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Measurement of Ultrafast Phenomena in the Femtosecond Time Domain

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Summary. Considerable progress has taken place in the generation and application of ultrashort optical pulses. The methods and techniques for extending time-resolved measurements into the femtosecond (10^{-15} second) time domain are described, and recent applications and fertile areas for investigation with femtosecond pulses are discussed.

Dramatic advances have taken place in the generation and application of ultrashort optical pulses. Laser measurement techniques have progressed to the point where investigations of ultrafast phenomena in condensed matter can now be accomplished on the femtosecond (10^{-15} second) time scale. Optical pulses as short as 30 fsec have been generated (*1*) by pulse compression techniques. The application of these advanced techniques is expected to produce new insights into dynamic processes in condensed matter and to have an impact on physics, chemistry, and biology. In this article I describe the basic concepts and new techniques that permit experimental investigations in the femtosecond regime and review the implications and potential areas of application of these measurement tools.

As we move into the femtosecond realm, a whole new range of problems becomes accessible for investigation. If we consider that a 30-fsec pulse corresponds to 1000 cm^{-1}, it is clear that we can study the properties of liquids and solids in a time less than the period of many important vibrations and well under a typical collision time in a liquid. In essence, with these ultrashort optical pulses it should be possible to coherently excite a liquid or solid and resolve the fundamental dephasing mechanisms. On a sufficiently short time scale we should be able to observe the evolution of non-Markovian processes to the statistical limit.

Although picosecond optical pulses have been very important for studying many dynamic processes, increased resolution can make the difference between qualitative and quantitative observations. A good example is the study of the nonradiative relaxation of the molecule azulene (*2*). Early picosecond work could only set limits for the process (*3*), but with the advent of higher resolution techniques detailed quantitative studies were accomplished (*4*). But while increased resolution is often valuable for refining our understanding, I believe that the most important effect of femtosecond spectroscopy will be to open up doors to the discovery of new phenomena.

Ultrashort Optical Pulses

During the decade and a half since the first generation of ultrashort laser pulses, optical pulse generation techniques have continued to improve. In Fig. 1 the shortest reported optical pulse width is plotted against year. The first publication on optical pulses in the picosecond range was in 1966 (*5*). By 1972 pulses on the order of a picosecond were generated with the continuously mode-locked dye laser (*6*). Improvements of this laser led to the generation of optical pulses shorter than 1 psec in 1974 (*7*). Within the past 2 years, a new type of passively mode-locked dye laser has extended the reach of attainable pulse widths to less than 100 fsec (*8*). Most recently, optical pulse compression techniques have led to the shortest reported optical pulse width yet attained, 30 fsec (*1*). Even shorter optical pulses appear on the horizon. However, since an optical pulse 30 fsec in duration corresponds to only 14 cycles of light, it is clear that we are fast approaching fundamental limits.

Femtosecond Pulse Generation Techniques

Passive mode locking of the continuous wave (CW) dye laser is now a well-established technique for producing ultrashort optical pulses (*9*). Figure 2 shows a new kind of dye laser pulse generator called a colliding pulse mode-locked laser (*8*). This configuration consists of a series of mirrors forming a ring cavity that contains only two essential elements: an optically pumped saturable gain dye (rhodamine 6G) and a saturable absorber dye (diethyloxacarbocyanine iodide) at the two focal points in the cavity. An argon laser operating at 514.5 nanometers is used as an optical pump. The lack of complexity of this configuration accounts in part for its ability to generate femtosecond optical pulses. By minimizing the amount of material in the cavity, the effects of group velocity dispersion are reduced, allowing the cavity to sustain a broad bandwidth of oscillating frequencies necessary to form a short optical pulse.

The mechanism for pulse shortening (*10*) in this laser configuration is very similar to that in the passively mode-locked dye laser, but with some additions. If we consider an optical pulse

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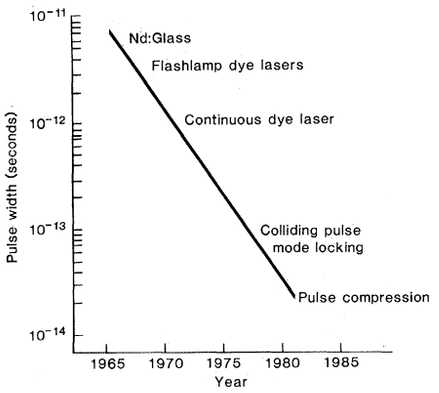


Fig. 1. Plot of the logarithm of the shortest reported optical pulse width versus year. Note that each reduction in pulse width has been accompanied by an advance in pulse generation technology.

traveling around the ring, the pulse is shaped each time it is amplified by the gain dye and absorbed by the saturable absorber. The leading edge of the pulse is preferentially clipped by the saturable absorber. Preferential amplification of the leading edge of the pulse, combined with cavity loss, effectively clips the rear edge of the pulse with each pass around the cavity until a limiting pulse width is achieved. An additional mechanism operative in the colliding pulse ring configuration results from the fact that there are two equally stable but oppositely directed pulses which "collide" as they meet each other traveling around the ring. The energetically most favorable place for the two pulses to meet is in the saturable absorber. Since the pulses are coherent, they can interfere and set up a standing wave pattern in the absorber. The standing wave pattern minimizes the energy lost, because the field is most intense where the absorption is saturated and is weakest in the field minima where the absorption is not saturated. The shortest optical pulses are produced with a thin absorbing region that confines the standing wave field. Figure 3 shows the experimentally measured autocorrelation function obtained with second-harmonic generation in a crystal of potassium dihydrogen phosphate (KDP). The full width at half-maximum (FWHM) of the optical pulse determined from the autocorrelation function is 65 fsec.

With optical pulse compression techniques even shorter optical pulses can be produced. More than a decade ago, Gires and Tournois (*11*) and Giordmaine *et al.* (*12*) proposed that optical pulses be shortened by adapting microwave pulse compression techniques to the visible spectrum. Optical pulse compression is accomplished in two steps. In the first step, a "chirp" or frequency sweep is impressed on the pulse. Then the pulse is compressed by using a dispersive delay line. A chirp can be impressed on an intense optical pulse simply by passing the pulse through an optical Kerr medium. When an intense optical pulse is passed through a nonlinear medium, the refractive index, n, is modified by the electric field, E,

$$n = n_0 + n_2 \langle E^2 \rangle + \ldots$$

A phase change, $\delta\phi$, is impressed on the pulse

$$\delta\phi = n_2 \langle E^2 \rangle \frac{\omega z}{c}$$

where ω is the frequency, z is the distance traveled in the Kerr medium, and c is the velocity of light. As the intensity of the leading edge of the optical pulse rises rapidly, a time-varying phase or frequency sweep is impressed on the pulse carrier. Similarly, a frequency sweep in the opposite direction occurs as the intensity of the pulse falls on the trailing edge. The amount of frequency sweep is given approximately by

$$\delta\omega = \left(\frac{\omega z n_2}{c}\right)\frac{d}{dt}\langle E^2(\tau) \rangle$$

A more rigorous approach to this problem requires a solution of the wave equation with the addition of a nonlinear term to account for the Kerr nonlinearity. The problem can be reduced to the solution of the nonlinear Schroedinger equation.

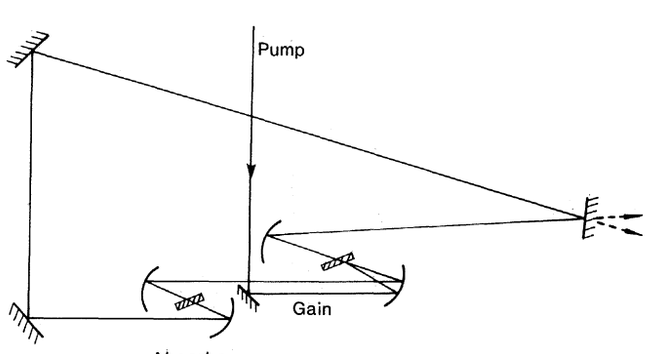


Fig. 2. Laser cavity configuration for a colliding pulse mode-locked dye laser.

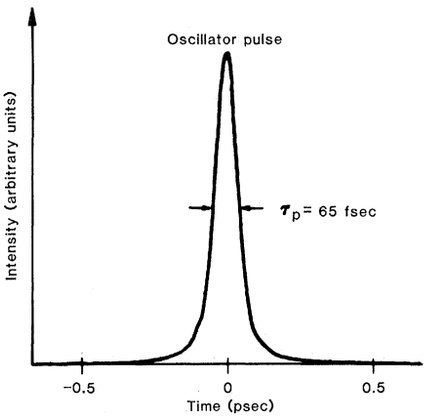


Fig. 3. Autocorrelation function of a 65-fsec optical pulse from a colliding pulse mode-locked dye laser. This autocorrelation measurement was obtained with second-harmonic generation in a KDP crystal.

Solutions of these equations by numerical techniques have been reported (*13–15*).

Thus far I have only discussed a plane wave solution to the nonlinear frequency problem. In addition, I have neglected self-focusing effects, which are a natural consequence of perturbing the index of refraction of the medium. These problems can be overcome by using a single-mode optical fiber as the Kerr medium (*14, 16, 17*).

Once a chirp has been applied to a pulse, the pulse is passed through a dispersive delay to reassemble all its frequency components in order to achieve compression. A nearly ideal pulse compression device is a pair of parallel gratings (*18*). Each wavelength passing through the grating pair is diffracted at a different angle and follows a different path, giving rise to a wavelength-dependent optical path delay. By properly adjusting the grating spacing, we can provide the right amount of group delay to form the compressed pulse. Figure 4 shows the experimental arrangement for compressing a 90-fsec optical pulse. The optical pulse is focused into a 15-centimeter piece of single-mode polarization preserving optical fiber. The pulse is recollimated with a lens, passed through a grating pair, and sent to the pulse measuring apparatus. The measured autocorrelation function for the compressed pulse is plotted in Fig. 5. It is interesting to note that a 30-fsec optical pulse is significantly broadened when it passes through all the optical elements used for recollimating and directing pulses into the measuring apparatus. Fortunately, the grating pair compresses the chirped pulse and provides a means of compensating the other dispersive ele-

ments in the beam as well. Care must be taken when such short pulses are used to make measurements to eliminate possible artifacts resulting from dispersion. Pulse compression has a significant advantage over direct pulse generation in a laser cavity for the generation of optical pulses in the femtosecond time regime. As shorter pulses are generated, increasing spectral width is required. In a laser, the gain bandwidth of the lasing medium and the optical cavity determine the lasing bandwidth. In contrast, the Kerr effect is operative from the ultraviolet to the infrared. It appears feasible to compress optical pulses to a few femtoseconds, which is nearly a single optical cycle.

Often it is desirable to amplify short optical pulses and to use nonlinear optical techniques to generate pulses at new frequencies. The peak pulse power coming directly from the dye laser oscillator is in the kilowatt range. An amplifier design (*19*) that can amplify optical pulses to gigawatt power levels and yet preserve the femtosecond pulse width is shown in Fig. 6. A frequency-doubled Nd:YAG (neodymium:yttrium aluminum garnet) laser at 530 nm is synchronized to a mode-locked dye laser and used to pump a four-stage dye amplifier. A saturable absorber dye isolates each stage. A grating pair is used to compensate the dispersion in the dye amplifiers and optical components. Figure 7 shows the autocorrelation function of an amplified pulse with gigawatt peak power and a pulse width of 70 fsec.

Shortly after the first generation of ultrashort optical pulses, Alfano and Shapiro (*20*) discovered that by focusing an intense optical pulse into several centimeters of almost any clear liquid, a white light continuum pulse could be generated. The precise mechanisms of this generation process are still the subject of some controversy (*21*).

One of the most severe problems with extending the white light continuum into the femtosecond regime is a sweep in time of the various frequency components brought about by group velocity dispersion. Some time sweep is inevitable because of the broad frequency range over which the continuum extends. We can greatly reduce the sweep by generating the continuum in the shortest possible path length and eliminating lenses by use of reflective optics. We have succeeded in generating an 80-fsec white light pulse by focusing an intense gigawatt 70-fsec optical pulse into a 400-micrometer-thick free-flowing stream of ethylene glycol (*22*). With an excitation wavelength of 620 nm the generated continuum pulse extended from 0.19 to 1.6 μm.

The measured frequency sweep in the continuum is shown in Fig. 8. Note that over the entire range of the measurement, the time sweep is less than or comparable to the pulse width. We think that most of the observed frequency sweep is a result of the generation process. The shift to lower frequencies at early times, and to higher frequencies at later times, suggests that the self-phase-modulation process described in the section on pulse compression may play an important role in generating white light pulses as well. The spectral width of the white light pulse is too large to be completely described by self phase modulation. At the intensities used to generate this continuum pulse (10^{11} watts per square centimeter) it is not surprising that other nonlinear effects would contribute to the generation process (*21*).

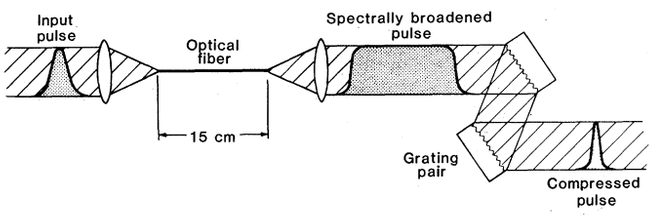


Fig. 4. Experimental arrangement for compressing femtosecond optical pulses.

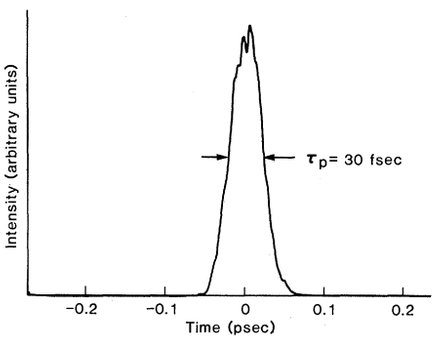


Fig. 5. Measured pulse autocorrelation function of the compressed 30-fsec optical pulse.

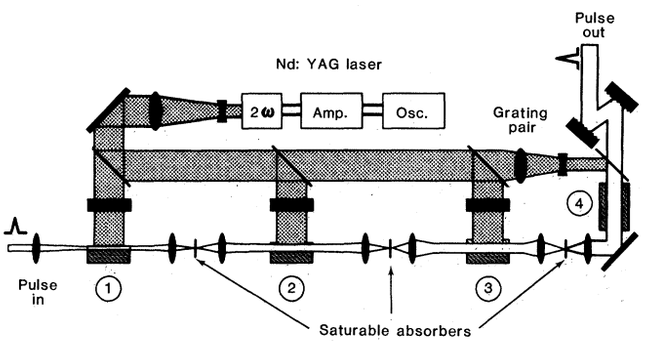
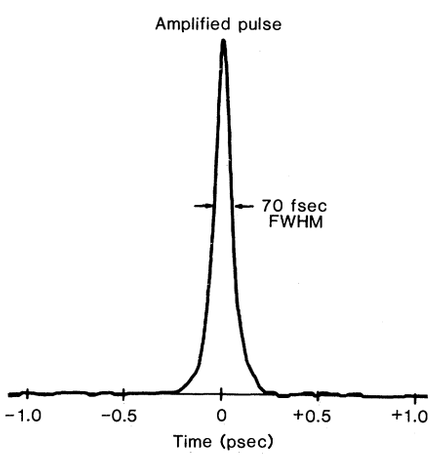


Fig. 6. Diagram of a four-stage dye amplifier for femtosecond optical pulses. With this amplifier a 70-fsec optical pulse can be amplified to gigawatt power levels.



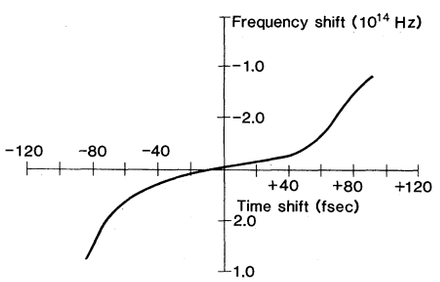


Fig. 7 (left). Pulse autocorrelation function of a 70-fsec amplified optical pulse. Fig. 8 (right). Measured time shift as a function of frequency for a white light femtosecond continuum pulse generated in a 400-μm-thick ethylene glycol stream.

Femtosecond Spectroscopy

The discussion in the foregoing section was limited to the pulse generation process itself. Now we turn to the application of these short pulses to measurement. A number of novel and clever techniques have been developed in the past decade to measure dynamic processes with short optical pulses (*23*). Many of these techniques can be directly adapted to measurements in the femtosecond time regime.

An experimental arrangement for measuring time-resolved spectra with femtosecond optical pulses is shown in Fig. 9. Optical pulses of wavelength 620 nm are generated with a colliding pulse mode-locked dye laser. These pulses are then amplified to gigawatt powers with the four-stage amplifier described previously. The amplified pulses are divided into two parts, one for exciting and the other for probing a sample. The excitation pulses are passed through a nonlinear frequency-shifting medium to generate the desired frequency. The frequency shifting can be achieved by using the stimulated Raman effect or some other nonlinear process. The probing pulses pass through a variable path or time delay controlled by a stepper motor and are then focused into an ethylene glycol stream to generate a white light continuum pulse. The white light continuum pulse is further divided into a measuring pulse and a reference pulse, which are directed into a spectrometer with a vidicon or optical multichannel analyzer on the output of the spectrometer. In this way, measurements of optically induced changes in absorption can be performed over a broad spectral range at different time delays following excitation as determined by the path delay controlled by the stepper motor. The resolution is determined by the convolution of the pumping and probing pulse widths. Care must be taken to limit artifacts caused by group delay in the various parts of the white light continuum spectrum.

The application of these measurement techniques is illustrated by some recent work on the dynamics of absorption and gain in a highly excited semiconductor multiquantum well structure made of thin, 200-angstrom layers of GaAs and GaAlAs (*24*). Time-resolved absorption measurements provide a unique means of observing the influence of hot electrons in optically excited semiconductors (*25, 26*). In this experiment, we sought to determine the distribution of hot carriers in a two-dimensional semiconductor multiquantum well within the first few hundred femtoseconds after optical excitation. In Fig. 10 time-resolved absorption spectra are plotted at various times after excitation. Note that the scale has been expanded for "gain" or negative absorption spectra. The noise level on these curves is ± 0.005 change in optical density. The solid curve is the optical absorption spectrum before excitation.

The sharp peaks in the absorption spectra are due to free excitons associated with each quantum sublevel. These sharp peaks disappear after intense optical excitation because Debye screening from the dense (10^{13} cm^{-2}) electron-hole plasma screens the electron-hole correlation that gives rise to the bound excitons.

The observation of gain within 200 fsec reveals that a population inversion has been produced on this time scale. At the very earliest times, gain is observed well above the fundamental band edge (1.51 electron volts). Typically, semiconductor lasers emit just below the band edge. With short optical excitation pulses a transient population inversion is produced. As time progresses the carriers cool and recombine, causing the band edge gain to begin return to absorption within the first 1.5 psec. As the carrier population cools the gain moves closer to the band edge. Spectra of this type can be used to determine the temperature of the electron-hole plasma as a function of time (*27*).

Another example which illustrates the resolving power of our femtosecond measurement system is a recent measurement of the absorption dynamics of optically excited polyacetylene. This material is of interest because it is a prototype one-dimensional semiconductor, and there has been a great deal of work on its optical and electronic properties (*28, 29*).

Optical excitation of polyacetylene can induce symmetry-lowering distortions in this simple polymer chain that can give rise to induced optical absorptions. Calculations have shown that the time scale for the formation of these induced states can be on the order of 10^{-13} second (*30*). Figure 11 shows the optical absorption induced at 1.55 μm in polyacetylene following excitation with a 70-fsec optical pulse at 620 nm (*31*). Note the exponential decay with a time constant of 160 fsec—the shortest time con-

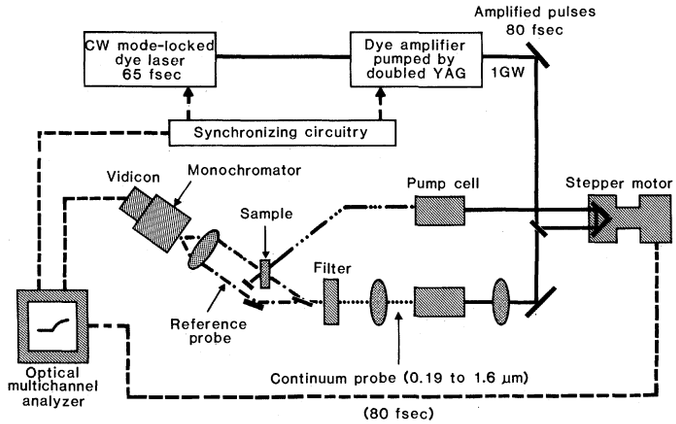


Fig. 9. Schematic of apparatus for femtosecond time-resolved spectroscopy.

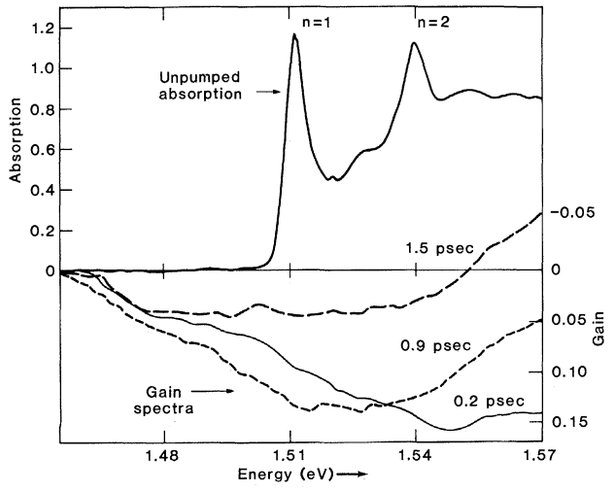


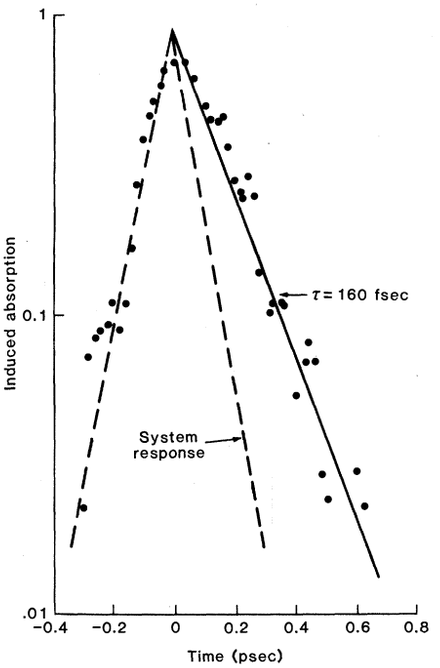
Fig. 10. Time-resolved absorption and gain spectra of an optically excited GaAs-GaAlAs multiquantum well structure.

Fig. 11. Measurement of excited state relaxation in polyacetylene. The points are experimental and yield a 160-fsec exponential relaxation time. The dashed curve is the instrument response.

stant yet measured by optical techniques. We consider the rapid recovery of this induced absorption to be the result of a transient excited state absorption produced as the optically excited polymer chain undergoes a dynamic distortion.

Limits

The question inevitably arises of just how short an optical pulse can be generated. Fundamentally, there is no limit other than that imposed by the uncertainty principle, $\Delta\omega\Delta t \sim 1$, where $\Delta\omega$ is the frequency bandwidth and Δt is the pulse width. This requires that we establish coherence over a broad range of frequencies. Typically, for a dye laser the gain bandwidth is on the order of 100 nm, which corresponds to a minimum pulse of a few femtoseconds. Maintaining a fixed phase relationship over such a broad range of frequencies is difficult. Material and optical cavity dispersion tend to broaden the optical pulse. In fact, using such a short pulse to make measurements requires special consideration. Linear dispersion alone will significantly broaden a pulse of a few femtoseconds after it traverses 100 μm in almost any material. In principle, it is possible to compensate for linear dispersion by the pulse compression techniques described earlier, but these techniques become more difficult to apply as the pulses get shorter. New techniques and methods will have to be devised to



account for all these problems in order to make meaningful measurements with optical pulses only a few femtoseconds in duration.

Conclusion

I have outlined the latest progress in generating ultrashort optical pulses in the femtosecond time domain and have shown how these advances can be used to make measurements of dynamic processes in solids on this extremely short time scale. These new measurement tools give us a chance to peer into the as yet unexplored world of processes that take place in femtoseconds. Discoveries in a broad range of fields including physics, chemistry, and biology lie ahead.

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