and their transformation as a result of "hard" and "soft" spontaneous polarization symmetry breaking. This paper presents a review of publications on polarization instabilities in passive nonlinear optical systems, including Fabry–Perot resonators, gyrotropic media, systems with strong two-photon absorption, birefringent crystals, fiber lightguides, and isotropic media.]

Articles

Ahmanov S.A., Bagratashvili V.N., Golubkov V.V., V,Zgursky F.V., Ischenko A.A., Krikunov S.A., Spiridonov V.D., Tunkin A.G. (1985) The production in electronograph EMR-100 of picosecond pulses of fast electrons by photoemission in laser field. *JTP Lett*., **11**, 157. [Generation of electron bunches, received for the account of photoemission from the cathode, lightened with picosecond laser pulse was described.]

Ahmanov S.A., Gladkov S.M., Zheltikov A.M., N.I.Koroteev N.I. (1988). Generation harmonics of optical radiation under electron scattering on ions. *Preprint Phys.Dep.MSU* No.5. [Authors observed very strong nonlinear response of an electron scattered on ion in the field of superhigh

light wave, that can lead to generation of many well phasing intensive harmonics.]

Ahmanov S.A., Vorontsov M.A., Ivanov V.Yu. (1988). Large-scale transverse light waves in systems with two-dimensional feedback, generation of structures, optical turbulence. *LETP*

Lett., **12**, 898. [Authors showed that full use of three-dimensional character of a light field in systems with a two-dimensional feedback allows to observe a wide class of the new phenomena — spatial optical bistability and multistability, generation of dynamic periodic spatial structures and optical turbulence.]

Assion A., Baumert T., Bergt M., Brixner T., Kiefer B., Seyfried V., Strehle M., Gerber G. (1998). Control of Chemical Reactions by Feedback-Optimized Phase-Shaped Femtosecond Laser Pulses., *Science*, **282** pp.919-922 [Tailored femtosecond laser pulses from a computer-controlled pulse shaper were used to optimize the branching ratios of different organometallic photodissociation reaction channels.]

Burke D.L., Field R.C., Horton-Smith G., Spencer J.E., Walz D., Berridge S.C., Bugg W.M., Shmakov K., Weidemann A.W., Bula C., McDonald K.T., Prebys E.J., Bamber C., Boege S.J., Koffas T., Kotseroglou T., Melissinos A.C., Meyerhofer D.D., Reis D.A., and Ragg W. (1997). Positron Production in Multiphoton Light-by-Light Scattering. *Phys.Rev.Lett*., **79,** pp.1626-1629 [It was the first direct observation of material particles produced by nothing but photons.]; see also Schwarzschild B. (1998). Gamma Rays Create Matter Just by Plowing into Laser Light. *Physics Today*, **51**, No.2, 17.

Cavalieri A.L., Müller N., Uphues Th., Yakovlev V.S., Baltuška A., Horvath B., Schmidt B., Blümel L., Holzwarth R., Hendel S., Drescher M., Kleineberg U., Echenique P.M., Kienberger R., Krausz F. & Heinzmann U. (2007). Attosecond spectroscopy in condensed matter. *Nature*, **449**, No.7165, pp.1029-1032 [The authors extend the attosecond techniques previously used to study isolated atoms in the gas phase to observe electron motion in condensed-matter systems and on surfaces in real time. They demonstrate ability to obtain direct time-domain access to charge dynamics with attosecond resolution by probing photoelectron emission from single-crystal tungsten.]

Evans M.G. and Polanyi M. (1935). Some applications of the transition state method to the calculation of reaction velocities, especially in solutions. *Trans.Faraday Soc*., **31,** 875; Eyring H. (1935). The activated complex in chemical reactions. *J.Chem.Phys*. **3**, 197.

Freeman R., Bucsbaum P.H., Milchberg H., Drack S., Schumacher D., Geusic H. (1987). Above threshold lonization with subpicosecond laser pulses. *Phys.Rev.Lett.* **59**, 1092 [Experiment shows that above-threshold ionization with intense linearly polarized light occurs via Stark-shifted bound-state resonances.];

Hentschel M., Kienberger R., Spielmann Ch., Reider G.A., Milosevic N., Brabec T., Corcum P., Heinzmann U., Drescher M., Krausz F. (2001). Attosecond metrology. *Nature*, **414,** 509 – 513. [Presented measurement indicates at attosecond response of the atomic system, a soft X-ray pulse duration of 650±150 as and an attosecond synchronism of the soft X-ray pulse with the light field. The demonstrated experimental tools and techniques open the door to attosecond spectroscopy of bound electrons.]

Hirschbach d.r.. Le Prix Nobel, 1986. Molecular dynamics of elementary chemical reactions.*Elsevier*, *Amsterdam*, 1987.

Hirschfelder I.O., Eyrnig H., Toplev B. (1936). *J.Chem. Phys.*, **4,** 170.

Judson R.S. and Rabitz H. (1992). Teaching lasers to control molecules. *Phys.Rev.Lett*, **68,** No.10, 150-1593 []; Warren W.S., Rabitz H., and Dahley M. (1993). Coherent Control of Quantum Dynamics: The Dream is Alive. *Science*, **259**, 1581. [

Kapteyn H.C., Murhane M.H., Falcone R.W. (1987). Time-resolved measurements of short wavelength fluorescence from X-ray excited ions. *Optics Lett.* **12**, 663. [Some applications of optically induced X-ray pulses are described.]

Karplus M., Porter R.N., Sharma R.D. (1965). *J.Chem.Phys*., **43**, 3258 [In this article authors considered, in particular, the process of bond breaking in a molecule and bond formation.]; see also Laidler K.J. Theories of Chemical Reaction Rates. *McGraw-Hill*, New York, 1969.

Keldysh L.V. (1964). Ionization in the field of intensive electromagnetic wave. *JETP*, **47,** 11 [Theoretical consideration for intensity of light leading to tunnel ionization of atoms, i.e. intensity at which atom at the expense of tunneling of electron is ionized during an order of the light period.]

Kuhlke D., Herpers V., D. von der Linde (1987). Soft X-ray emission from subpicosecond laser produced

plasma. Report at V Int. Symp. "Ultrafast processes in spectroscopy", Vilnus, 1987, p.25. [Observation of soft X- rays from a tungsten plasma produced by intense subpicosecond laser pulses is reported. X-radiation of several keV photon energy was observed with just a few millijoules of laser energy. Using two consecutive pulses for the generation of the plasma the X-ray emission is maximal for a delay of about 30 to 50 ps between the laser pulses.]

Leonhardt R., Holzapfel W., Zinth W., Kaiser W. (1987). Terahertz beats of vibrational modes studied by femtosecond coherent Raman spectroscopy *Rev.Phys.Appl.* **22**, 1735. [It is shown that with ultrashort pulses of less than 100 fs it is possible to excite coherently several vibrational modes of polyatomic molecules simultaneously. The femtosecond time resolution of the experiment allows the study of pronounced high-frequency beat phenomena up to 10 THz. The frequency difference between vibrational modes separated by more than 300 cm^{-1} may be determined with high precision.]

Ruhman S., Joly A.G., Kohler B., Williams L.R., Nelson K.A. (1987). Intramolecular and intermolecular dynamics in molecular liquids through femtosecond time-resolved impulsive stimulated scattering. *Rev. Phys. Appl.* **22**, 1717. [Femtosecond time-resolved impulsive stimulated scattering experimental results from molecular liquids are reviewed and new data are presented. Three main areas are discussed. First, the inertial molecular motions of simple liquids (CS2, benzene) are observed. The results can be interpreted in terms of intermolecular librations, which in some cases are clearly manifest in the form of oscillatory time-dependent responses. The temperature-dependent intermolecular librational frequency and dephasing dynamics in CS2 liquid are determined. The data suggest that dephasing is predominantly inhomogeneous, and permit estimation of the extent of inhomogeneity in the librational frequency. Second, intramolecular vibrational oscillations are monitored directly in real time. The data are influenced by both molecular vibrational and orientational dynamics. These experiments make possible time-resolved spectroscopy of vibrationally distorted molecules in well defined nonequilibrium configurations. Finally, the general occurrence of impulsive stimulated scattering whenever an ultrashort light pulse passes through a Raman-active medium is discussed.]

Sah R.C., Attwood D., Sabersky A.P. (1984). Picosecond pulses from future synchrotron radiation sources. *Ultrafast Phenomena IV*/Eds. D.Auston, M.Eisenthal. – Berlin: Springer-Verlag, , p.49. [Methods of producing the short X-ray pulses from synchrotron radiations with duration of a pulse of the order of 10 ps discussed.]

Scherer N.F., Khundkar L.R., Bernstein R.B., Zewail A.H. (1987). Real-time picosecond clocking of the collision complex in bimolecular reactions: The birth of OH from H+CO_2. *J.Chem.Phys.*, **87**, 1451. [The authors discussed the method that involves the use of a beam of a van der Waals "precursor molecule" containing the potential reagents in close proximity. Weak molecular complexes were used, so the zero-of-time can be established and hence the course of the reaction can be followed in real time.]

Weiner A.M., Leaird D.E., Wiederrecht G.P., Nelson K.A. (1990). Femtosecond pulse sequences used for optical manipulation of molecular motions. *Science*, **247**, 1327. [In this work femtosecond pulse sequences were used for optical manipulation of molecular motion.]

Weiner A.M., Leaird D.E., Wiederrecht G.P., Nelson K.A.. (1991). Femtosecond multiple-pulse impulsive stimulated Raman scattering spectroscopy. *JOSA* B, **8**, 1264 [Possibility of resonant excitation of oscillations of substance with the help of a train of femtosecond pulses has been experimentally shown.]

Williamson S., Mourou G., Li J.C.M. (1984). Time-resolved laser induced phase transformation in aluminium. *Phys. Rev. Lett.* **52**, 2364−2367. [The technique of picosecond electron diffraction is used to resolve in time the laser-induced melting of thin aluminum films. It is observed that under rapid heating conditions, the long-range order of the lattice subsists for lattice temperatures well above the equilibrium point, indicative of superheating. The melting time is found to vary according to the degree of superheating. The initial density of nuclei is determined under the assumption of a two-dimensional expansion model. These results show for the first time the relationship between superheating and the rate of transformation.]

Wood O.R., Silfast W.T., Tom H.W. *et al.* (1987). Soft X-rays produced by picosecond target irradiance. *Proc.Int.Quant.Electron.Conf.* — Baltimore, Maryland 1987, p.187 [Generation of short pulses of radiation in a range of wavelengths of 10-70 nanometers at focusing laser pulses with duration 100 fs and intensity of 10^{14} W/cm^2 on a tantalum target.]

Zewail A.H.. (1988). Laser Femtochemistry. *Science*, **242** pp.1645-1653. [The author shows that with lasers it is possible to record snapshots of chemical reactions with sub-angstrom resolution. The strobing of the transition-state region between reagents and products provides real time observations that are fundamental to understanding the dynamics of the chemical bond.]

Biographical Sketch

Tsipenyuk Yuri Mikhailovich, graduated from the Moscow Institute of Physics and Technology (MIPT) in 1962, becoming candidate of sciences in 1969, and doctor of physico-mathematical sciences in 1979. From 1961 until the present time he has worked at the P.L.Kapitza Institute for Physical Problems, Russian Academy of Sciences, now are being the leading scientist of this Institute. In addition he is Professor of physics of the Moscow Institute of Physics and Technology. His scientific interests include: electron accelerators, fission of atomic nuclei, activation analysis, investigation of the solid state by neutron scattering, and superconductivity. In 1997 he was made Soros professor and in 1997 he became a Member of the New York Academy of Sciences. Y.M.T. has published more than 140 papers in scientific journals, and is the author of three monographs: "Physics of Superconductivity" (in Russian, 1995, MIPT Publishing, Moscow), "Nuclear Methods in Science and Technology" (IOP Publishing, 1997), "The Microtron: Development and Applications" (Harwood Academic Press, 2001), in addition to being the coauthor of a textbook on general physics for high school "Basics of Physics" (Fizmatlit, Moscow, 2001). In 2006 he published the monograph “Quantum micro- and macrophysics” (Fizmatkniga, Moscow).