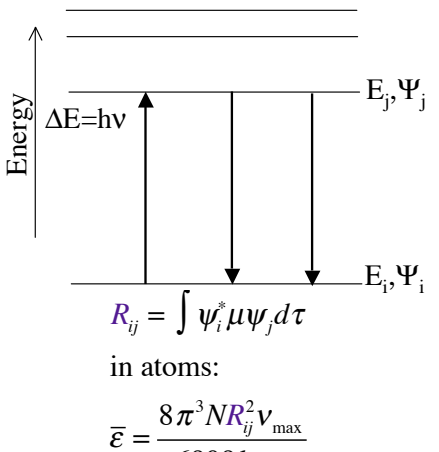
Resonant Light-Matter Interactions

What happens when photons encounter matter?

QM: If photon E (hν) is equal to ΔE between states -

absorption (excitation) spontaneous emission stimulated emission



$$R_{ij} = \int \psi_i^* \mu \psi_j d\tau$$

in atoms:

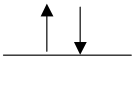
$$\bar{\varepsilon} = \frac{8\pi^3 N R_{ij}^2 \nu_{max}}{6909 hcg_i}$$

X-rays	inner shell e-	X-ray Photoelectron X-ray Diffraction
UV	valence shell e-	**UV Absorbance** **Fluorescence Spec.**
Visible	valence shell e-	**Visible Absorbance** **Fluorescence Spec.**
IR	vibrate atoms	**IR Absorbance Spec.** **Raman Spectroscopy**
μ & radio waves	rotations flip nuclei in **B**	EPR Spectroscopy NMR Spectroscopy

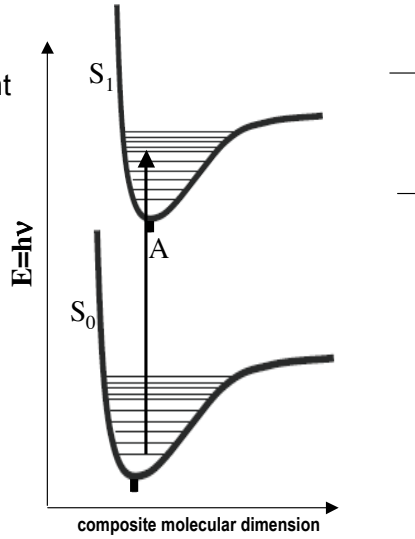
Photoinduced Electronic Transitions

$t < 10^{-15}$ s
scattered light
transmitted light

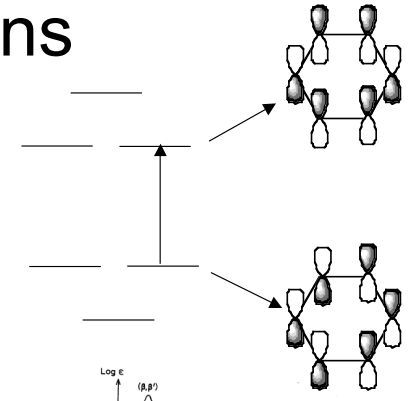
$t \sim 10^{-15}$ s
absorption

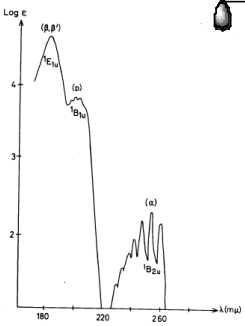


Singlet

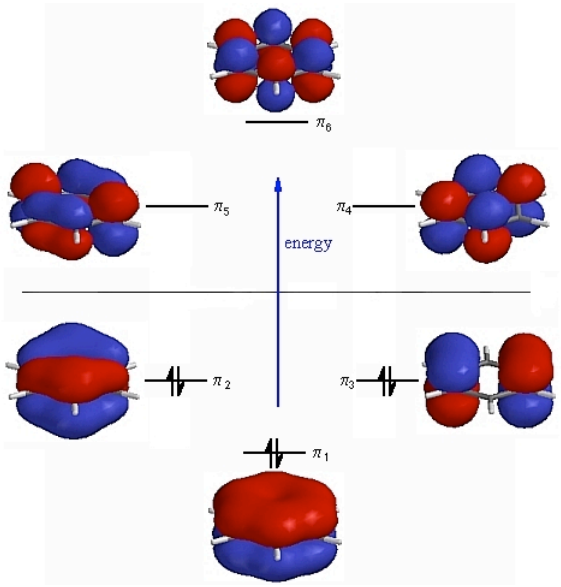


$E = E_{electronic} + E_{vibrational} + E_{rotational}$





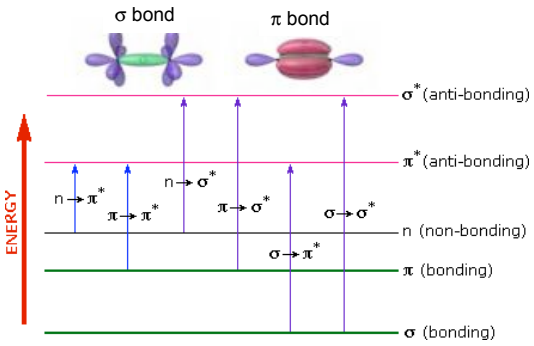
Molecular Orbitals of Benzene

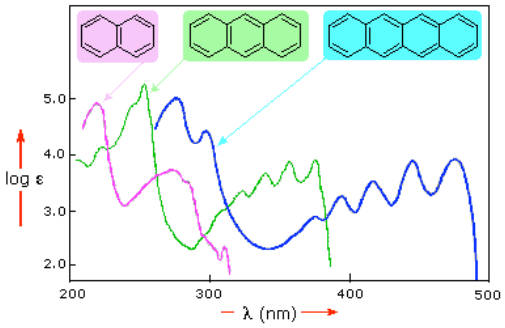


http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch11/ch11-4-1.html

Principles of UV/Vis Absorbance

UV/Vis hν (~180 -800 nm) are absorbed when valence electrons of molecules are <u>transiently</u> promoted into empty non-bonding or anti-bonding molecular (comb. of atomic) orbitals



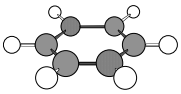
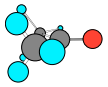


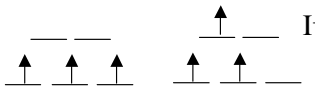
W. Reusch
http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/spectro.htm

Longer conjugated pi systems are more resonance stabilized
λ_{max} increases with molecule size

Principles of UV/Vis Absorbance

UV/Vis hν (~180 -800 nm) are absorbed when valence e- of molecules are transiently promoted into MT non-bonding and anti-bonding orbitals

Class	Example	λ	Transition	ε
Saturated heteroatomics	$H_3C-\ddot{N}H_2$	215	$n \rightarrow \sigma^*$	100
Aromatics		184	$\pi \rightarrow \pi^*$	10^4
Unsaturated heteroatomics		280	$n \rightarrow \pi^*$	20
Transition Metal Complexes	CrL_6^{3+6q}	varies	$d \rightarrow d^*$	10^4

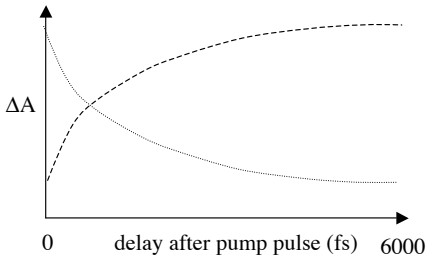


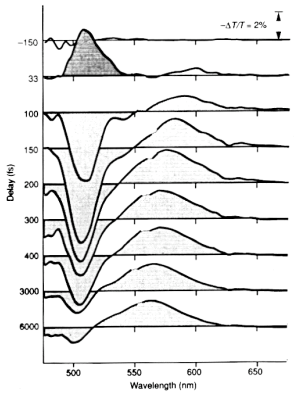
Cr^{3+} Cr^{3+*}

$I^- < Br^- < Cl^- < F^- < OH^- < C_2O_4^{2-} \sim H_2O < SCN^- < NH_3 < en < phen < NO_2^- < CN^-$

$\lambda = 736$ $\lambda = 573$ $\lambda = 456$ $\lambda = 380$

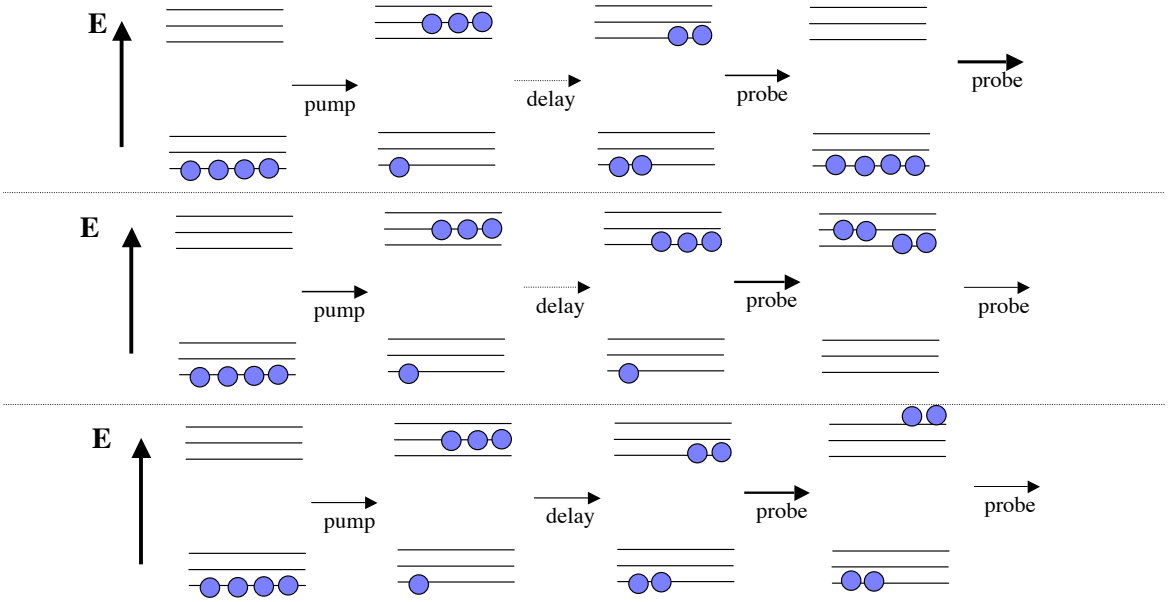
Transient Absorption



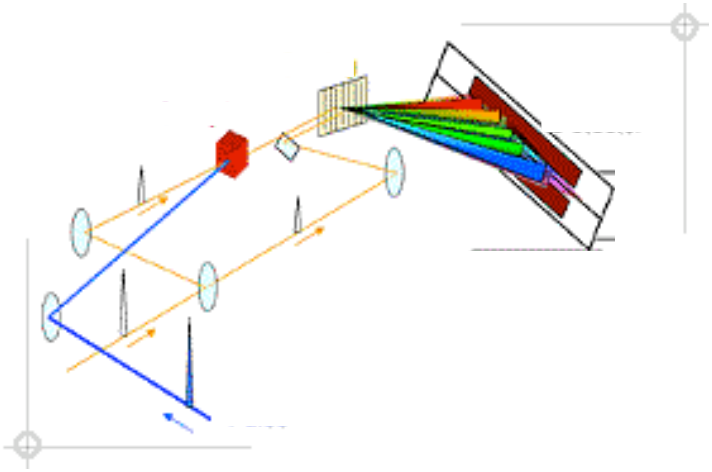


Source:

Transient Absorption



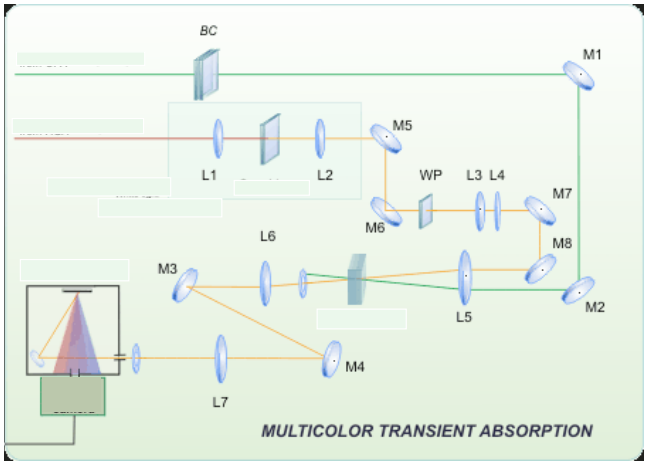
Single-Shot Transient Absorption Spectrometer



Adapted from

http://www.jaist.ac.jp/ms/research/htm/06/content-06-e.html

Fs Transient Absorption Spectrometer



http://www.chem.kuleuven.ac.be/mds/polychromatic_transient_absorption.htm

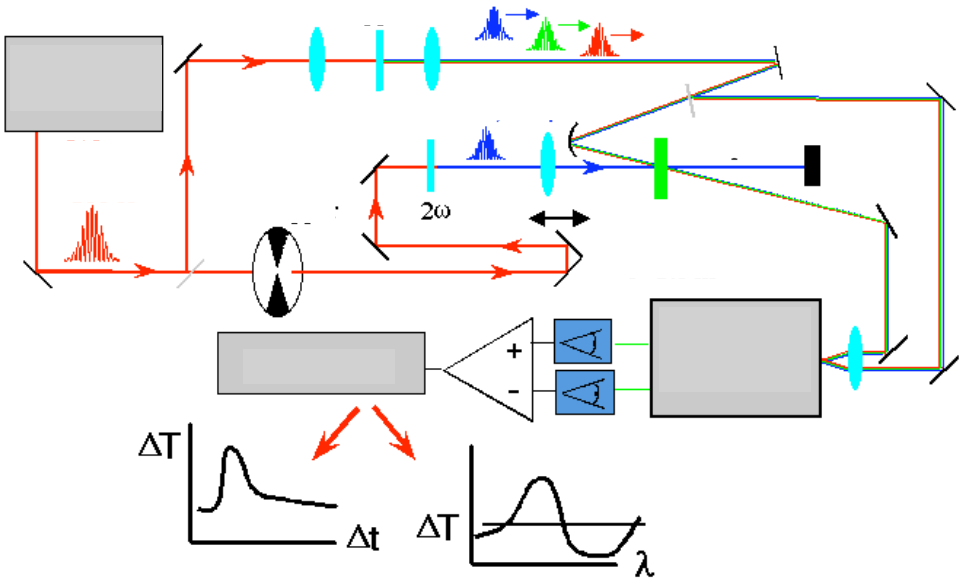
Paper I: Electronic Spec.

V. I. Klimov; D.W. McBranch, Femtosecond high-sensitivity, chirp-free transient absorption spectroscopy using kilohertz lasers, *Optics Letters*, **1998**, *23*, 277.

Objectives

Approach

Instrumentation



Results

Fig. 1

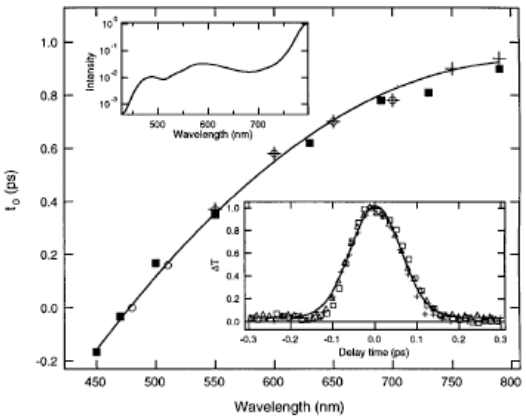


Fig. 1. Chirp of the probe pulse measured by TPA cross correlation with a reference pulse at 800 nm in 1-mm ZnS (squares) and 0.1-mm CdS (crosses) or 400 nm in 1-mm sapphire (circles). The solid curve is a fit (see text). Top inset, continuum intensity versus λ. Bottom inset, TPA cross correlation (continuum + 800 nm) at 550 (crosses), 650 (triangles), and 750 nm (squares). The solid curve is a fit to a Gaussian pulse with FWHM 140 fs.

Results

Fig. 2

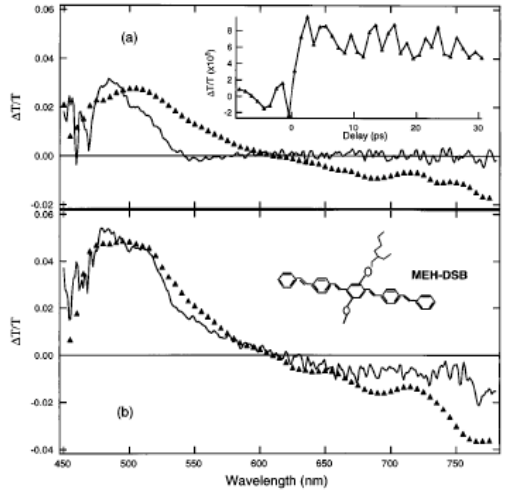


Fig. 2. DT spectra of MEH-DSB measured at (a) 300 fs and (b) 800 fs after excitation by use of a CCD camera (solid curves) and chirp-free spectral scanning (triangles). Inset, DT dynamics at 780 nm, showing a standard deviation of 1.4×10^{-5}.

Results

Fig. 3

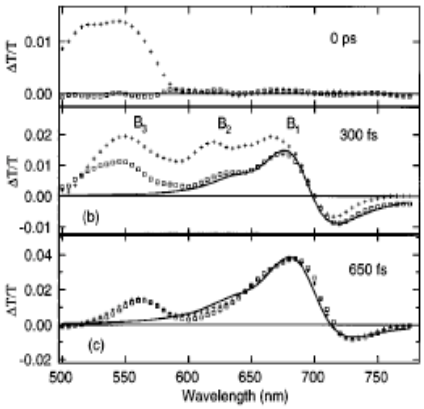


Fig. 3. Comparison of DT spectra of CdSe NC's measured in scanning mode with (squares) and without (crosses) chirp correction. Solid curves, fits to a model describing the population redistribution between B_1 and B_2 transitions.

Conclusions

Authors Conclusions

Critique