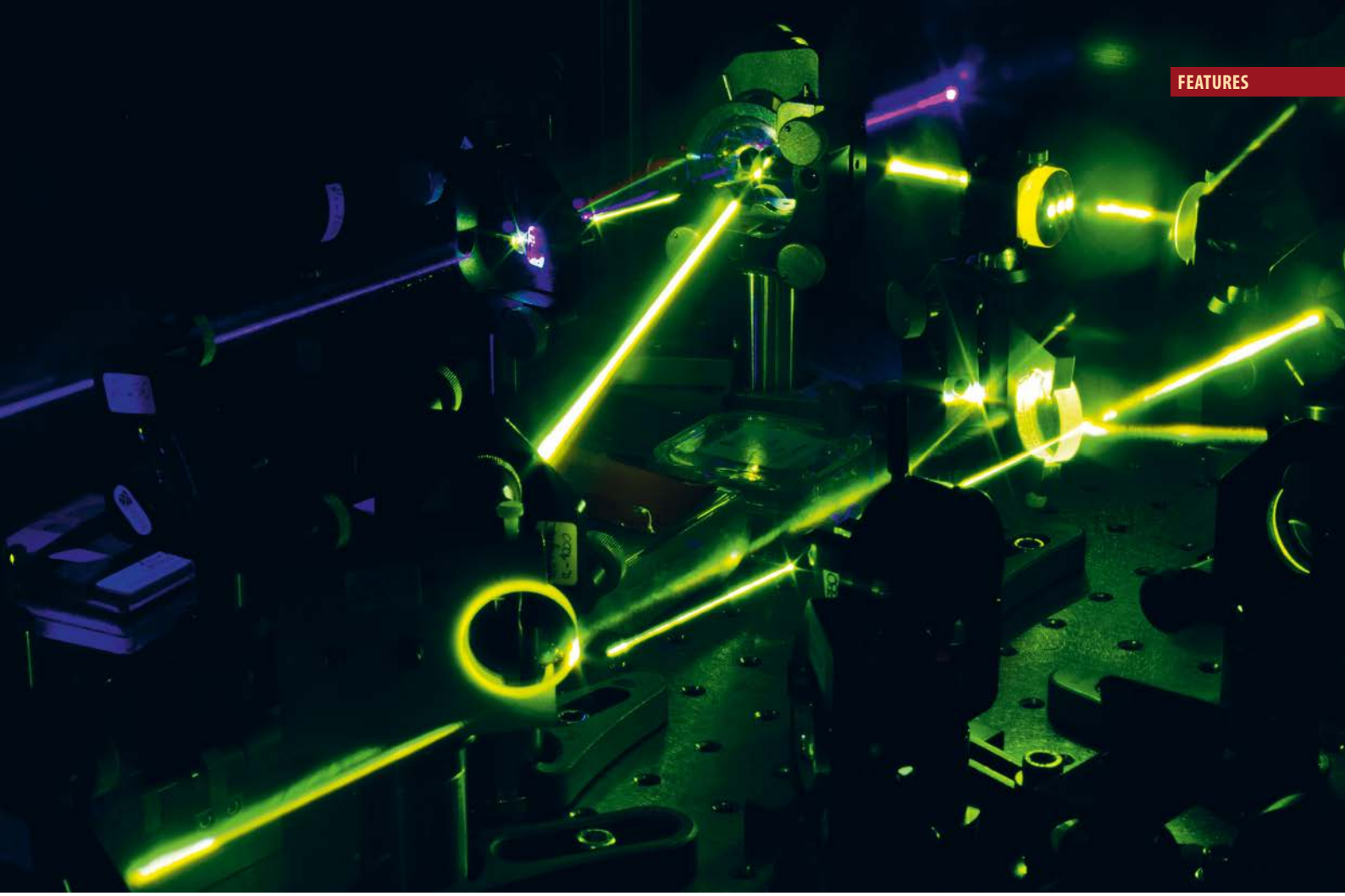

ULTRAFAST LASERS: FROM FEMTOSECONDS TO ATTOSECONDS

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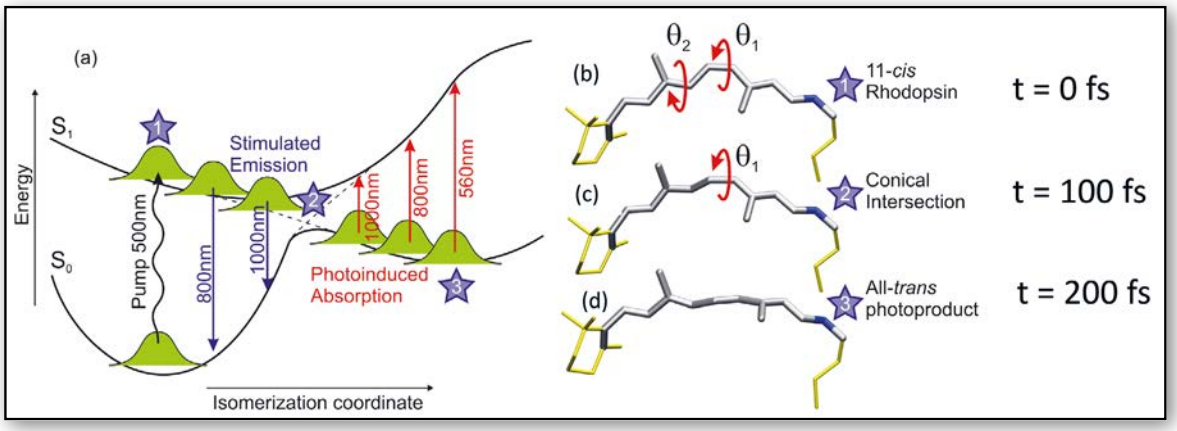
We review the capability of lasers to generate light pulses of incredibly short duration, from a few femtoseconds (1 fs = 10^{-15} s) in the visible down to a few tens of attoseconds (1 as = 10^{-18} s) in the extreme-ultraviolet, reaching peak powers up to several petawatts (1 PW = 10^{15} W).

Ultrashort laser pulses

One of the properties of lasers is the capability of generating a coherent monochromatic light beam, as opposed to incoherent, natural light, which is typically polychromatic, being emitted over a broad spectrum of frequencies. Soon after the advent of lasers, however, it was discovered that they can also produce broadband light in the form of trains of pulses, with duration ranging from the nanosecond down to the femtosecond temporal domain. The most widely used technique for the generation of short light pulses, in the picosecond and femtosecond range, is known as *mode-locking*, since the laser cavity modes are made to oscillate with some definite relation among their phases [1]. The light emitted from a mode-locked laser thus consists of the coherent superposition of many sine waves of different frequencies, corresponding to the longitudinal modes, which interfere destructively except at the times when they are all in phase. This interference



▸ **FIG. 1:** Molecular movie of isomerization of rhodopsin. (a) wavepacket motion from the excited state potential energy surface of the reactant (with stimulated emission) to the ground state potential energy surface of the product (with photoinduced absorption). (b)-(d) calculated snapshots of the structure of retinal during the process at the initial 11-*cis* (b, $\theta_1 = -12.8°$, $\theta_2 = 173.9°$), conical intersection (c, $\theta_1 = -87.8°$, $\theta_2 = -144.6°$) and final *all-trans* (d, $\theta_1 = -141°$, $\theta_2 = -142°$) configurations [8].

pattern results in the emission of a train of ultrashort light pulses, spaced by the cavity roundtrip time, which is the time it takes for light to travel back and forth between the cavity mirrors. Each of these pulses has an ultrashort duration which, according to the Fourier transform theorem, is inversely proportional to the number of locked modes and therefore to the width of the frequency spectrum emitted by the laser. Already in 1965, after the discovery of laser mode-locking by DeMaria and co-workers [2], it was possible to generate light pulses with a duration of 10 ps, which is three orders of magnitude shorter than the shortest pulses of incoherent light, obtained with the electro-optic Kerr shutter. In the two following decades, there was an intense race to shorten the pulse duration, exploiting liquid dyes as optical amplification media because of their broad gain bandwidth. The pulse duration dropped by three additional orders of magnitude [3], to the femtosecond regime, until the milestone result by Shank and coworkers, who generated in 1986 visible pulses with 6-fs duration by using a post-compression technique based on the nonlinear optical process of self-phase modulation in an optical fibre [4]. **This is a remarkable achievement because such pulses contain just a few cycles of oscillation of the carrier light wave (for visible light at λ = 600 nm the oscillation period is T = 2 fs) and are thus close to the ultimate limit of pulse duration in the visible range**.

Applications of femtosecond pulses

In the following decades, important technical advances were introduced which greatly improved the reliability and the accessibility of femtosecond laser technology. Liquid gain media were replaced with solid-state ones, such as Ti:sapphire crystals and Yb:doped crystals and fibers, greatly increasing long-term stability and average power of the laser sources [5]. Second- and third-order nonlinear optical effects, such as self-phase-modulation and optical parametric amplification, were used to further broaden the spectrum of the pulses and to tune their frequency, enabling to cover an extremely broad range from the mid-infrared to the ultraviolet [6]. Exploiting this tunability, femtosecond pulses have become invaluable tools for physicists, chemists and biologists in order to investigate the ultrafast non-equilibrium processes occurring in atoms, molecules and solids, using a variety of spectroscopic techniques [7]. Femtosecond laser pulses can be used to shoot "slow-motion movies" of key photoinduced processes in bio-molecules, such a photosynthesis and vision, as well as to get insight into the non-equilibrium charge carrier dynamics underlying the operation of (opto)-electronic devices. As an example, Figure 1 shows a schematic sketch of the primary event of vision, which is *cis-trans* isomerization (*i.e.* structural rearrangement) of retinal ($C_{20}H_{28}O$), which is the visible light-absorbing chromophore covalently bound within rhodopsin , the light-sensitive receptor protein involved in visual phototransduction in humans and many vertebrates. A wavepacket, created in the excited state of the 11-*cis* reactant, slides on its potential energy surface until it reaches, within 200 fs, the ground state of the all-*trans* photoproduct (Fig. 1a). Ultrafast laser spectroscopy with 10-fs time resolution allows to record the characteristic signals of the isomerization [8] and, combined with ab-initio numerical simulations, to derive the structural dynamics of the retinal molecule during the process (Figs. 1b-d).

Increasing the pulse energy

Mode-locked lasers produce pulses with relatively low energy, of the order of a few nanojoules (1 nJ = 10^{-9} J), which cannot be directly amplified due to damage occurring in the optical gain medium when the intensity exceeds a certain threshold. This problem was elegantly solved by the invention of the Chirped Pulse Amplification (CPA) technique [9]. In CPA laser systems the ultrashort pulses are first temporally stretched, by sending them to an optical system in which their frequency components travel with different speeds and become temporally separated, resulting in a pulse-width lengthening by several orders of magnitude. The stretched pulses are then safely amplified without damaging the optical amplifier material and finally sent to a pulse compressor, which is an optical system where the relative delays of the different frequency components are reversed, thus restoring the original

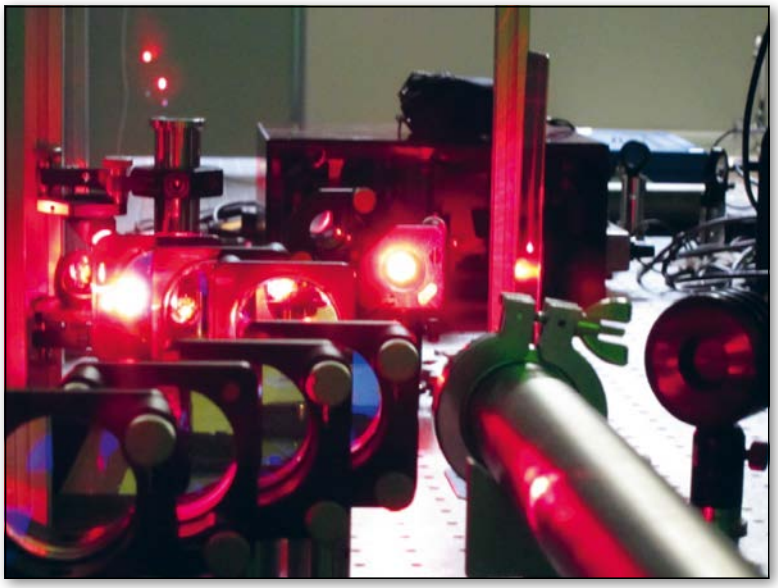
pulse duration. **The CPA technique, for which Donna Strickland and Gerard Mourou were honored with the Physics Nobel Prize in 2018, allowed to increase the energy of ultrashort pulses by over 10 orders of magnitude, resulting in peak powers reaching the petawatt regime.** Such incredibly high instantaneous powers, which exceed by more than two orders of magnitude the combined power of all the world electrical grids, enable completely new regimes of light-matter interaction, where electrons and ions can be accelerated by the laser light to relativistic speeds. Besides their huge scientific impact, ultrashort light pulses are finding more and more real-world applications in materials processing, as they allow depositing energy in the irradiated volume in a very short time, avoiding heat diffusion and resulting in clean ablation without collateral damage. High intensity femtosecond lasers are used for drilling holes in metals, such as in the injectors of diesel engines or the stents used in vascular surgery. They find also medical applications in refractive eye surgery, using the laser-assisted in situ keratomileusis (LASIK) procedure (where keratomileusis means surgical reshaping of the cornea) to correct myopia and astigmatism. It is worth mentioning that in the last few years the European Commission funded the Extreme Light Infrastructure (ELI), a pan-European infrastructure completely devoted to the generation and application of ultra-intense laser sources.

Attosecond pulses

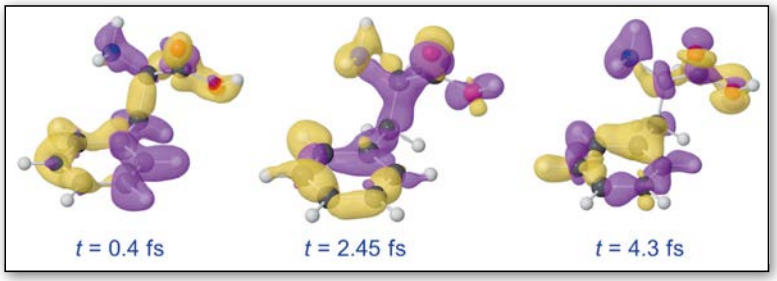
A further conceptual breakthrough in ultrafast optics was achieved with the discovery of high-harmonic generation (HHG) from noble gas atoms illuminated by ultrashort light pulses with a peak intensity of the order of 10^{13}-10^{15} W/cm^2. The process of HHG can be intuitively understood in terms of the so-called "three-step model" [10-11]. When the electric field of the driving light pulse is intense enough, an outer-shell electron is tunnel ionized from the atom into the continuum (first step). The freed electron is then accelerated by the light electric field, gaining kinetic energy (second step); when the electric field of light points in the opposite direction in the course of an oscillation cycle, the electron is accelerated back to the parent ion and, with a small probability, recollides with it. If the recolliding electron recombines with the parent ion, the kinetic energy acquired during its motion in the continuum can be released in the form of a burst of high-energy photons with attosecond temporal duration (third step). Since this process is periodically repeated every half optical cycle of the fundamental radiation, a train of attosecond pulses is generated, separated by half the optical cycle of the driving field. If the harmonic generation process is confined to a single event, by using few-cycle driving pulses with controlled electric field and employing suitable gating techniques, isolated attosecond pulses can be generated: this is important for a number of applications. Typically, sub-5-fs pulses with energy in the millijoule range are generated by using a post-compression technique based on spectral broadening in a gas-filled hollow-core fibre [12]. Figure 2 shows the spectrally-broadened beam at the output of a hollow fibre, which is reflected by a few chirped mirrors used for ultrabroadband dispersion compensation.

Applications of attosecond pulses

Since the first experimental demonstration of the generation of attosecond pulses in 2001 [13-14], such pulses have been used in time-resolved spectroscopy with extreme temporal resolution. **The main target of attosecond science is to get direct access to the electronic dynamics in atoms, molecules, nanostructures and solids, and the possibility to directly control such ultrafast processes.** A number of spectacular applications of attosecond pulses has been reported in the last 18 years, ranging from atomic physics to solid-state physics. The application of attosecond techniques to atomic physics has proven to be crucial for example for the measurement of the delay in photoemission and for the analysis of the process of tunnel ionization. Application of attosecond pulses in molecular physics has been pioneered in 2010, with the investigation of the charge localization process in hydrogen molecules initiated by isolated attosecond pulses (see Ref. [15] for a recent review on the application of attosecond pulses to the investigation of ultrafast dynamics in molecules). Attosecond pulses have been used more recently to investigate the process of charge migration in aminoacids [16]. Theoretical studies have pointed out that very efficient charge dynamics can be driven by purely electronic effects, which precede any rearrangement of the nuclear skeleton and which can evolve on a temporal scale ranging from few femtoseconds down to tens of attoseconds. This ultrafast charge dynamics, essentially driven by electron correlations, has been referred to as charge migration. The first experimental measurement



▼ FIG. 2: Spectrally-broadened beam at the output of a gas-filled hollow fibre, reflected by a set of chirped mirrors.



▲ FIG. 3: Charge dynamics calculated in phenylalanine after excitation by an isolated attosecond pulse at $t = 0$ [16]. Dark gray spheres represent carbon atoms, light gray spheres hydrogen atoms, blue sphere nitrogen and red spheres oxygen.

of charge migration in the α-amino acid phenylalanine ($C_9H_{11}NO_2$), after attosecond excitation was reported in 2014 [16]. An α-amino acid consists of a central carbon atom (α carbon), linked to an amine (-NH_2) group, a carboxyl acid (-COOH) group, a hydrogen atom and a side chain, which is specific to each amino acid. In particular, we investigated the aromatic amino acid phenylalanine, where the side chain is a methylene (-CH_2-) group terminated by a phenyl ring. The molecular structure of the most abundant conformer of phenylalanine is shown in Figure 3. Phenylalanine plays a key role in the biosynthesis of other amino acids and is important in the structure and function of many proteins and enzymes. Figure 3 shows the calculated evolution of the charge density in phenylalanine after prompt ionization induced by an attosecond pulse: a notable rearrangement of the charge is already visible 2 femtosecond after the excitation. The application of attosecond technology to the investigation of electron dynamics in biologically relevant molecules represents a multidisciplinary work, which can open new research frontiers: those in which few-femtosecond and even sub-femtosecond electron processes determine the fate of bio-molecules.

The extension of attosecond methods to solid-state physics is still limited, but important results have been already achieved. The experimental results reported so far demonstrate that the application of attosecond techniques to solids offers the possibility to investigate important physical processes, not accessible by using longer temporal resolution. The measured delays in photoemission from various solids are of the order of a few tens of attoseconds [17]; the intra-band motion of charges leading to the Franz-Keldysh effect in dielectrics evolves on the attosecond time scale [18]; the measured upper limit for the carrier-induced band-gap reduction and the electron-electron scattering time in the conduction band of silicon is of the order of a few hundreds of attoseconds [19]. These results clearly demonstrate the advantages offered by the application of attosecond techniques.

Finally, we mention that an alternative way for generating intense ultrashort pulses in the VUV/X-ray energy region is provided by X-ray free-electron lasers (FELs): several techniques have been proposed in the last years to generate high-energy attosecond pulses with these lasers. ■

About the authors

Giulio Cerullo is Full Professor of Physics at the Politecnico di Milano. His research activity deals with the generation of tunable few-optical-cycle light pulses and their application to the study of photoinduced processes in biomolecules and nanostructured materials. He is Chair of the Quantum Electronics and Optics Division of the European Physical Society.

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