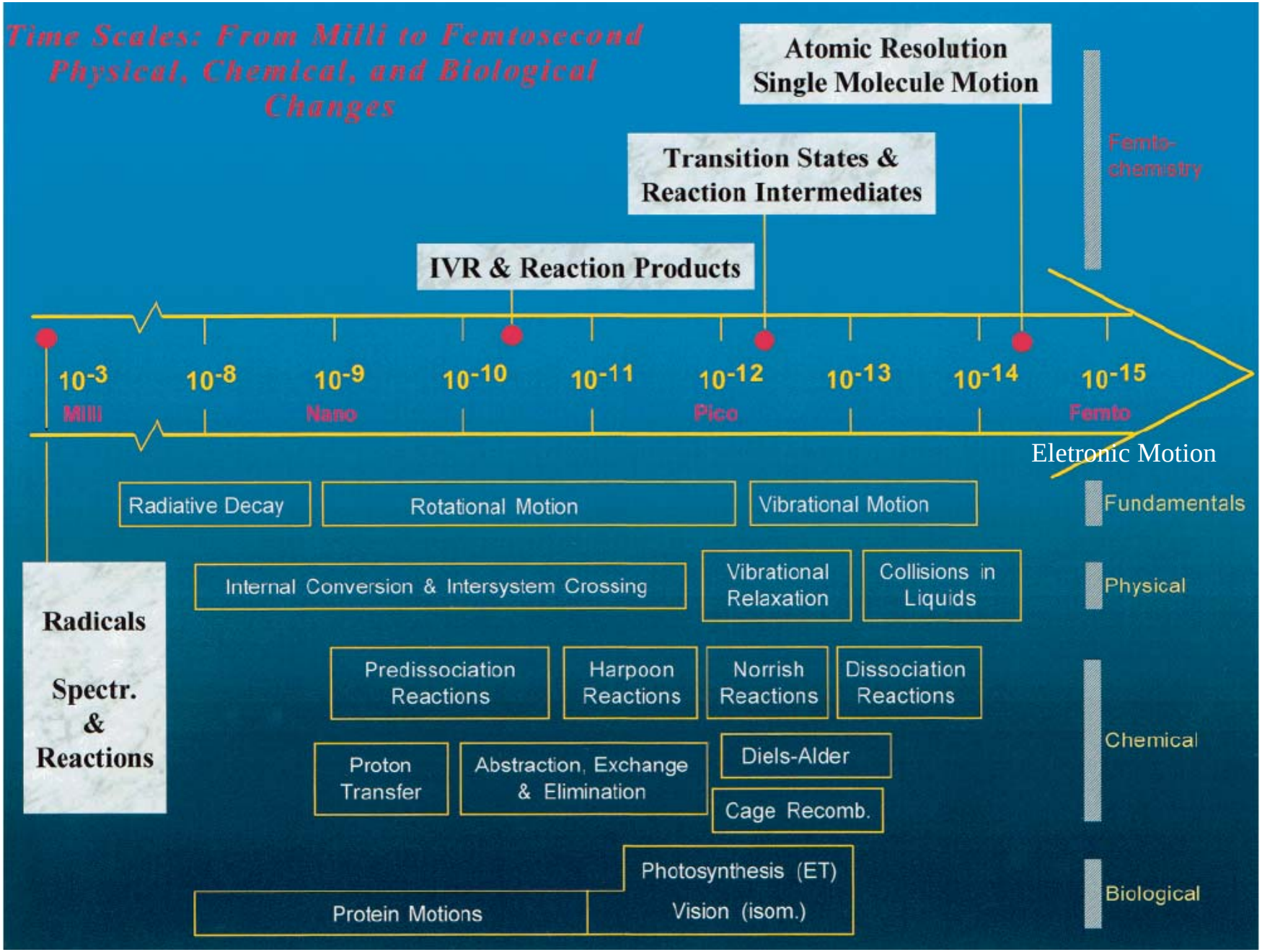
Chapter 17. Time-Resolved Laser Spectroscopy

The investigation of fast processes, such as radiative or collision-induced decays of excited levels, isomerization of excited molecules, or the relaxation of an optically pumped system toward thermal equilibrium, opens the way to study in details the dynamic properties of excited atoms and molecules. A thorough knowledge of dynamical processes is of fundamental importance for many branches of physics, chemistry, or biology.

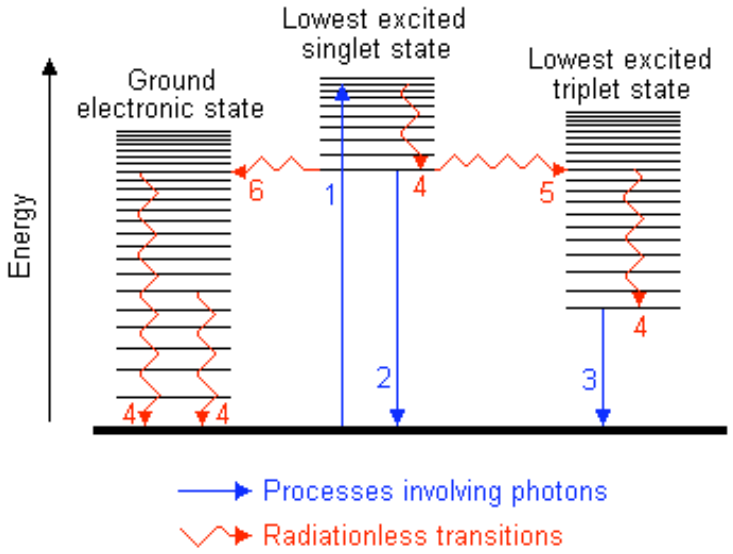
In order to study these processes experimentally, one needs a sufficiently good time resolution, which means that the resolvable minimum time interval Δt must be shorter than the time scale T of the process under investigation. Thus, this chapter emphasizes the high time resolution.

The development of ultra-short laser pulses and of new detection techniques has allowed a very high time resolution in the study of fast processes. The achievable time resolution has been pushed into the femtosecond range (1 fs = 10^{-15} s). The spectral resolution of most time-resolved techniques is confined by the Fourier limit $\Delta\nu = a / \Delta T$, where ΔT is the duration of the short laser pulse and the factor $a \approx 1$ depends on the profile I(t) of the pulse.

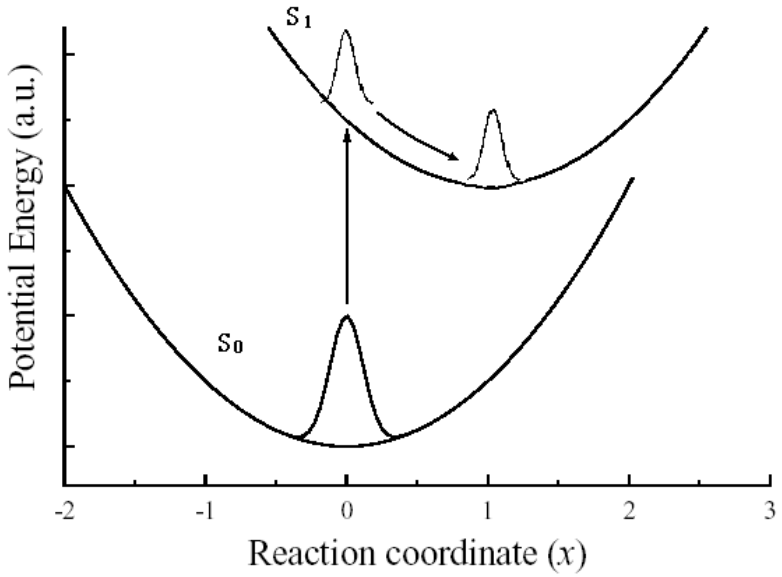


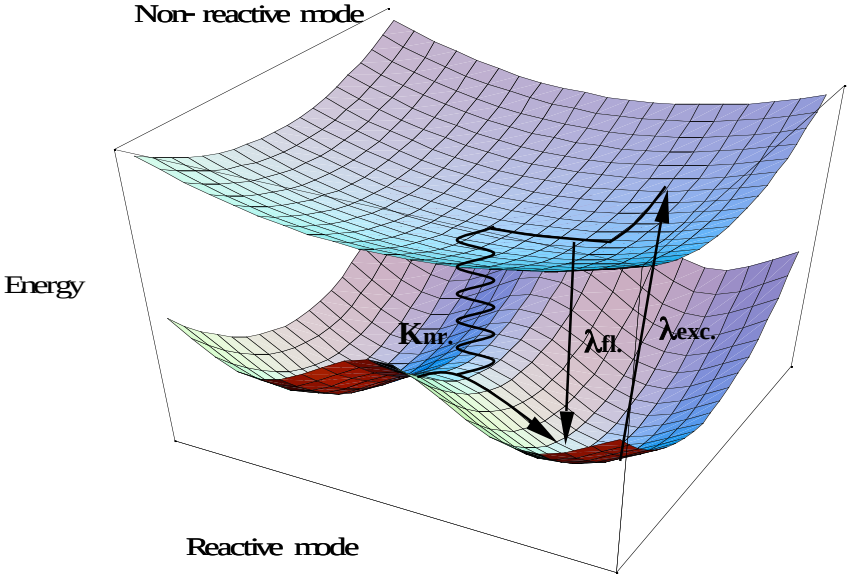
Ahmed H. Zewail, *J. Phys. Chem. A* **2000,** *104*, 5660-5694

Possible physical process following absorption of a photon by a molecule



1. Absorption
2. Fluorescence
3. Phosphorescence
4. Vibrational relaxation
5. Intersystem crossing
6. Internal conversion





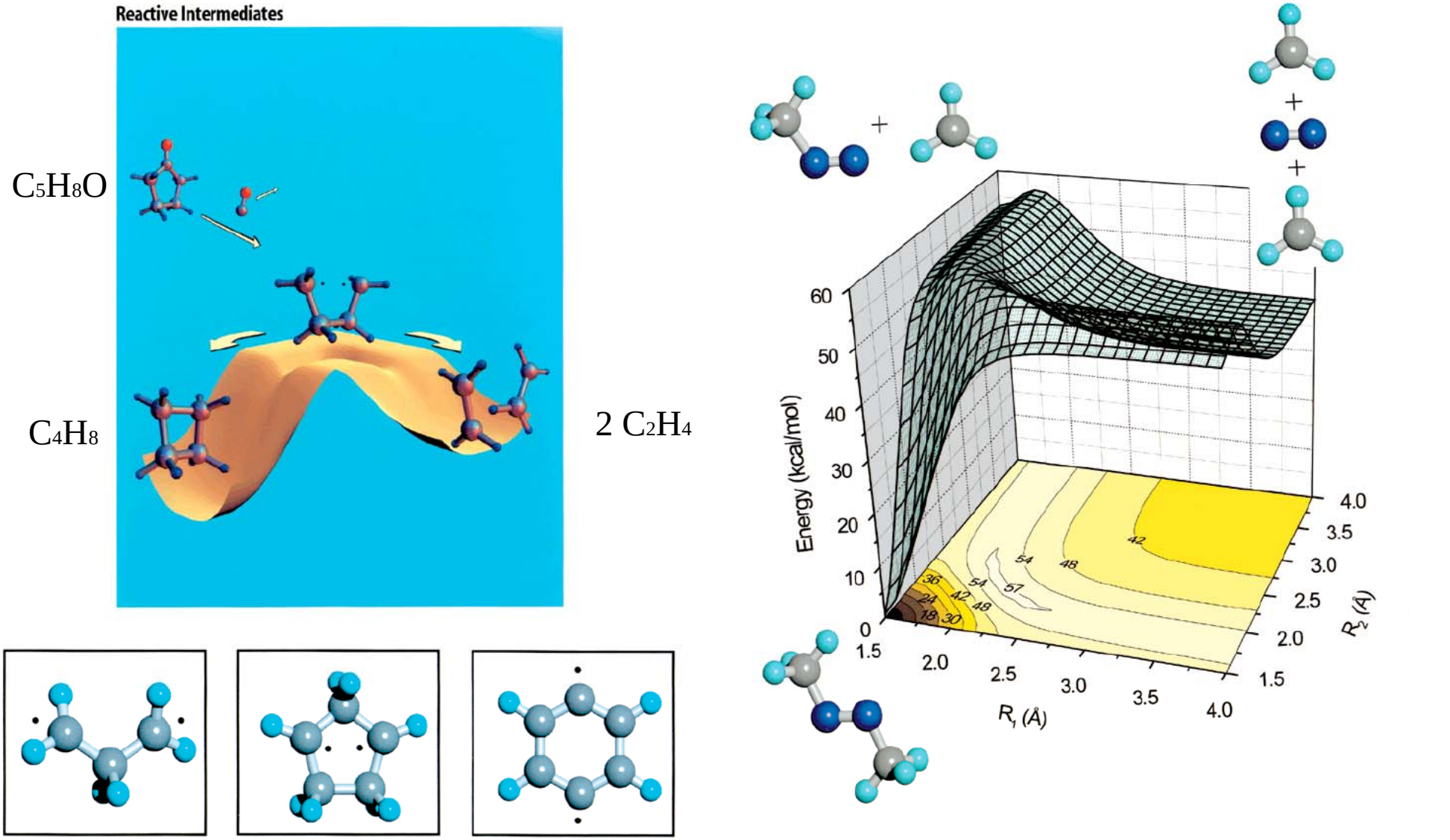


Figure 14. Reactive intermediates on the femtosecond time scale. (Left) Here, tetramethylene, trimethylene, bridged tetramethylene and benzyne are examples of species isolated on this time scale (see Figure 12 for others). (Right) Reaction dynamics of azomethane, based on the experimental, femtosecond studies. The ab initio PES was obtained from state-of-the-art calculations (E. Diau, this laboratory) which show the two reaction coordinates (C−N) relevant to the dynamics. A third coordinate, which involves a twisting motion, was also studied. Note the concerted and nonconcerted pathways. Reference 48.

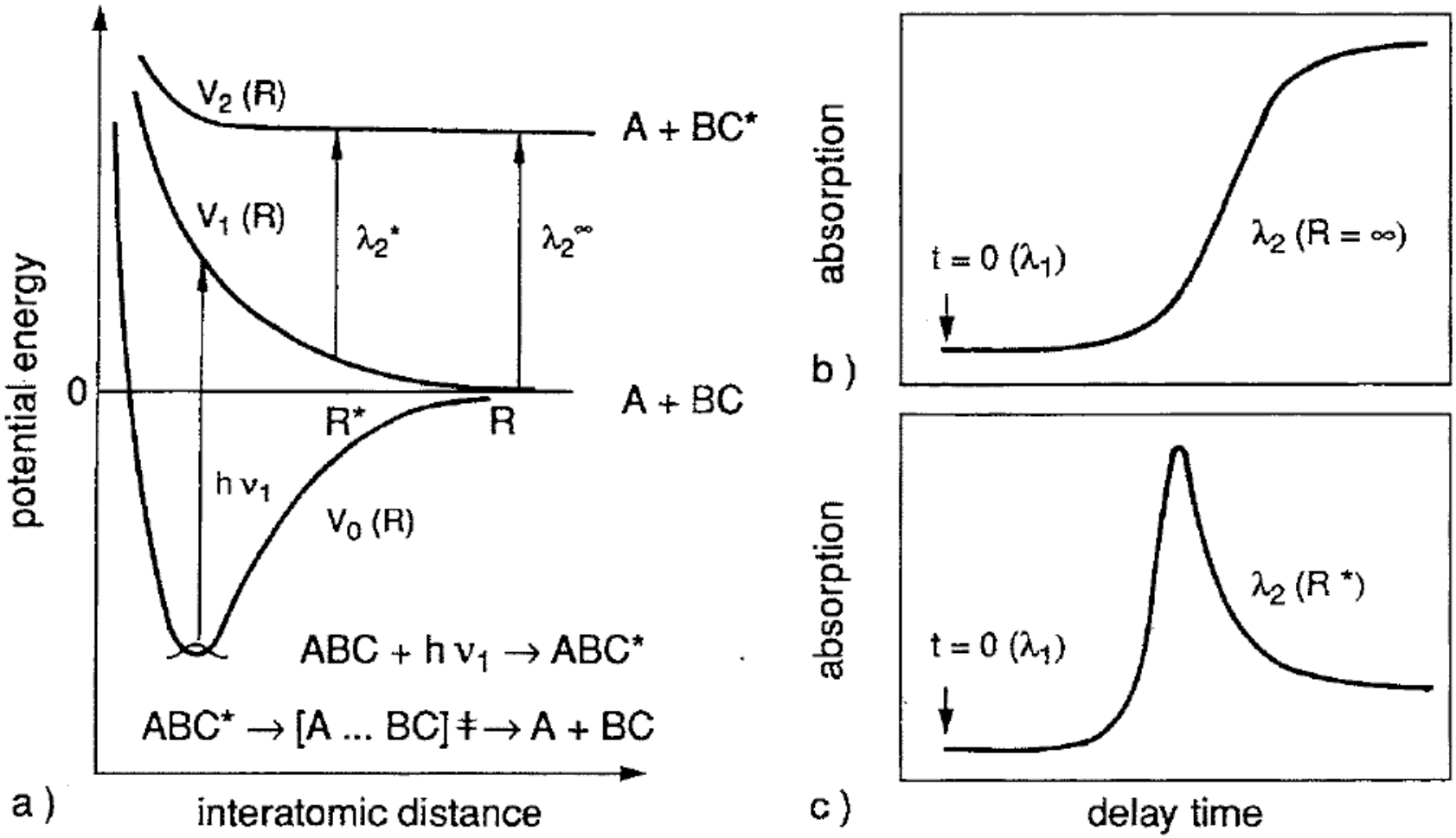
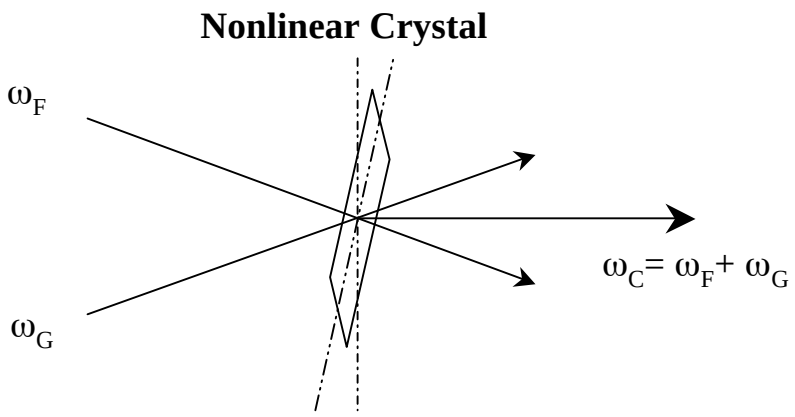


Fig. 15.8. (**a**) Potential energy curves for a bound molecule (V_0) and the first and second dissociative curves V_1, V_2; (**b**) the expected femtosecond transient signals $S(\lambda_2, t)$ versus the delay time t for $\lambda_2(R = \infty)$ and (**c**) for $\lambda_2(R^*)$ [15.43]

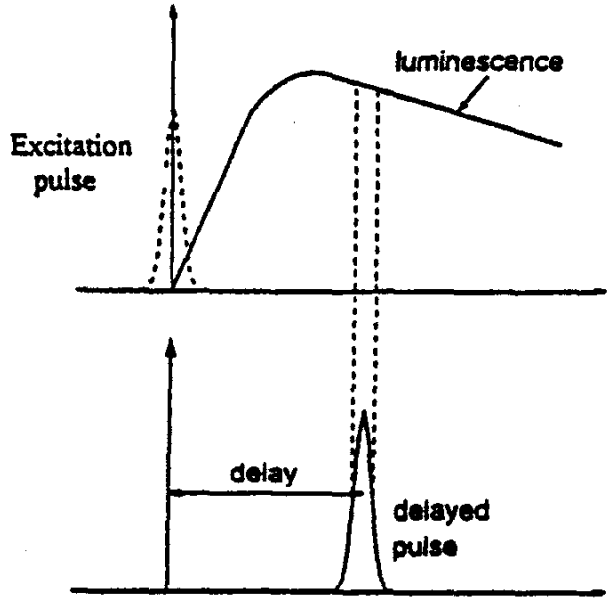


P331-359

5.8 Nonlinear Optical Mixing Techniques

$$\omega_C = \omega_F + \omega_G$$

$$\frac{n_C}{\lambda_C} = \frac{n_F}{\lambda_F} + \frac{n_G}{\lambda_G}$$

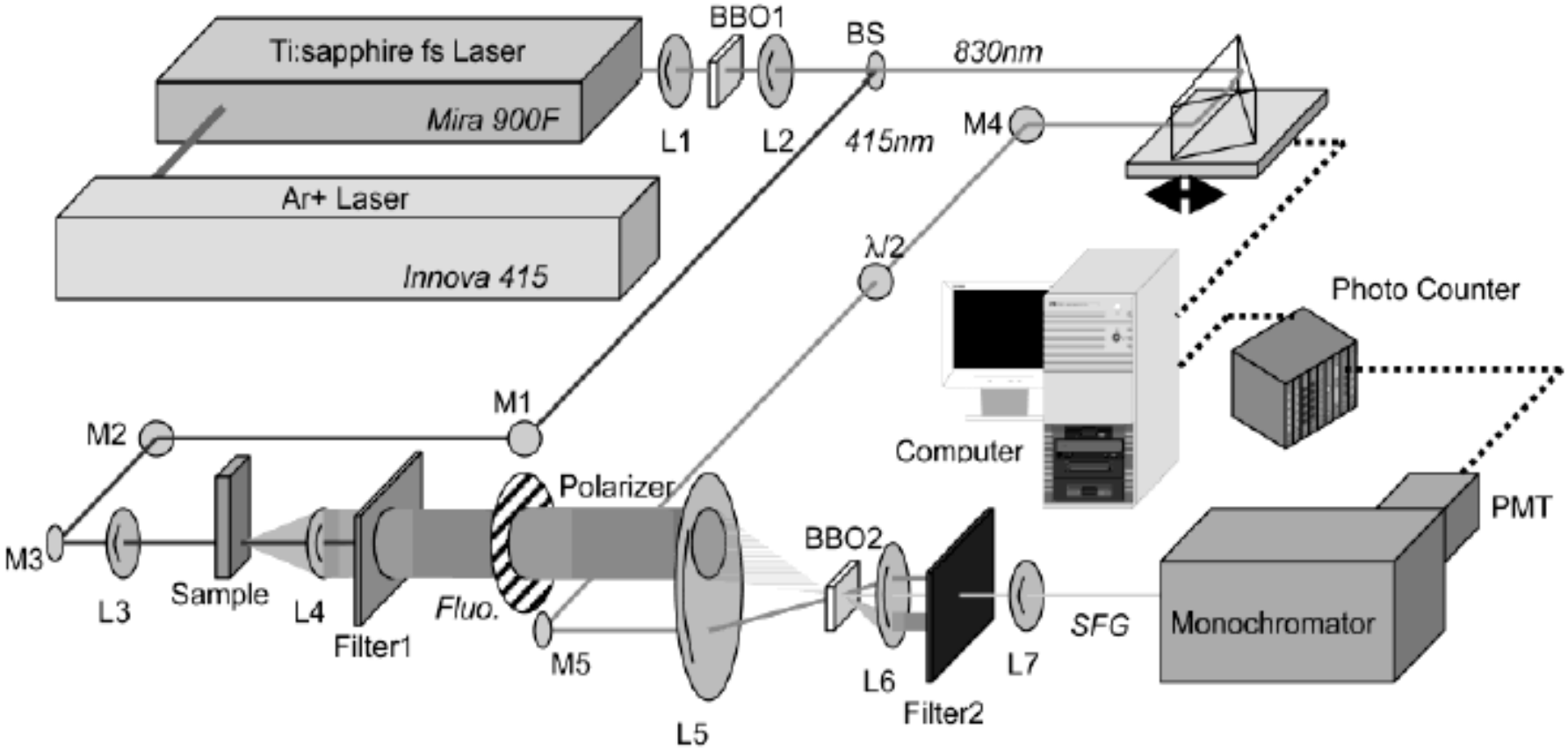


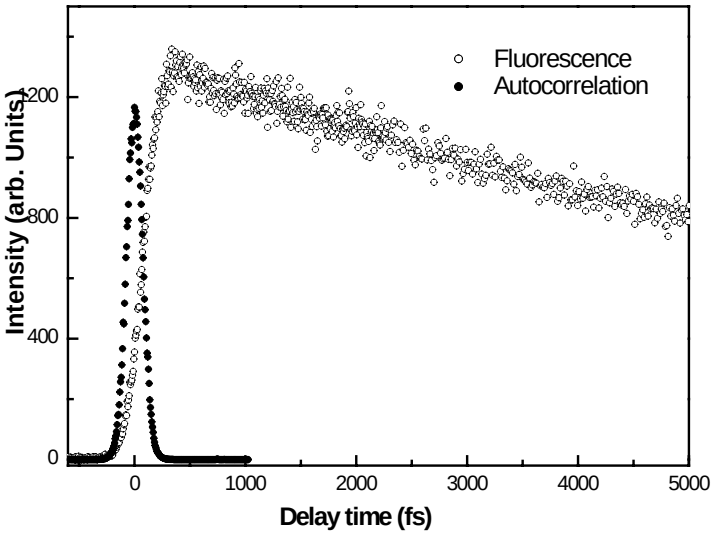
$$I_C \propto \left[I_F(\Delta t) + I_G \right]^2$$

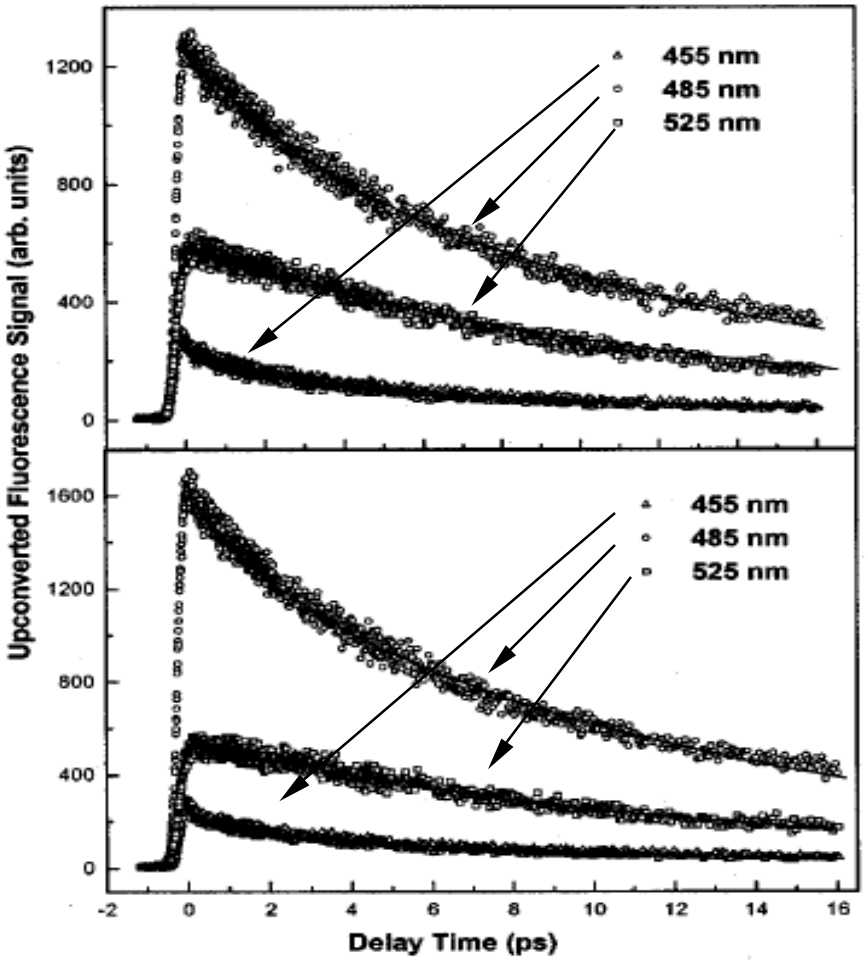
$$= I_F{}^2 + I_G{}^2 + 2 I_F(\Delta t) I_G$$

(Δt is the delay time)

Femtosecond Fluorescence Up-conversion Setup




Fluorescence
Autocorrelation
Intensity (arb. Units)
0
400
800
1200
0
1000
2000
3000
4000
5000
Delay time (fs)


455 nm
485 nm
525 nm
455 nm
485 nm
525 nm
Upconverted Fluorescence Signal (arb. units)
0
400
800
1200
1600
-2
0
2
4
6
8
10
12
14
16
Delay Time (ps)

Generation of Short Laser Pulse

1. Short laser pulse introduced by gain material
   About μs
2. Q-Switched laser (Q quality factor)
   Keep low Q, prevent laser power build up.
   Suddenly increase Q in a very short period, build up laser.
   Spinning mirror, Pockels cell…
   About ns
3. Cavity Dumping
   Keep high Q, keep high power lasing.
   Kick out the laser in a very short period.
   Pockels cell, Acoustic-optical Switch…
   About ns

4. Mode Locking Laser

   Active, Passive, Synchronous Pumping

   About ps

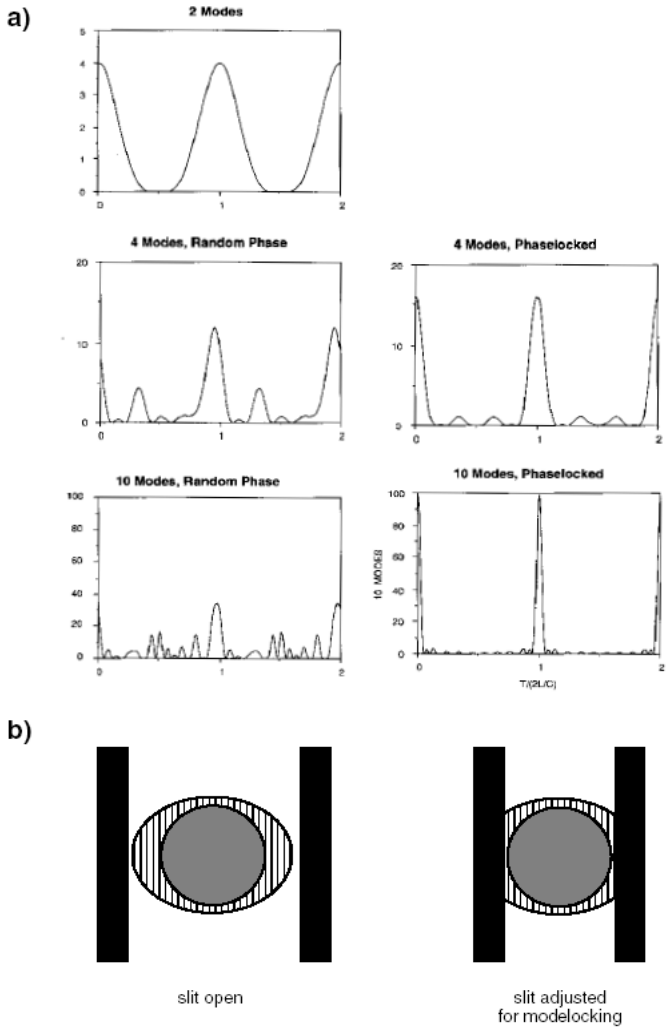
5. Create femtosecond laser pulse (optical process)

   Colliding-pulse mode locking

   Kerr lens Mode locking

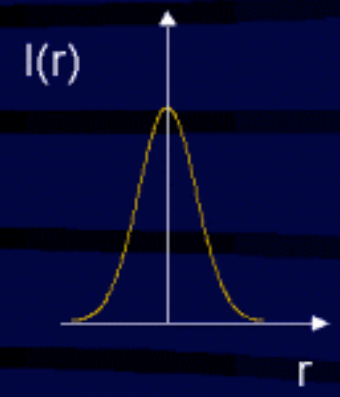
10-fs full width at half-maximum Gaussian pulse centered at 800nm has a bandwidth of 94nm

P625 Table 11.1

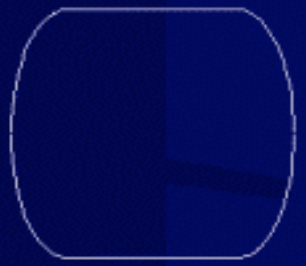


P630 Fig.11.21

Self-focussing



$n' = n + n_2 I(r)$

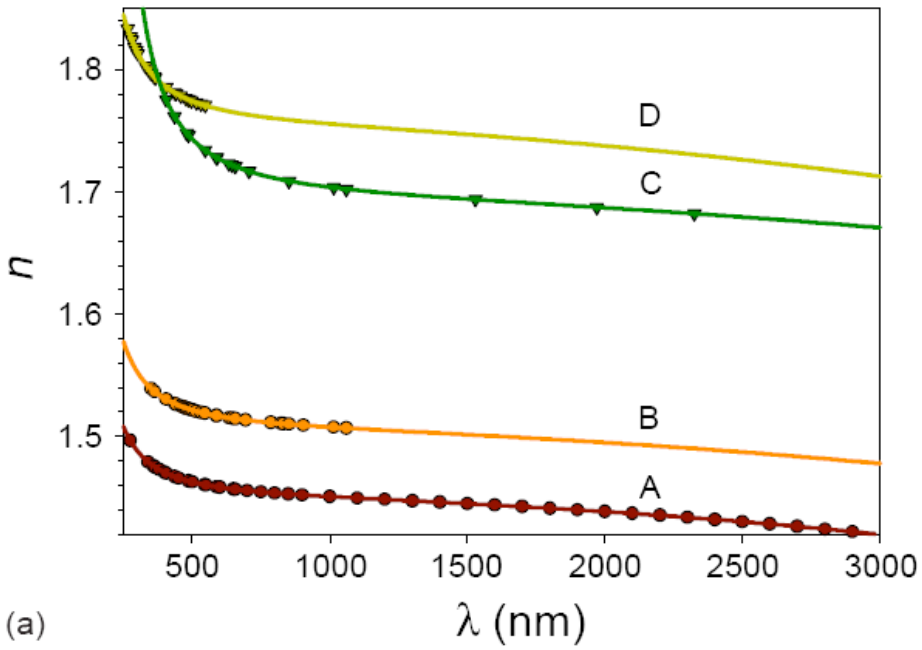


Optical thickness

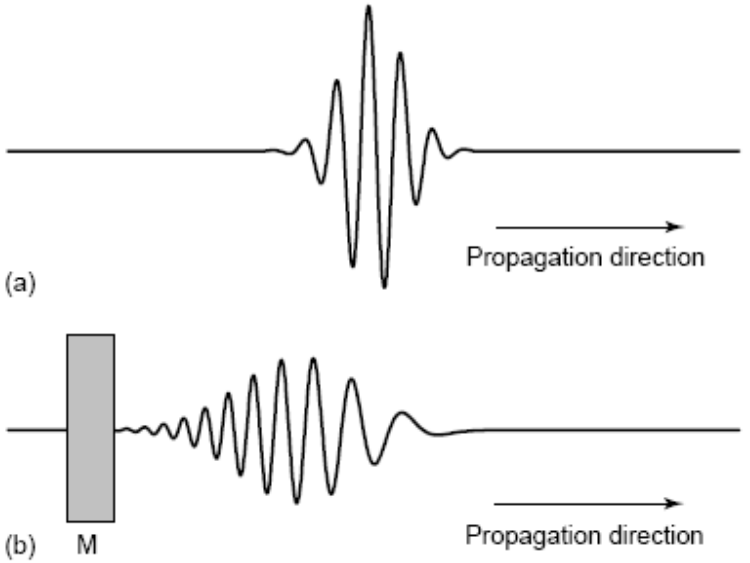
Self guiding

- **It is possible to balance the effects of self-focussing and diffraction to produce a self-guided beam**

$n' = n + nI(r)$



Refractive index versus wavelength data for some common materials: (A) fused silica, (B) Schott BK7, (C) Schott SF10 and (D) sapphire.
(Negative Dispersion)
Causing by Group delay dispersion.



Blue Red

$v = c_0/n$

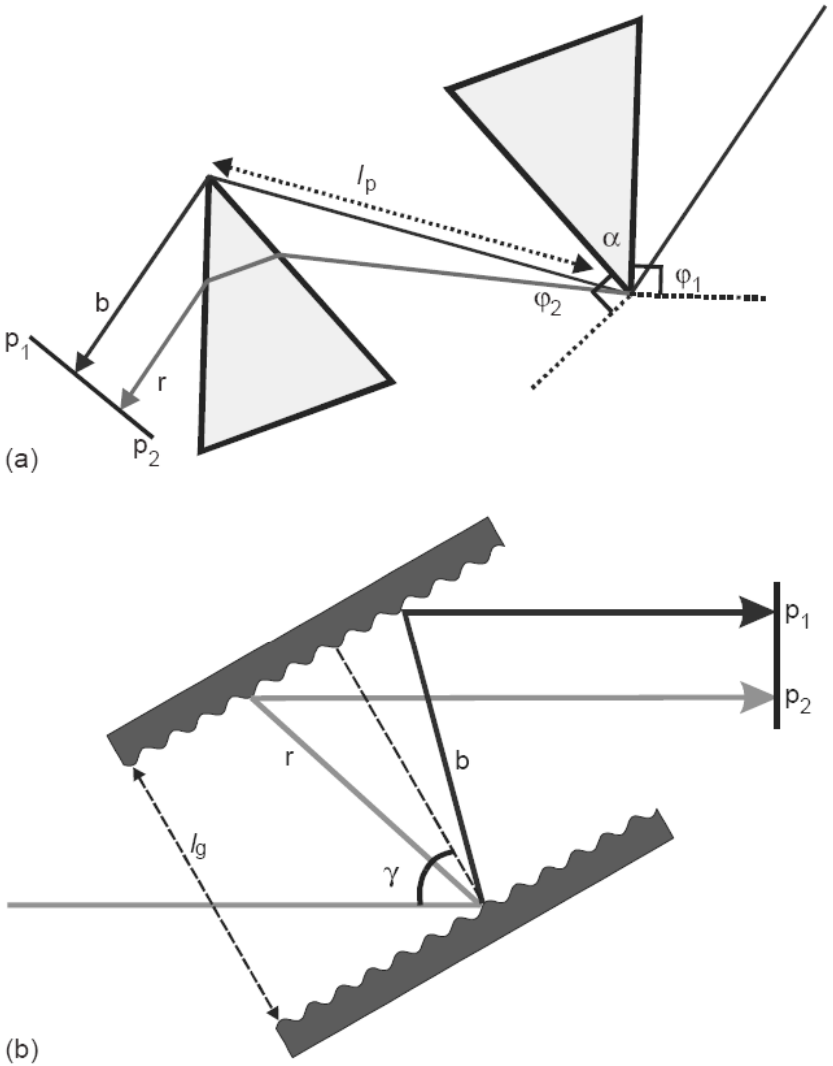


Figure 5 (a) Prism and (b) grating pairs used in the control of dispersion; r and b indicate the relative paths of arbitrary long- and short-wavelength rays. φ_1 is the (Brewster) angle of incidence at the prism face. The light is reflected in the plane $p_1 - p_2$ in order to remove the spatial dispersion shown.

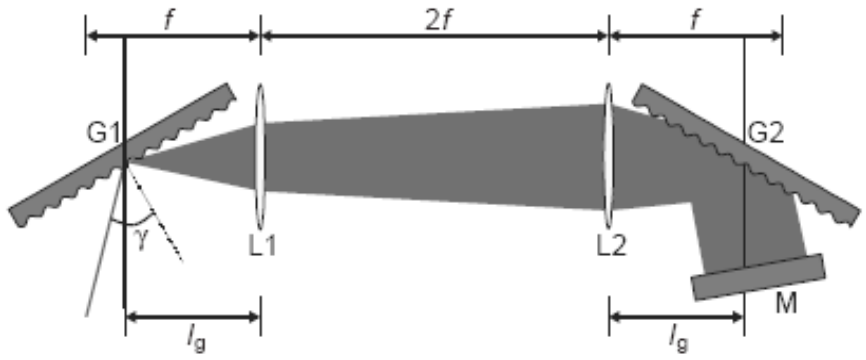


Figure 6 Schematic diagram of a grating-pair pulse stretcher showing the arrangement for positive dispersion. G1 and G2 are diffraction gratings, L1 and L2 are identical lenses separated by twice their focal length, f, and M is a mirror acting to double-pass the beam through the system. The distance $l_g - f$ determines the total dispersion.

Femtosecond Laser Pulse Amplification

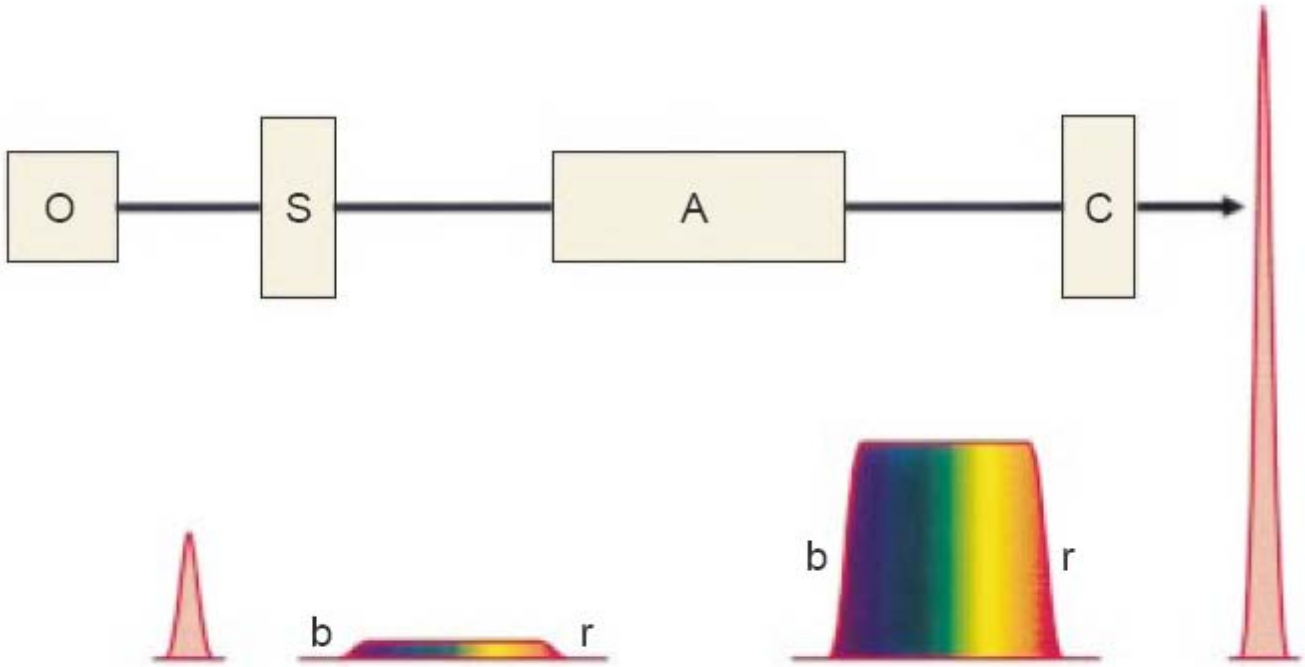
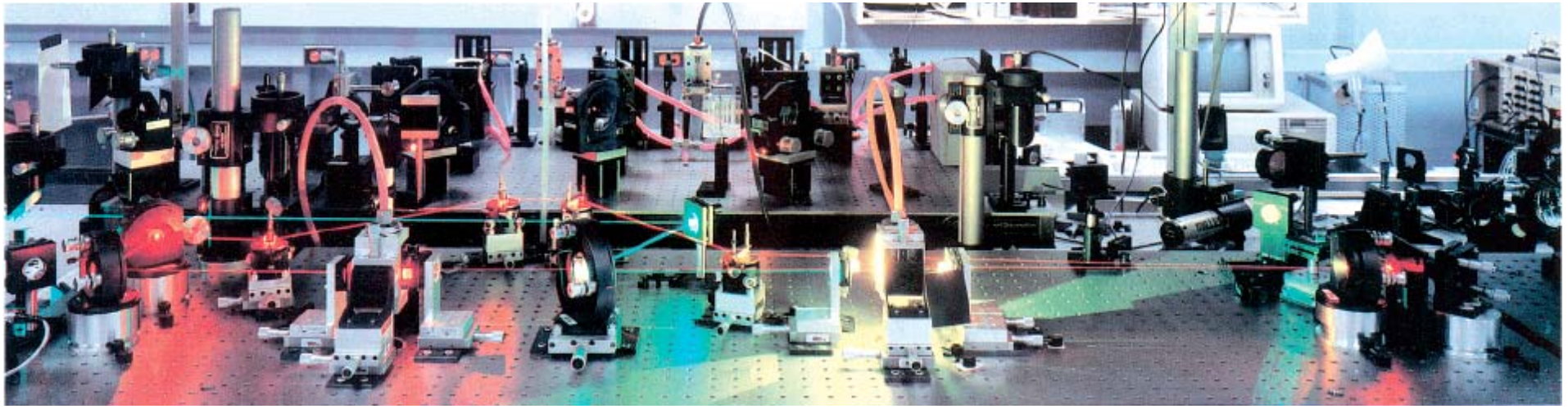
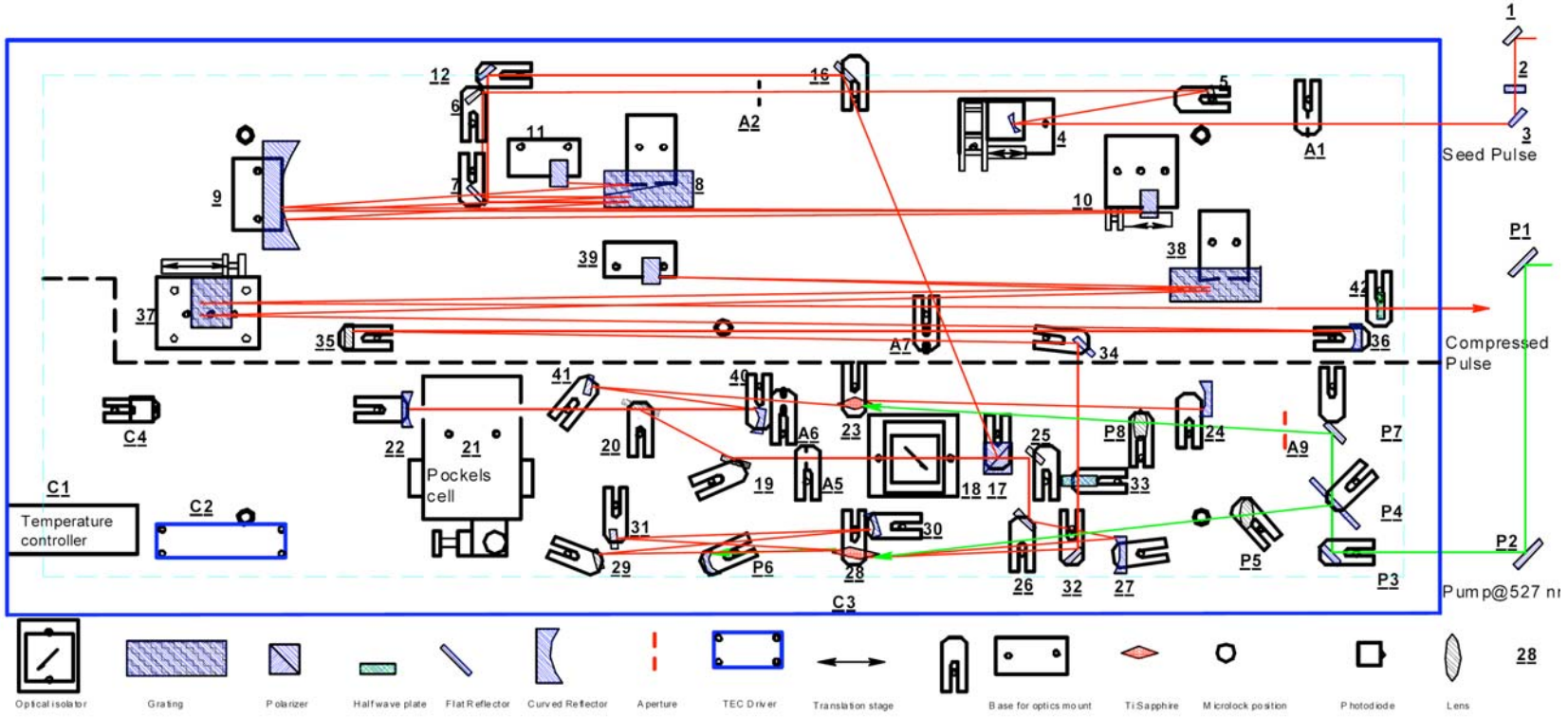


Figure 8 Diagram showing the principle of CPA. The oscillator output (O) is stretched in the grating stretcher (S) such that the red frequency components (r) travel ahead of the blue (b). The peak intensity is reduced in the process. The stretched pulse is then amplified in a regenerative or multipass amplifier (A) before recompression in a grating-pair compressor (C).

Ultra Short Time Duration	1w CW	1
Ultra High Peak Intensity	1w 100fs 1kHz	10,000,000,000



Ahmed H. Zewail's Dye Femtosecond Laser



QUANTRONIX Titan Ti:Sapphire Amplifier

Measurement of Ultrashort Pulse

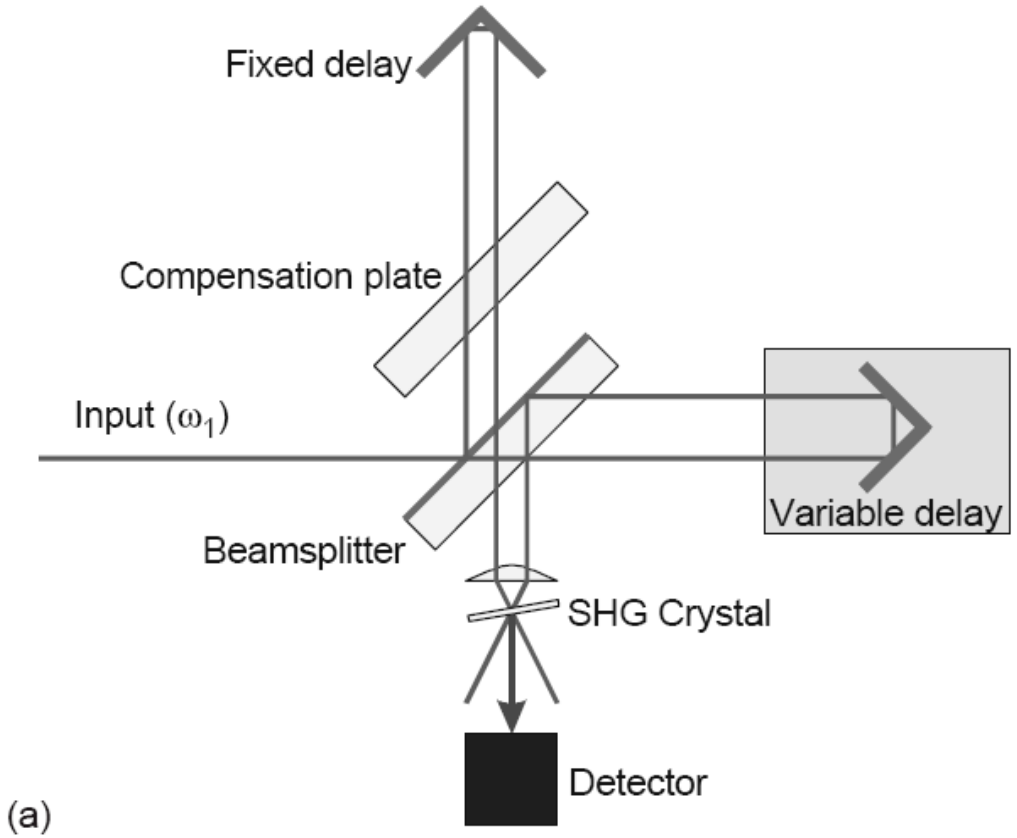
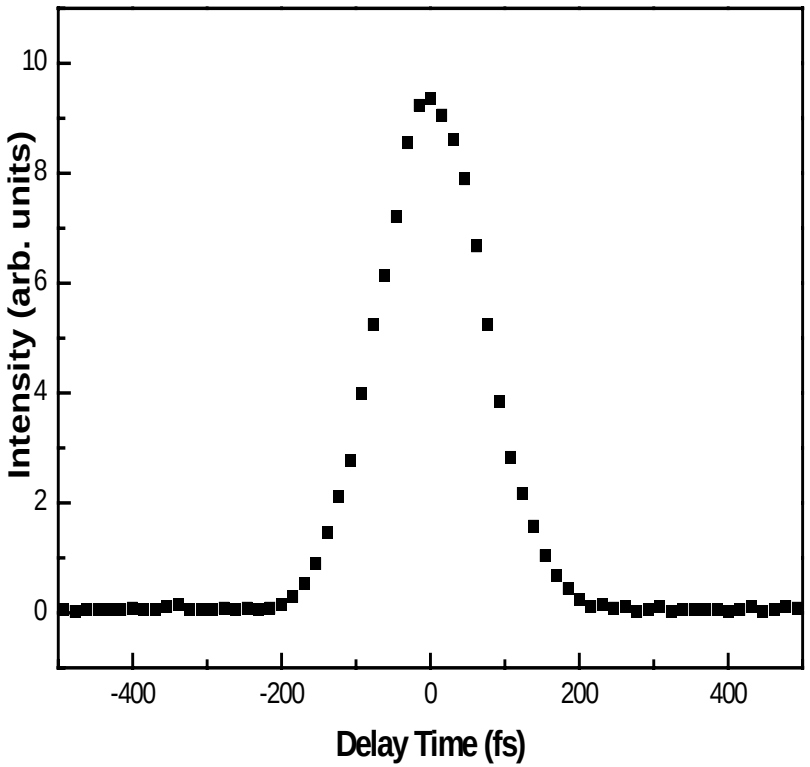
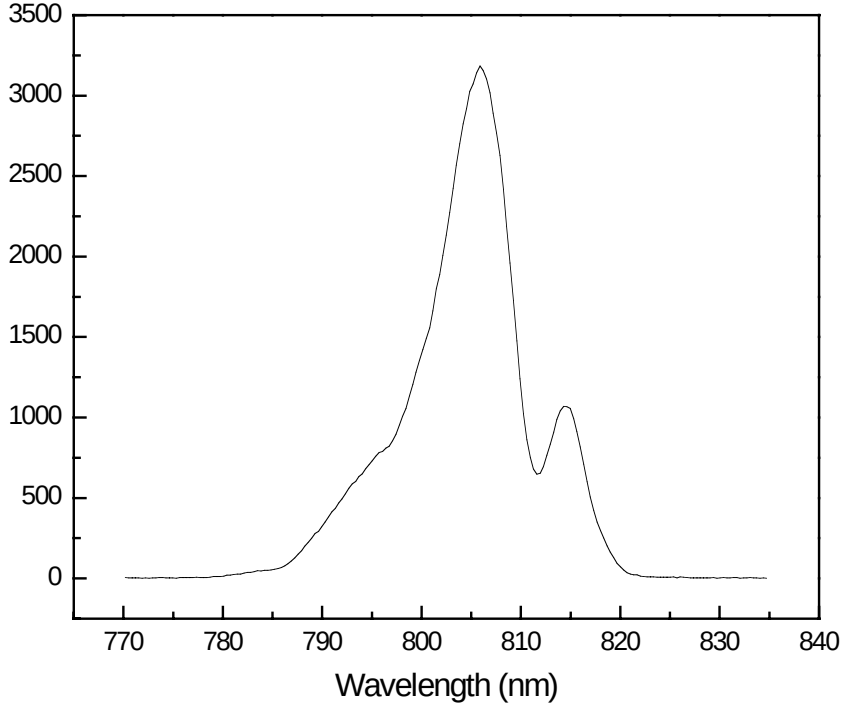


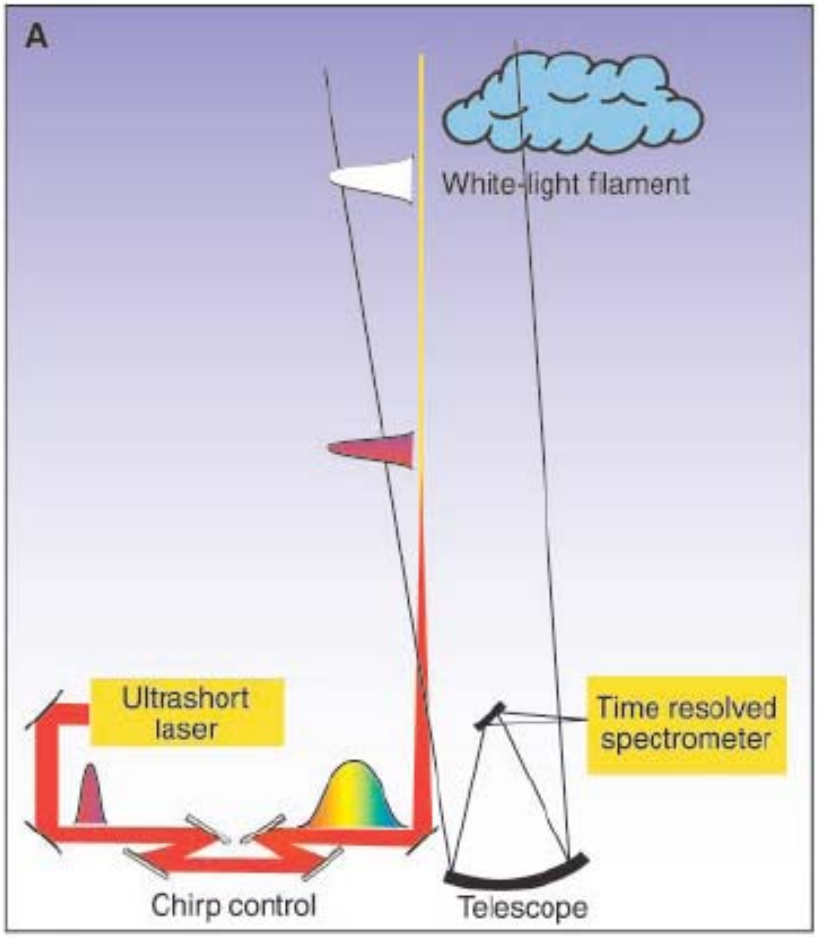
Figure 16 (a) Schematic diagram illustrating the layout of an autocorrelator. Two laser beams of femtosecond pulses at frequency w_1 are overlapped in a nonlinear crystal such as BBO. The sum-frequency signal at frequency $2w_1$ as a function of relative time delay is proportional to the shape of the pulse.



Typical Autocorrelation Signal



Typical Amplified Pulse Spectrum
(After a beam spliter, 450fs)



White-Light Lidar

Kasparian J. et al, *Science*, 301, 61, 2003

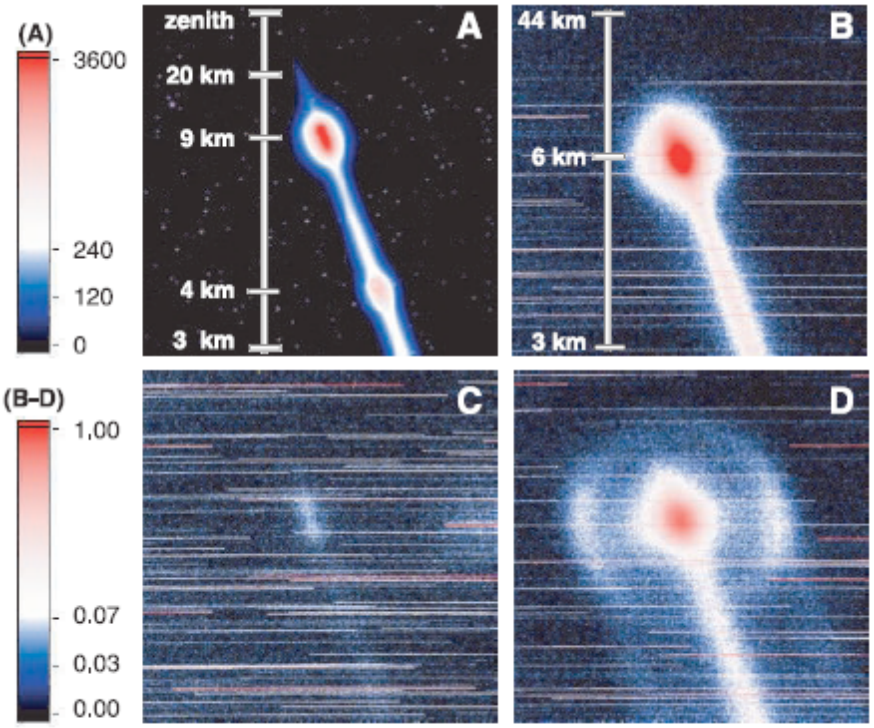


Fig. 1. Long-distance white-light propagation and control of nonlinear optical processes in the atmospheres. Images of the Teramobile fs laser beam propagating vertically were taken with the charge-coupled device camera at TLS observatory. (**A**) Fundamental wavelength, exhibiting signals from more than 20 km and multiple-scattering halos on haze layers at 4- and 9-km altitudes. (**B** to **D**) White light (385 to 485 nm) emitted by the fs laser beam. These images have the same altitude range, and their common color scale is normalized to allow direct comparison with that of (A). (B) With GVD precompensation. (C) Without GVD precompensation. (D) With slight GVD precompensation. The conical emission imaged on a haze layer is apparent.