united nations educational, scientific and cultural organization

international atomic energy agency

the
abdus salam
international centre for theoretical physics

SMR 1302 - 11

WINTER SCHOOL ON LASER SPECTROSCOPY AND APPLICATIONS

19 February - 2 March 2001

Experimental Methods for the Observation of Ultrafast Dynamics

Lecture III

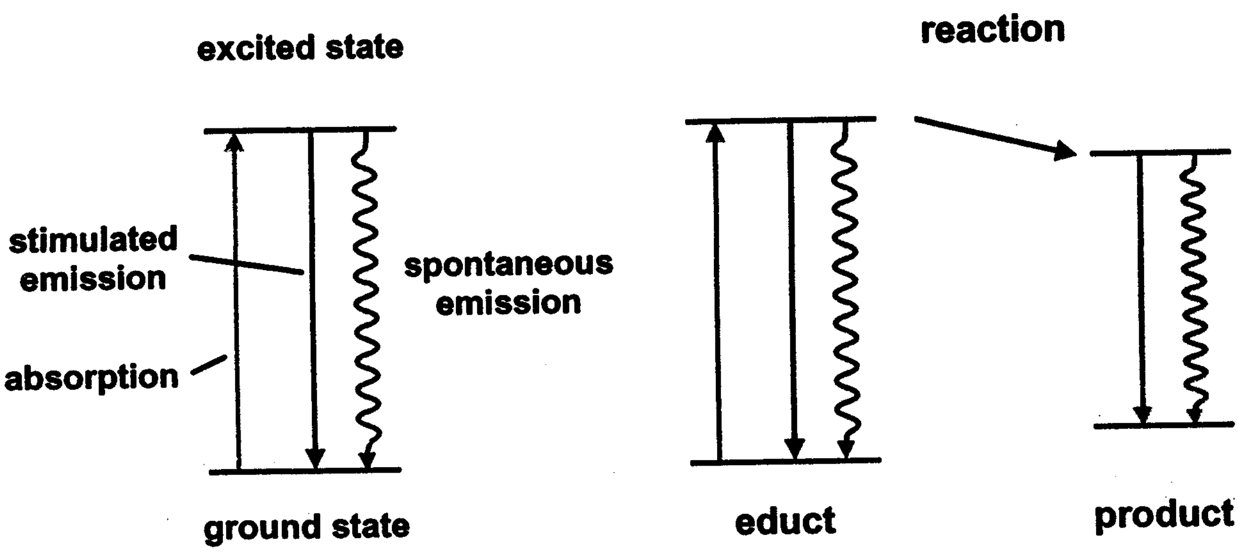
E. RIEDLE
Ludwig-Maximilians-Universitaet Munich
Lehrstuhl fuer Biomolekular Optik - Sektion Physik
Munich, Germany

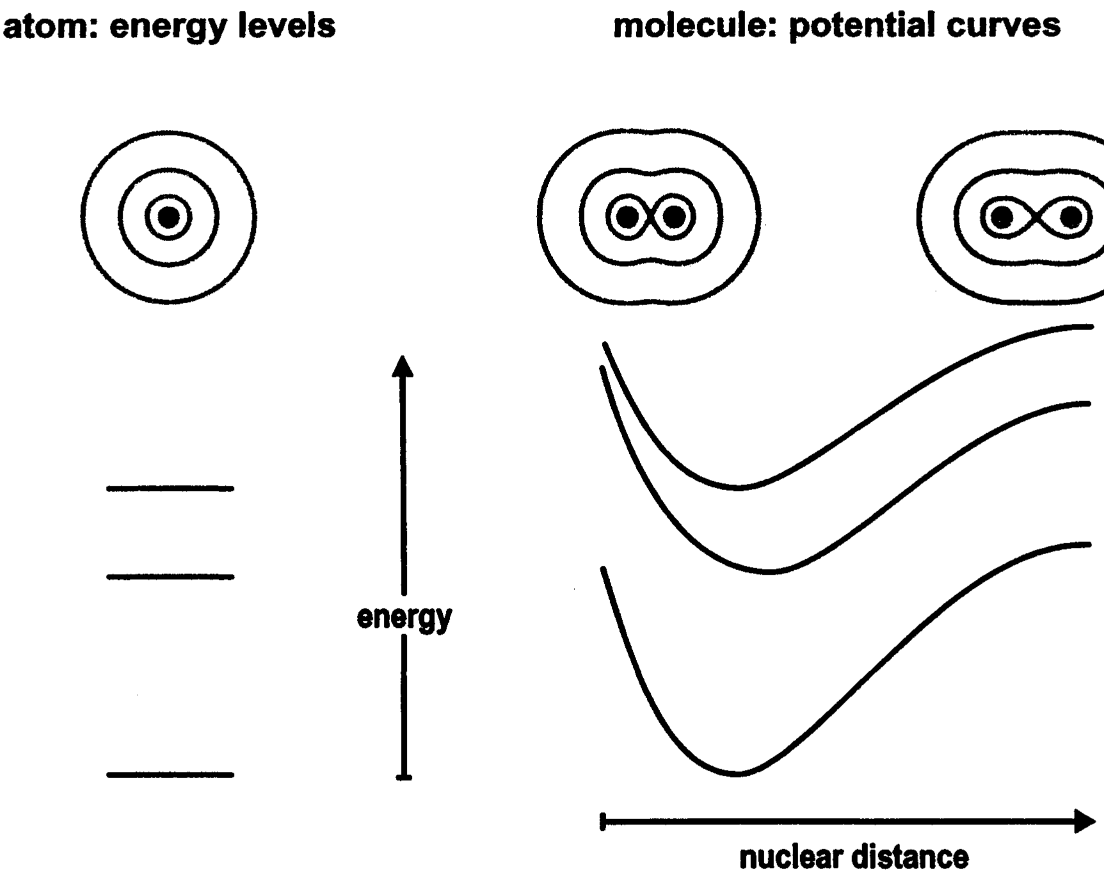
These are preliminary lecture notes, intended only for distribution to participants.

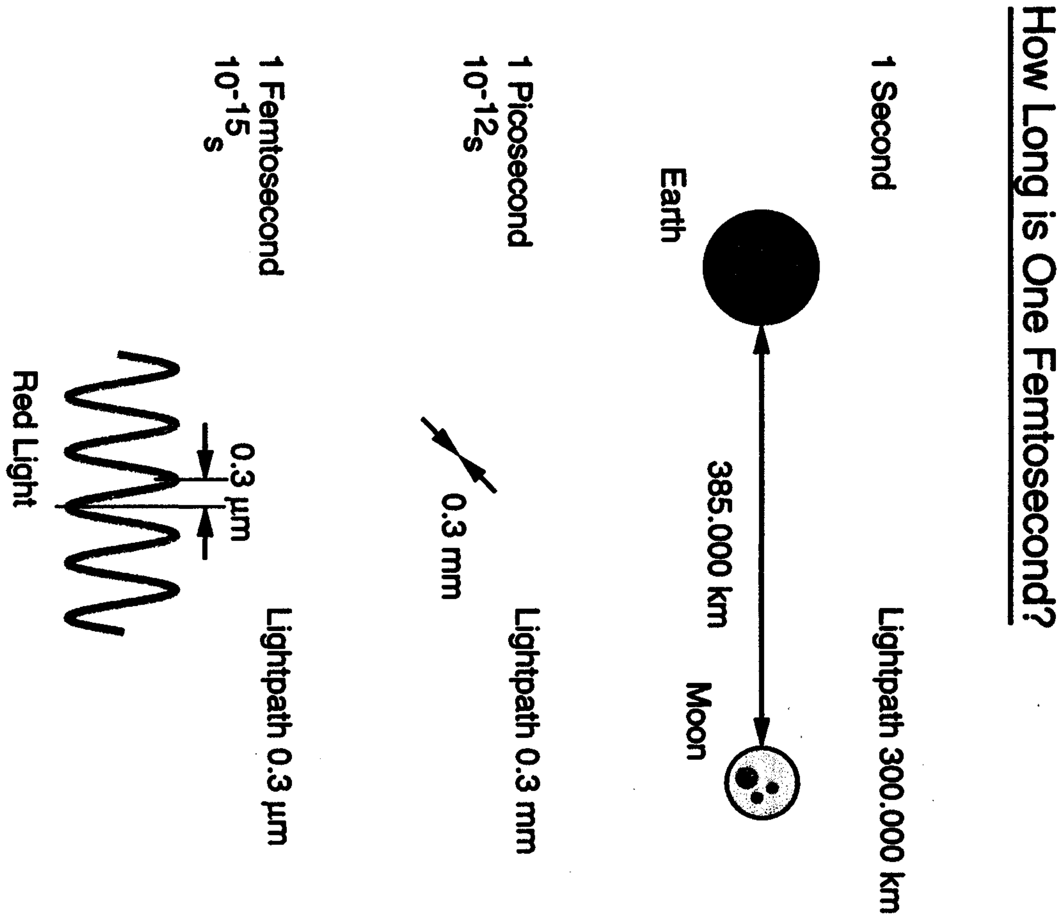
Experimental methods for the observation of ultrafast dynamics

- real time observation of molecular processes
- pump-probe spectroscopy
- group velocity dispersion and mismatch
- pulse compression
- transient absorption: single colour and broadband
- fluorescence detection
- ionisation detection
- time resolved photoelectron spectroscopy
- fluorescence up-conversion
- degenerate four-wave-mixing
- free induction decay and photon echo

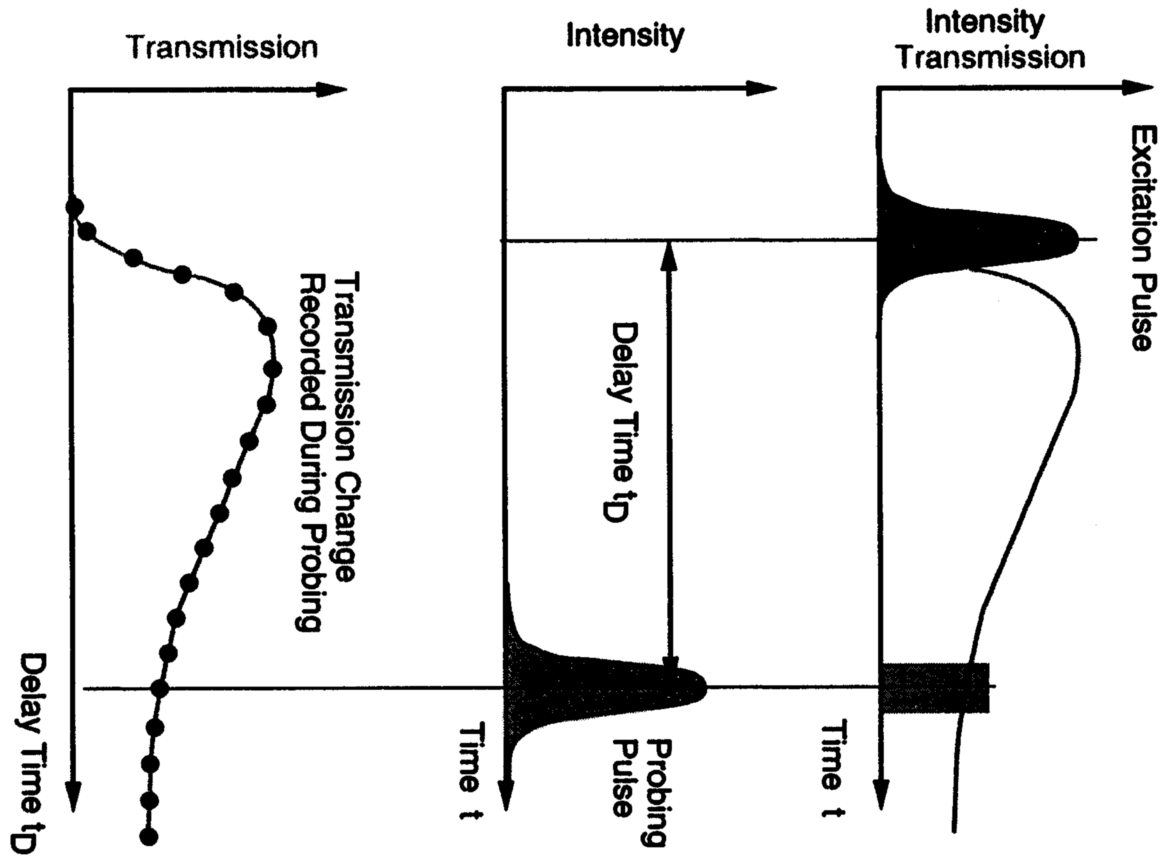
Interaction of Light and Matter

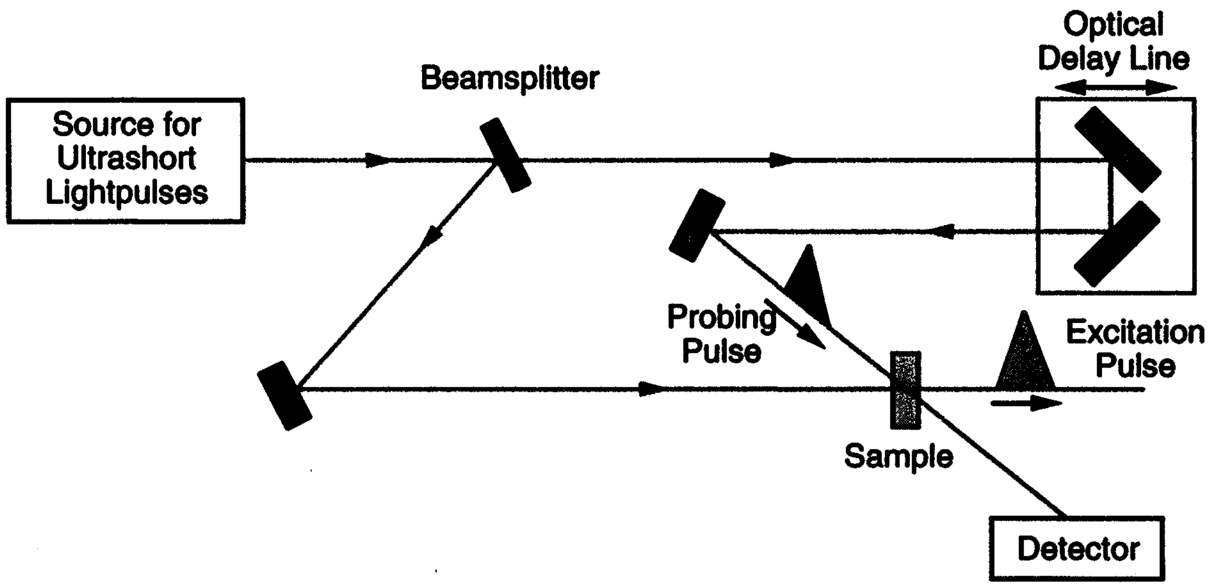






Zeitskala neu





Prinzip Zeitaufgelöst

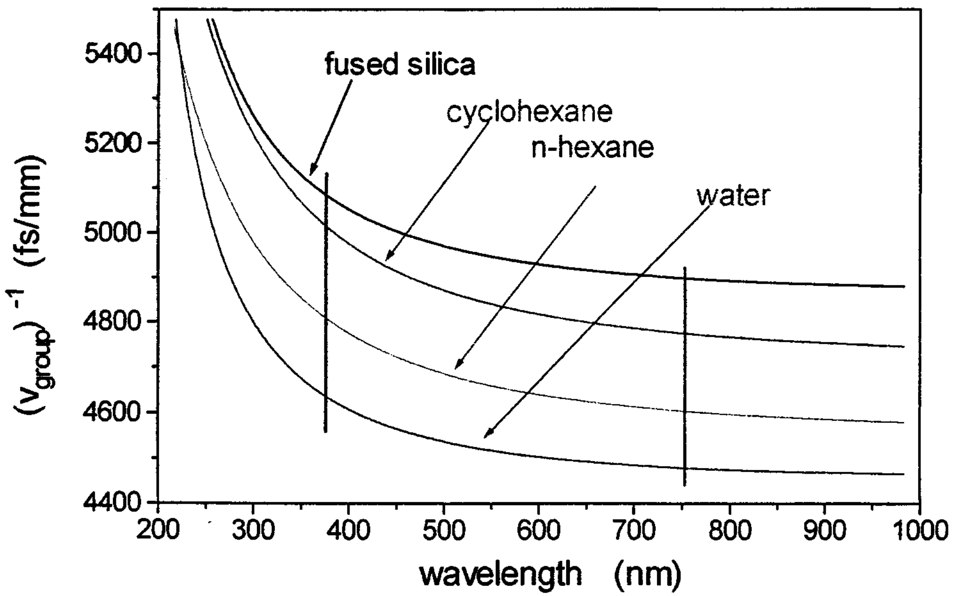
Group Velocity Dispersion

$$v_{phase} = \frac{c}{n} \qquad v_{group} = v_{phase}\left(1 + \frac{\lambda}{n}\frac{dn}{d\lambda}\right)$$

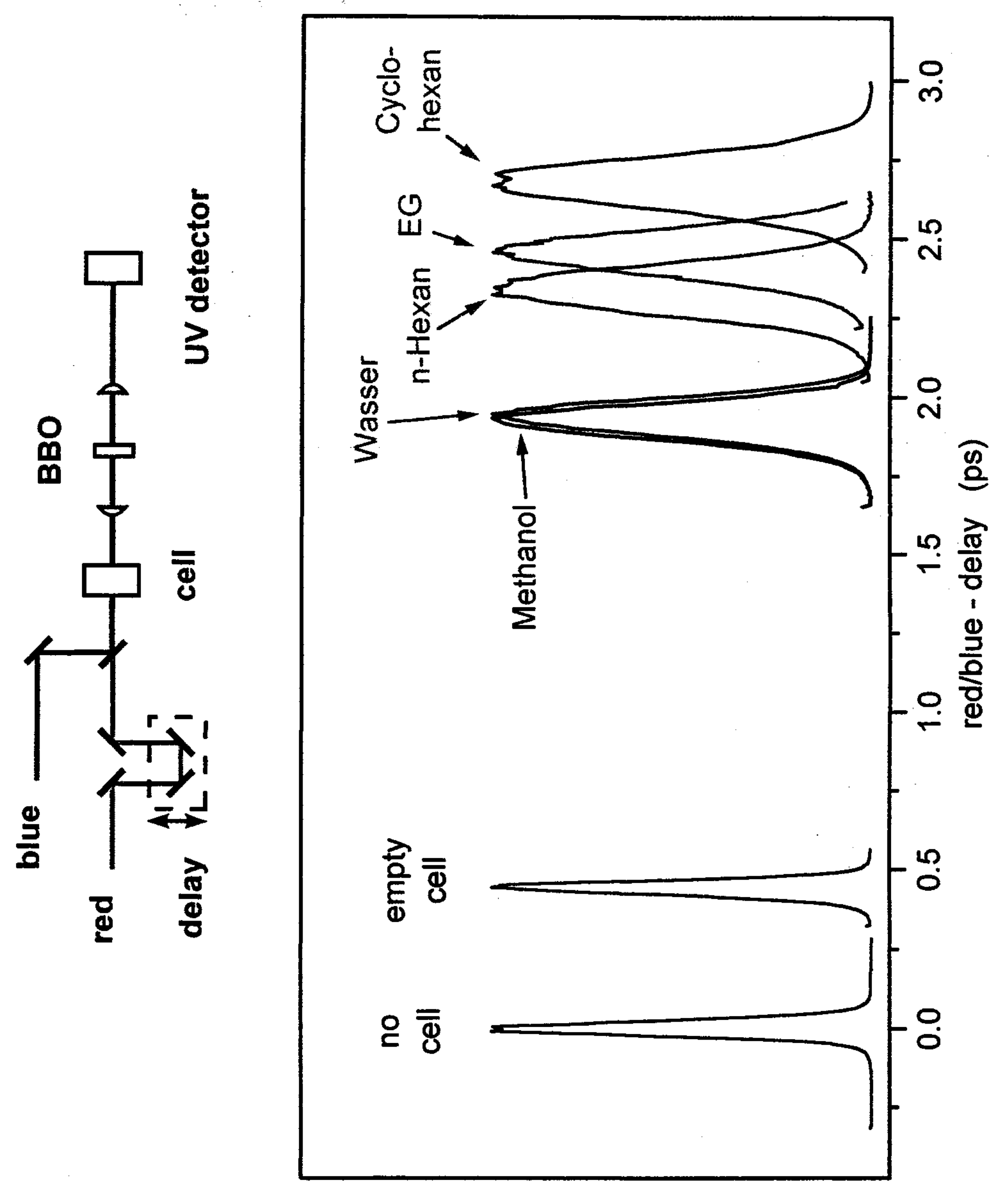
Delay: $$\Delta\tau_d = \left(\frac{1}{v_{group,1}} - \frac{1}{v_{group,2}}\right) L$$

Lengthening: $$\Delta\tau_p' = \Delta\tau_p \left[1 + \left(\frac{4 \ln 2\, \phi''(\omega_0)}{\Delta\tau_p^2}\right)^2\right]^{1/2}$$

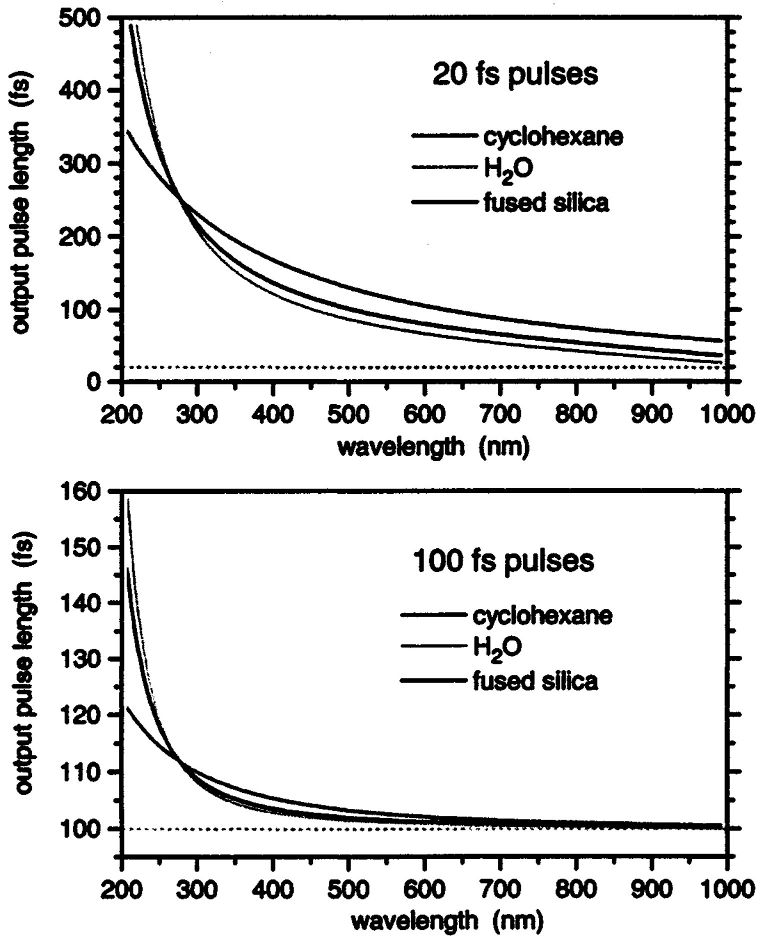
$$\frac{d^2\phi}{d\omega^2} = \frac{\lambda^3}{2\pi c^2}\frac{d^2 n}{d\lambda^2} L$$



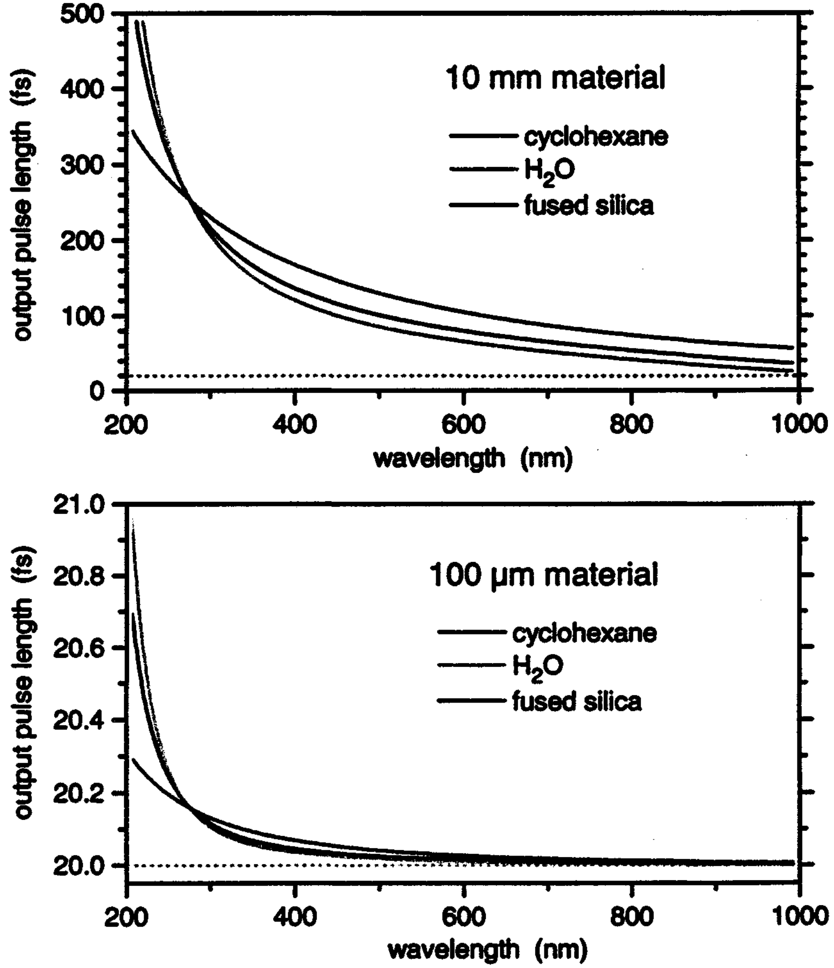
K. Kerl and H. Varchmin, J. Mol. Struct. **349**, 257 (1995)



Lengthening of pulses in 10 mm material



Lengthening of 20 fs pulses



Gruppengeschwindigkeitsdispersion

Laufzeitunterschied: $\Delta t = GVD_\lambda \times \Delta\lambda$

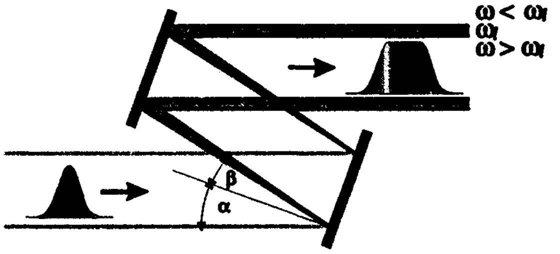
Material

$$GVD_\lambda = -\frac{l\lambda}{c} \times \frac{d^2 n}{d\lambda^2}$$

Quarz: -2.44 fs cm^{-1}nm^{-1}

SF6: 13.6 fs cm^{-1}nm^{-1}

Gitter



$$GVD_\lambda = \frac{l\lambda}{c} \times \frac{m^2}{\cos^3 \beta}$$

m = 600 Linien/mm

7.6 fs cm^{-1}nm^{-1}

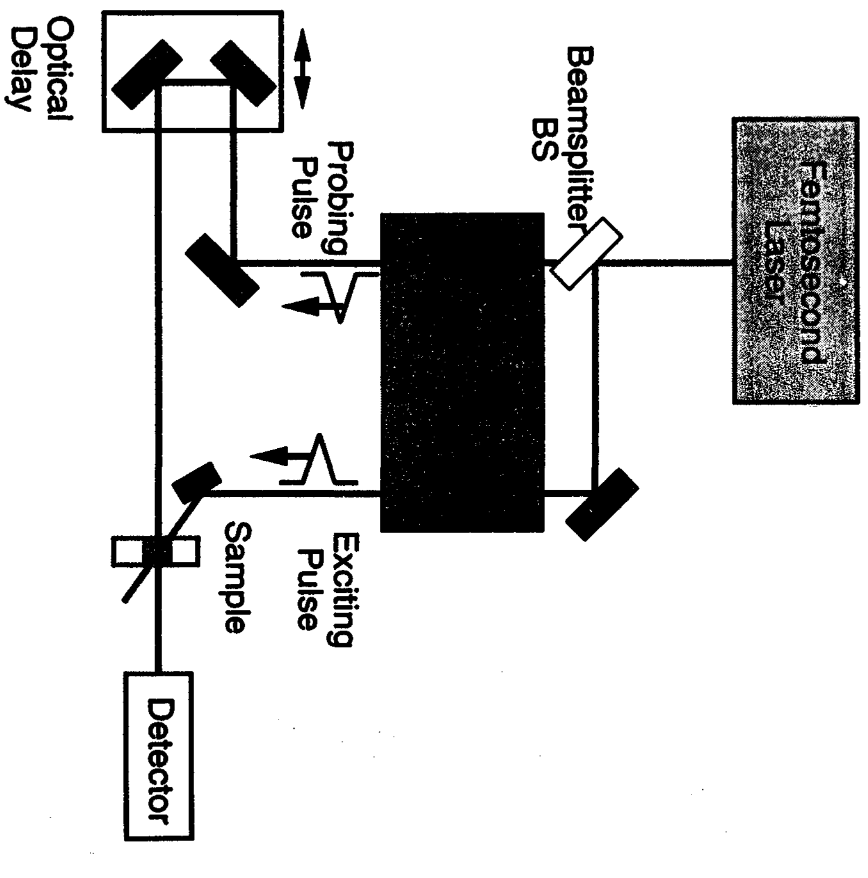
Prisma

$$GVD_\lambda = 4\frac{l\lambda}{c} \times \left(\frac{dn}{d\lambda}\right)^2$$

Quarz: 0.0712 fs cm^{-1}nm^{-1}

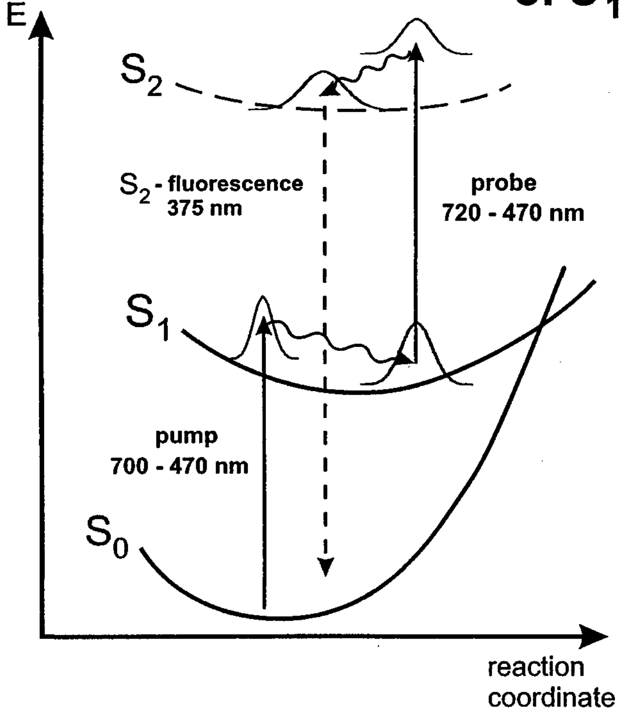
SF6: 1.3 fs cm^{-1}nm^{-1}

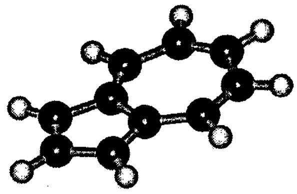
Femtosecond Excite-and-Probe Spectrometer

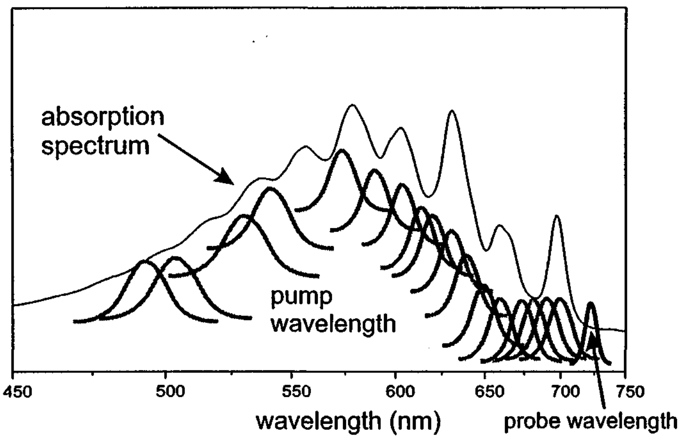


Schema-Meß- Aufbau.1

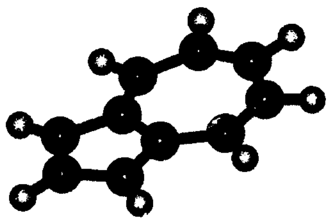
excess energy dependence of the radiationless relaxation of S_1- azulene

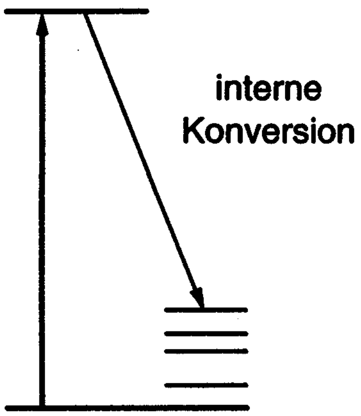


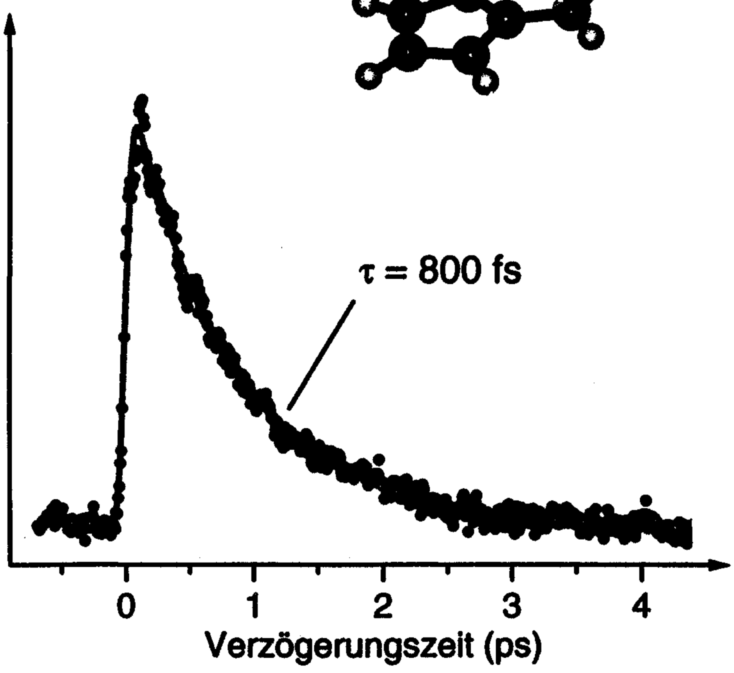


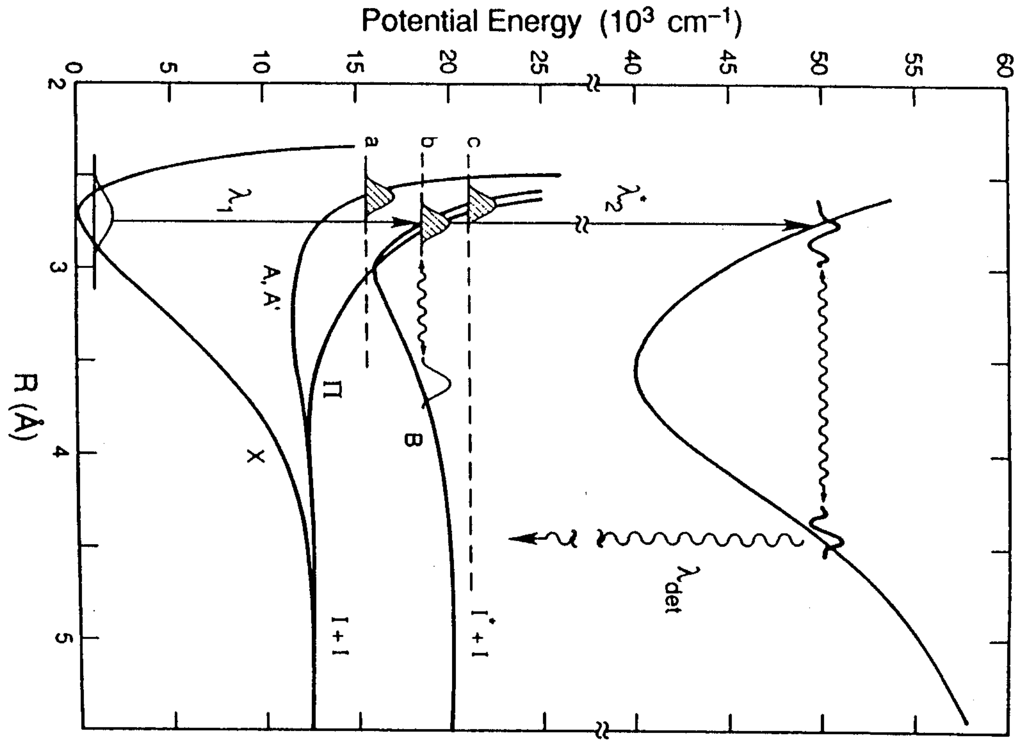


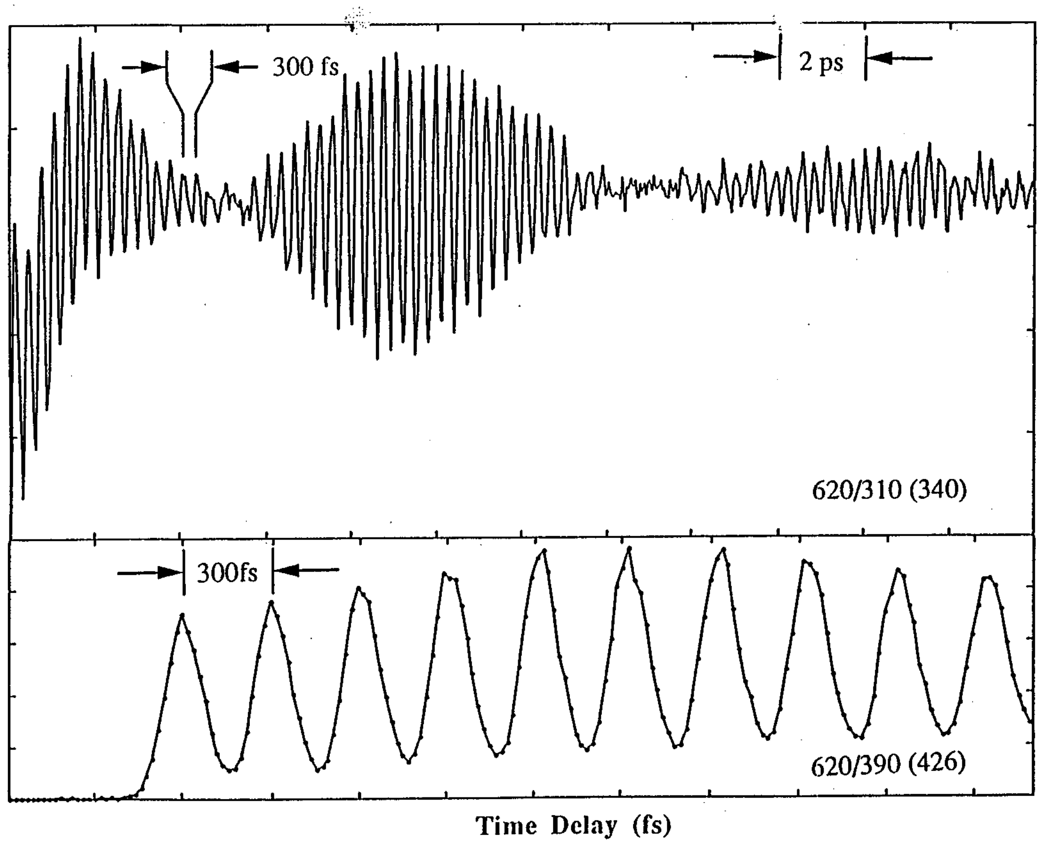
Ultraschneller exponentieller Zerfall des angeregten Azulens





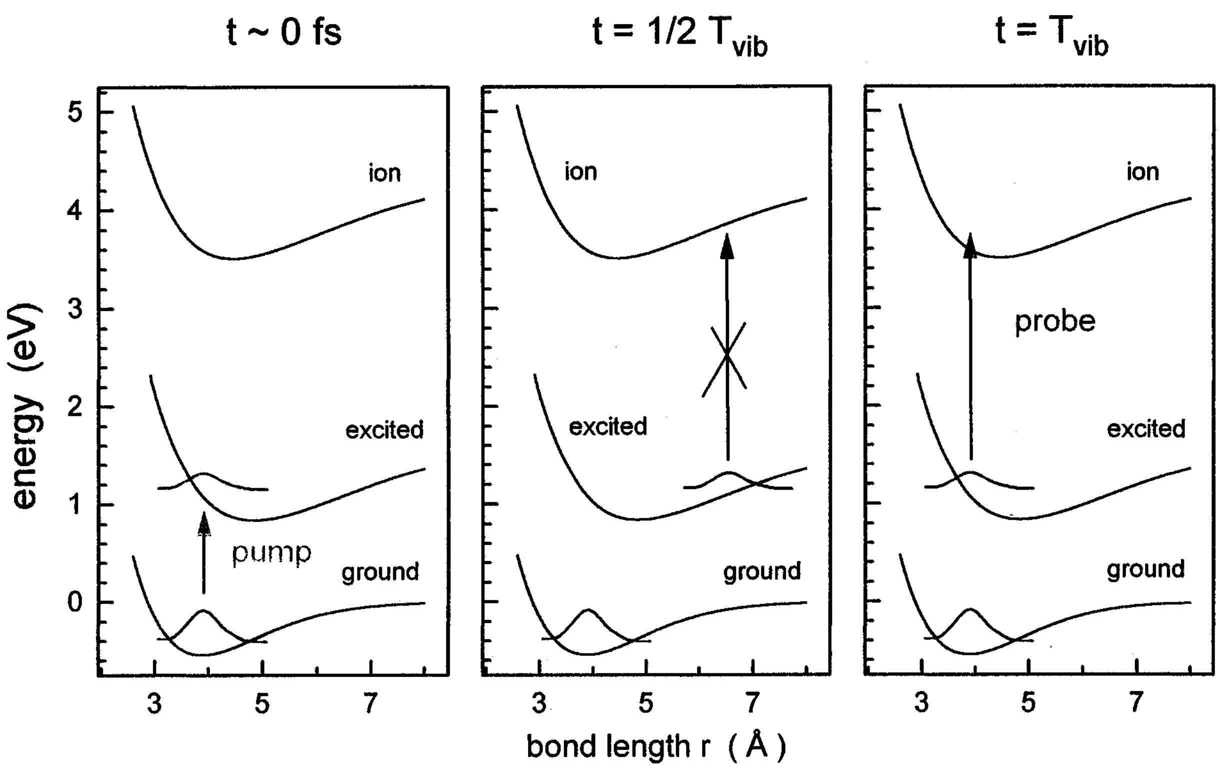




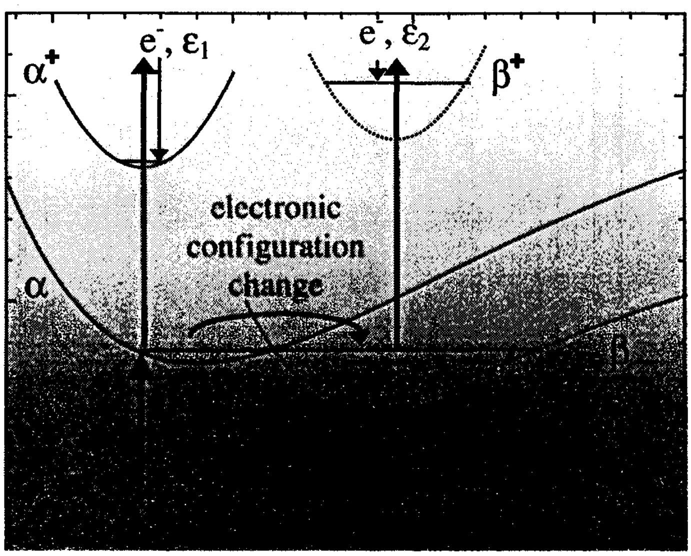


R.M.Bowman, M. Dantus, und A.H.Zewail, Chem.Phys.Lett. **161**, 297 (1989)

Detection of Wavepacket Motion by Ionisation



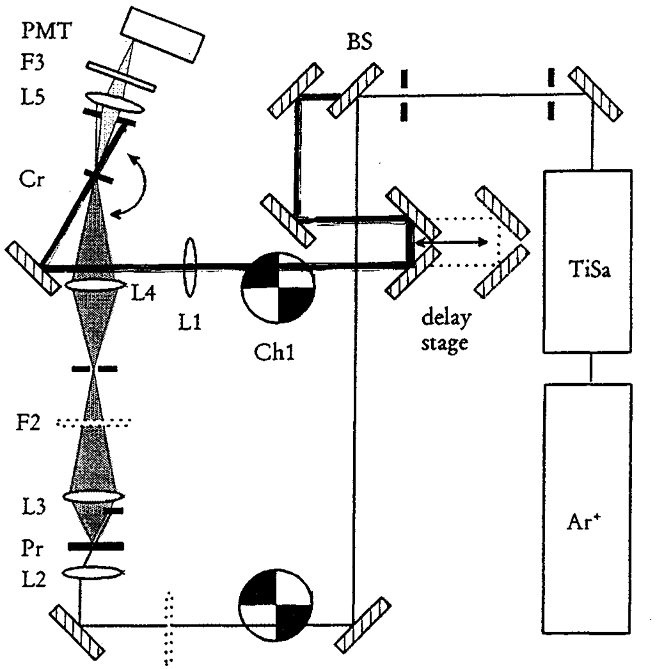
Time-Resolved Configuration Analysis by Photoelectron Spectroscopy



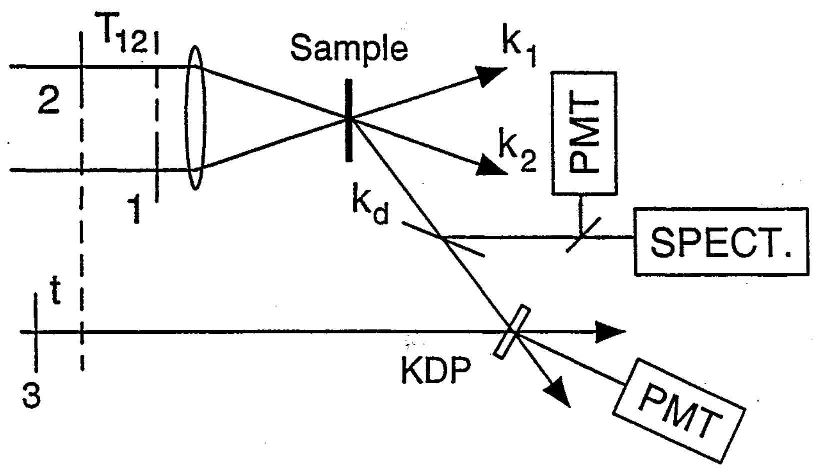
- Core does not like to rearrange during photoionization (frozen core).
- Excited neutral states correlate to a specific ion states upon removal of an electron. Ionization to other ion states is generally less favourable.
- Non-adiabatic effects should cause a switching of the electronic ionization channel.

⇒ **Disentangling of coupled nuclear and electronic dynamics is possible.**

Fluorescence Up-Conversion



Degenerate Four-Wave-Mixing (FWM) Using Femtosecond Pulses



Nonlinear third-order polarization :

$$\mathbf{P}^{(3)}(\omega_1, \omega_2, \omega_3) = \chi^{(3)}\colon\ \mathbf{E}_1(\omega_1)\ \mathbf{E}_2(\omega_2)\ \mathbf{E}_3(\omega_3)$$

$\omega_1 = \omega_2 = \omega_3 = \omega$ degenerate FWM

Diffracted intensity : $I_{FWM}(\omega,t) \propto |P^{(3)}(\omega,t)|^2$

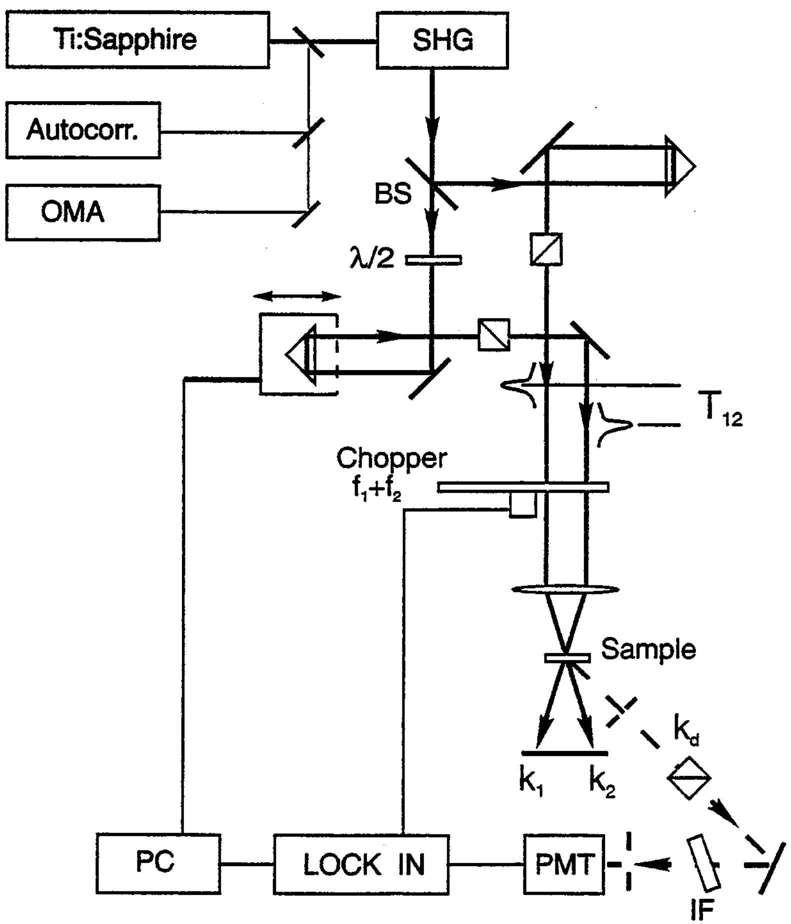
Phase-matching : $\mathbf{k}_d = 2\mathbf{k}_2 - \mathbf{k}_1,\ 2\mathbf{k}_1 - \mathbf{k}_2$

Ensemble of independent two-level systems :

Homogeneous broadening : $I_{FWM}(T_{12}) \propto \exp(- T_{12}/(T_2/2))$

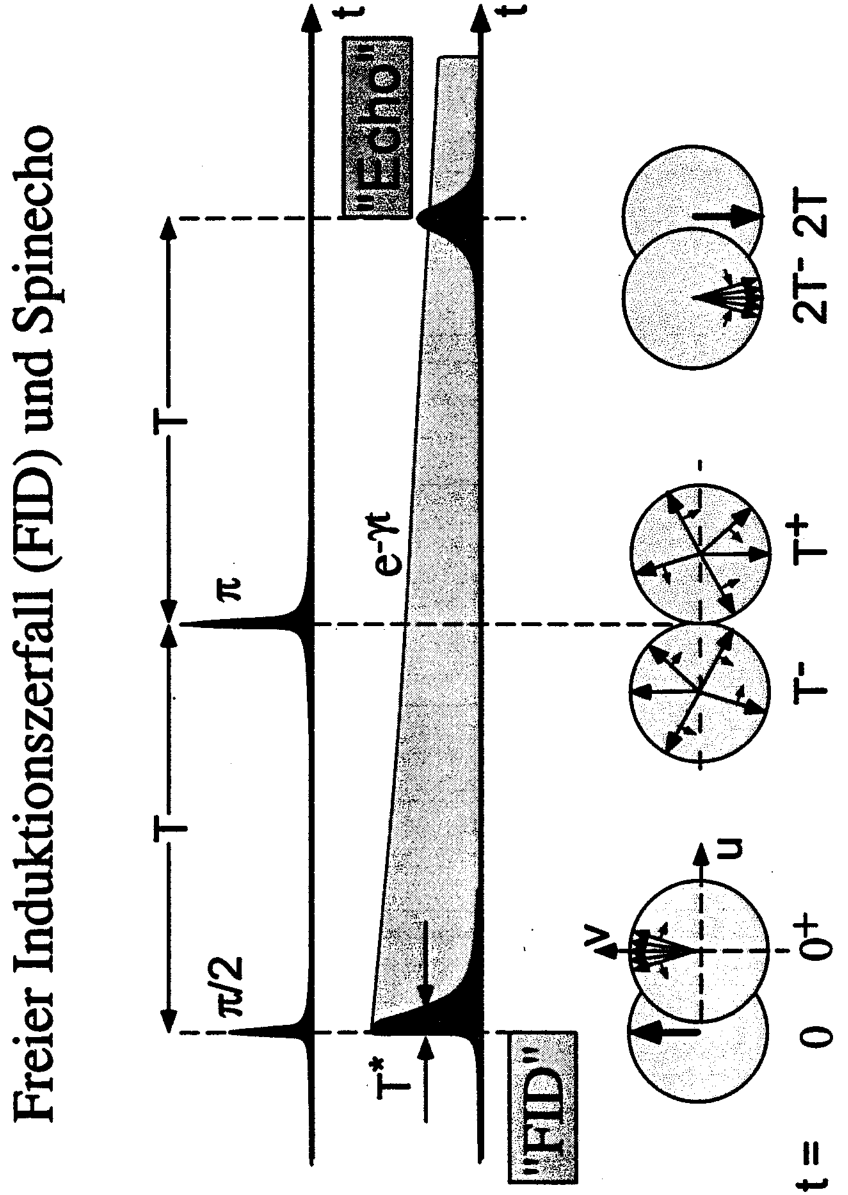
Inhomogeneous broadening : $I_{FWM}(T_{12}) \propto \exp(- T_{12}/(T_2/4))$

Experimental Setup for DFWM



$$P^{(3)}(\omega_1,\omega_2,\omega_3) = \chi^{(3)} : E_1(\omega_1)E_2(\omega_2)E_3(\omega_3)$$

Phase-matching: $\mathbf{k}_d = 2\mathbf{k}_2 - \mathbf{k}_1$



Aus: Optik, Licht und Laser, D. Meschede, Kap.11 © 1999 B.G. Teubner Stuttgart•Leipzig