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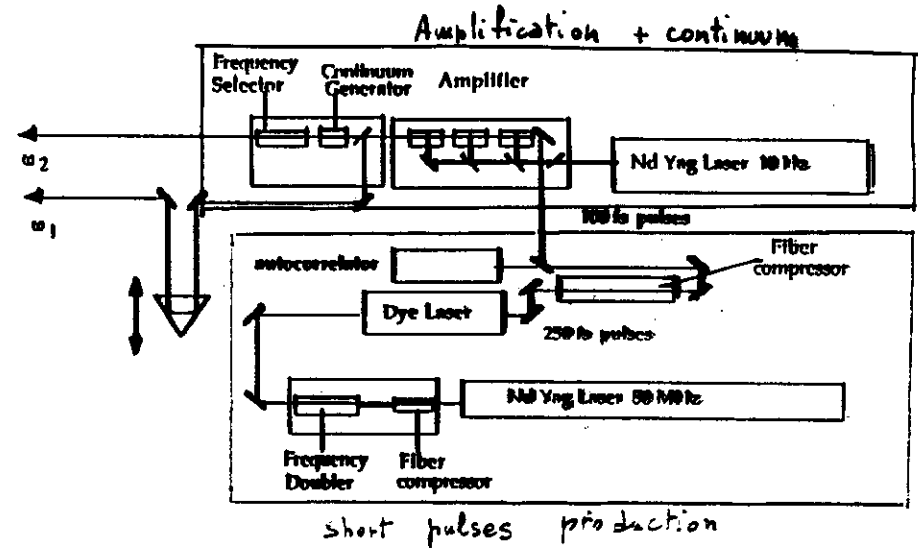
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Winter College on Ultrafast Phenomena

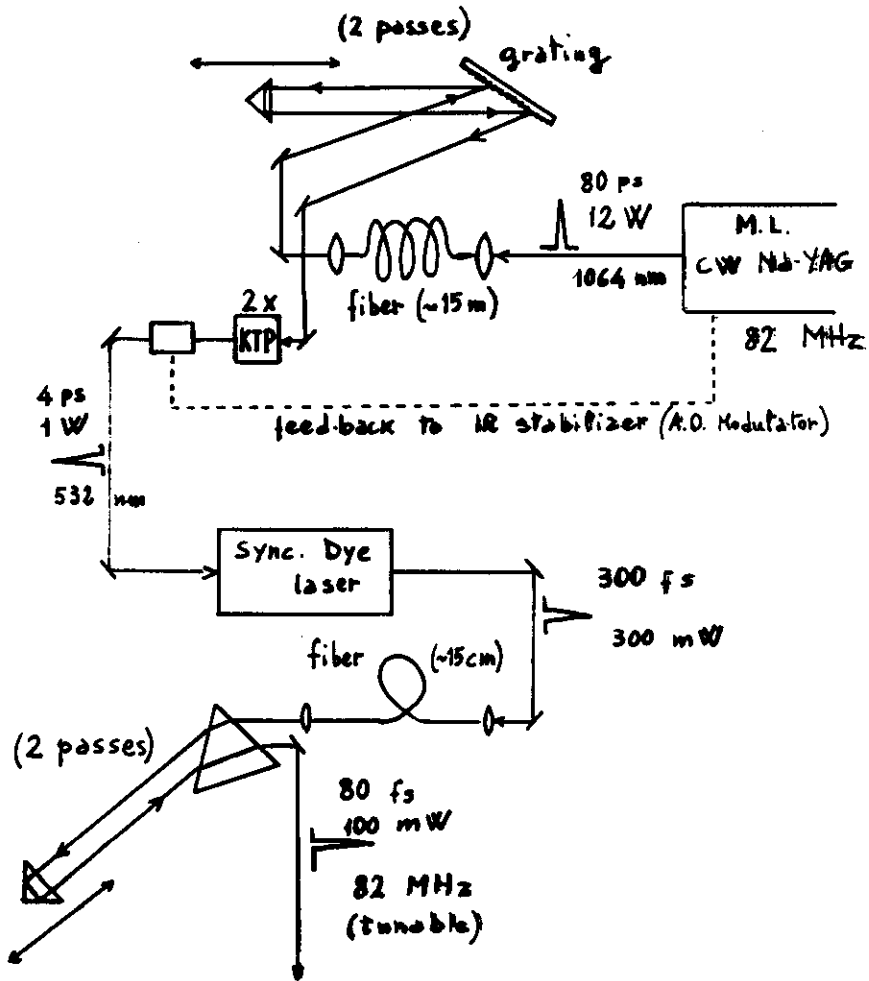
18 February - 8 March 1991

*Femtosecond Laser Facility
 in Florence*

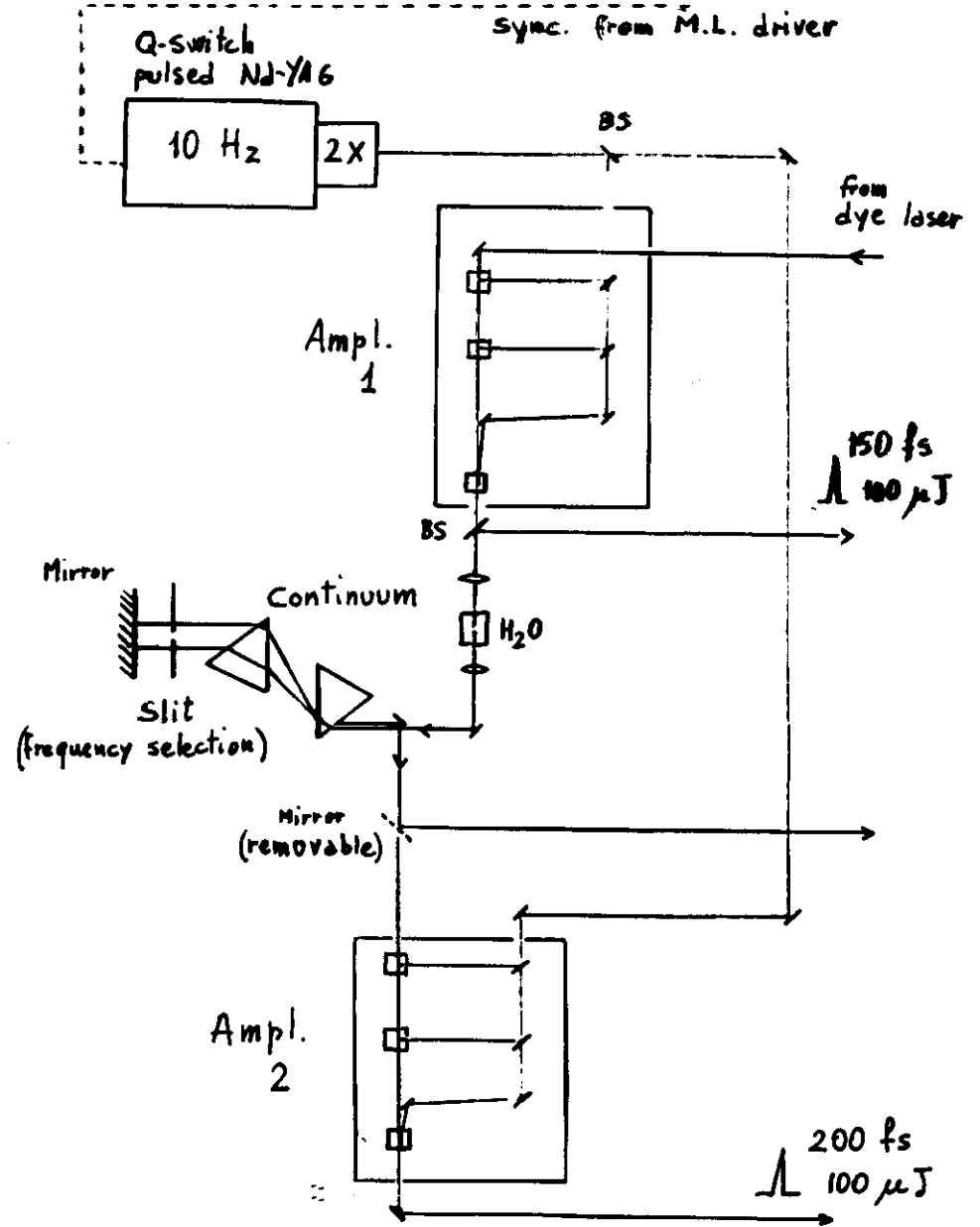
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Generation of short, low power, high repetition rate, tunable pulses



Amplification and generation of continuum



Transient Optical Kerr Effect in the Study of Molecular Dynamics in Diluted Solutions

Molecular dynamics in condensed phase can be conveniently studied by means of optical techniques exploiting the non-linear effects excited in the medium by intense laser pulses. The use of ultra-short laser pulses allows determining the sub-picosecond dynamics of molecular motions.

In centrosymmetric materials (and, of course, in isotropic samples, like liquids) the first non-linear term of the material susceptibility is $\chi_{ijkl}^{(3)}$, which accounts for the third order polarization $P_i^{(3)}(t)$ according to

$$P_i^{(3)}(t) = \int dt' \int dt'' \int dt''' \chi_{ijkl}^{(3)}(t, t', t'', t''') E_j(t') E_k(t'') E_l(t''') ,$$

$E_j(t)$ being the electric field of the j -polarized e.m. radiation.

In the Born-Oppenheimer approximation the third-order polarization can be written as the sum of two parts:

- i) an electronic contribution, described by a tensor σ_{ijkl} ; in case of non-interacting molecules it coincides with the molecular hyperpolarizability $\langle \gamma_{ijkl} \rangle$;
- ii) a molecular part, $d_{ijkl} = i/2\hbar \langle \chi_{ij}(t) \chi_{kl}(0) \rangle$; for non interacting molecules, it is the correlation function of the molecular polarizability.

The two terms correspond to two different material responses to the applied electric fields: the electronic contribution is due to the electron cloud distortion, with a practically instantaneous response time. The nuclear part is due to partial orientation of the polarizable molecules in the electric field of the radiation. This contribution is absent when the molecular polarizability is isotropic.. The third order polarization is then

$$P_i^{(3)} = \sigma_{ijkl} E_j(t), E_k(t), E_l(t) + E_j(t) \int_{-\infty}^t dt' d_{ijkl}(t-t') E_k(t') E_l(t') .$$

The transient birefringence induced in the sample by the two effects described above is responsible for the Optical Kerr Effect (OKE).

In a transient OKE (see Fig. 1) an excitation pulse ω_1 , polarized along x , propagates in the z direction. A probe pulse ω_2 , polarized at 45° with respect to ω_1 , coincides spatially with ω_1 in the sample; the delay between the two pulses can be varied. The probe pulse experience a transient birefringence according to

$$\Delta n(t) = 2\pi n/l \int_{-\infty}^t dt' |E_1(t')|^2 (\chi_{xyxy} + \chi_{xyyx}) R(t-t') ,$$

where n is the non linear refractive index and $R(t)$ is the material response function, containing both the instantaneous (electronic) and time-dependent (nuclear) contributions.

The phase difference for the probe pulse is

$$\delta\phi(t) = \omega_2 \Delta n l/c .$$

If the transmitted probe beam is analyzed through a crossed polarizer, the detected intensity as a function of the time delay τ is given by

$$I(\tau) = \int_{-\infty}^{\infty} I_0(t-\tau) \sin^2(\delta\phi(\tau)/2) dt .$$

The time profile of $I(t)$ gives, after deconvolution, the time behaviour of the material response function $R(t)$. The decay of the induced birefringence at $t > 0$ corresponds to the recovery of the equilibrium orientational distribution of the solute molecules; the OKE time profile then provides a direct measure of the orientational relaxation.

- Experimental set-up

The laser system utilized in the experiment is illustrated in Fig.2. A mode-locked cw Nd-YAG laser produces a train of 80 ps pulses (80 MHz rep. rate) at $\lambda = 1.06 \mu\text{m}$. The infrared pulses are compressed in a 15m long optical fiber and rephased by quadruple passing through a grating rephasing module. After frequency doubling in KTP crystal, green pulses 4 ps long are obtained (1 W average power). The green beam is used to synchronously pump a dye laser (Rhodamine 6G), from which a train of pulses 300 fs long is obtained. The tunable dye pulses are compressed by means of a short fiber (15 cm) compressor, equipped with a four-prisms rephasing unit. An average power of 100 mW is obtained, with pulses as short as 80 fs. The compressed pulses are sent to a low rep. rate (10 Hz) amplification system, consisting of a pulsed Nd-YAG laser which pumps a three-stage amplifier. Two transvers and one longitudinal amplification units are used, with sulphorhodamine solution as an active medium. Half of the amplified beam (100 μJ per pulse, 150 fs duration) is directly utilized as the pump beam. The remaining is focused in a water cell, producing white light covering the entire visible spectrum. The rephasing of the white light is achieved by means of a four-prisms set-up, in which a slit is inserted to select the desired frequency. The pulse extracted from the continuum is sent to a computer driven, encoder controlled optical delay line, and finally used as probe pulse. The detection of the transmitted probe beam is performed by means of a photomultiplier; the dynamic range of the measure is increased by using a set of neutral filters. The data acquisition is performed by means of a BOX-CAR integrator; which also monitor the intensities of the pump and probe beams. Each experimental point is the average of a number (typically 50-100) pulses.

- Transient OKE of β -carotene in diluted solution

β -carotene is a large organic molecule (see Fig. 3) whose spectroscopic properties have been widely studied for many years. Its long conjugated chain gives the molecule large non-linear optical parameters, thus making β -carotene a prototype of a large family of organic molecules of interest under this respect. In spite of the wide interest, no data are presently available on the molecular dynamics of this molecule in diluted solution. In fact, the third order susceptibility of a diluted solution can be written as

$$\chi^{(3)} = \chi_s^{(3)} + \chi_m^{(3)}$$

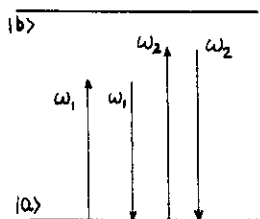
the s and m suffixes indicating the solvent and solute contributions, respectively. The intensity of the OKE signal depends quadratically on the concentration of the active species: the solute contribution $\chi_m^{(3)}$ then quickly disappears as concentration decreases.

In normal conditions it is not observable in diluted ($\sim 10^{-3}$ M) solutions.

On the other hand, much more sensitive techniques involving absorption processes, like transient absorption, transient dichroism (resonant OKE), fluorescence depolarization, cannot be used because of the very short lifetime of the first electronic excited state of β -carotene (we'll go back to this point later).

The modified OKE technique we are going to discuss here has been proposed in order to overcome all these difficulties. The transient birefringence is induced in the sample by an intense off-resonance polarized laser pulse; the frequency of the probe pulse instead is chosen to fall within the absorption band of β -carotene. In such a way a strong amplification of the OKE signal is obtained; on the other hand, the molecular electronic excited state contribute only to the detection of the transient optical anisotropy of the sample, and not to its set-up. The decay of the detected signal thus is not affected by the lifetime of the excited state.

The amplification mechanism can be understood by considering the perturbation treatment of the third order polarization. The energy level scheme for OKE is shown in the diagram on the right: ω_1 and ω_2 are the pump and probe frequencies, respectively. The relevant term of the third order polarization, oscillating at the ω_2 frequency, is $P_i^{(3)}(-\omega_2, \omega_1, -\omega_1, \omega_2)$.



The perturbation theory provides the following general expression for the third order susceptibility:

$$\chi_{ijkl}^{(3)}(\omega_1, \omega_2, \omega_3) = \pi/6(\hbar)^3 \sum_{abcd} I_{1,2,3} \times$$

$$\rho^{000} \left\{ \frac{R_{ab}^i R_{bc}^j R_{cd}^k R_{de}^l}{(\omega_{ab} + \omega_1 + \omega_2 + \omega_3) (\omega_{ac} + \omega_2 + \omega_3) (\omega_{ad} + \omega_3)} + \frac{R_{ab}^j R_{bc}^i R_{cd}^k R_{de}^l}{(\omega_{ab} - \omega_1) (\omega_{ac} - \omega_1 - \omega_2) (\omega_{ad} + \omega_3)} + \frac{R_{ab}^j R_{bc}^k R_{cd}^i R_{de}^l}{(\omega_{ab} - \omega_1) (\omega_{ac} - \omega_1 - \omega_2) (\omega_{ad} + \omega_3)} + \frac{R_{ab}^i R_{bc}^j R_{cd}^k R_{de}^l}{(\omega_{ab} - \omega_1) (\omega_{ac} - \omega_1 - \omega_2) (\omega_{ad} - \omega_1 - \omega_2 - \omega_3)} \right\}$$

where R_{ab} is the matrix element of the dipole operator, ω_1 , ω_2 and ω_3 are the frequencies of the incoming fields, a, b, c and d run over all the states of the system; the operator $I_{1,2,3}$ performs the commutations of the field indexes. ω_{ab} is a complex frequency such that $\text{Re}(\hbar\omega_{ab})$ is the energy difference of the two states, and the imaginary part is the corresponding damping. In the present case one of the frequencies is chosen to be in resonance with the $S_1 \leftarrow S_0$ electronic transition: all terms of the previous expression containing a one-photon resonance contribute to the amplification of the Kerr effect.

In the experiment a $5 \cdot 10^{-3}$ M solution of β -carotene in n-dodecane was employed. In order to minimize the depolarization due to glass surfaces, and the amount of stimulated Raman produced, the sample consisted of a 300 μm thick jet stream. The absorption spectrum of the solution is shown in Fig. 4. Different wavelengths between 470 and 570 nm were utilized for the probe beam, while the wavelength of the exciting pulse was kept at 604 nm, well below the first electronic transition of β -carotene. The frequency tuning of the probe pulse extracted from the white light was obtained by moving the slit in the beam path of the rephasing unit.

The time dependence of the OKE signal obtained with two different pump intensities are shown in Fig. 5. The result is quite surprising: at low intensity the optical anisotropy decays as a single exponential with time constant of 8 ± 1 ps. This time corresponds to the recovery time for the excitation - de-excitation cycle shown in Fig. 6. For high pump intensity the response changes dramatically. A very strong instantaneous response is observed, followed by a slowly decaying signal (time constant = 200 ps).

In order to find an explanation for the observed behaviour, we have to admit that, although the pump frequency is far from resonance, the absorption of the β -carotene solution at $\lambda = 604$ nm is not completely negligible (0.1% absorption was in fact measured at 604 nm in a 1 cm cell). Few solute molecules are thus excited in the B_u state, thus creating an "hole" in the orientational distribution of the molecules in the ground state, which is responsible for the depolarization of the probe beam. This effect is linear in the pump beam intensity, and is the dominant one at low intensity, when non-linear effects cannot set up. As already noticed, the short lifetime of the excited state makes the observation of molecular rotational relaxation impossible.

At high pump intensity instead non-linear effects become dominant, completely obscuring the very weak absorption discussed before. The third order susceptibility $\chi^{(3)}$

is then the source of the optical anisotropy. The strong sharp peak at $t=0$ is due to the electronic instantaneous response; the slow decay is due to the nuclear response. The situation is illustrated in Fig. 7, where the two extreme cases and an intermediate case (in which both kinetics can be observed), are shown.

In addition to the slow (200 ps) orientational relaxation, a very fast decay can be seen on the side of the instantaneous electronic response (see Fig. 8). To explain this feature we must consider that the bulk first order susceptibility χ_{ij} that appears in the molecular response $\langle \chi_{ij}(t) \chi_{kl}(0) \rangle$ can be written as

$$\chi_{ij} = \sum_a \alpha_{ij}^a + \sum_{ab} \alpha_{ij}^{ab} + \dots;$$

the first term is the contribution of the molecular polarizability; the second term represents the contribution of the two-body intermolecular interactions. Due to the low concentration of the solution, only solute-solvent interactions will be relevant. The intrinsic bandwidth of the very short laser pulses is wide enough ($\sim 80 \text{ cm}^{-1}$) to excite by stimulated Raman the low frequency librations of the solute molecules in the cage of the solvent molecules. The decay time obtained by deconvolution is 250 fs; it includes the effects of the librational damping and of the structural relaxation of the solvent cage.

It is interesting to notice (see Fig. 9) that the intensity of the OKE signal as a function of the probe wavelength follows a typical dispersive low, centered at the origin of the first electronic transition. Such a behaviour can be explained on the basis of the previously discussed perturbative expression for the third order susceptibility: when one of the field is in resonance with an electronic transition the corresponding term, proportional to $(\omega_{ab} - \omega_1)^{-1}$, can be singled out of the summation. ω_{ab} being a complex frequency, the calculation of the real part of the complex fraction produces the dispersive shape, which finally has to be added to the "background" of all the remaining non-resonant terms.

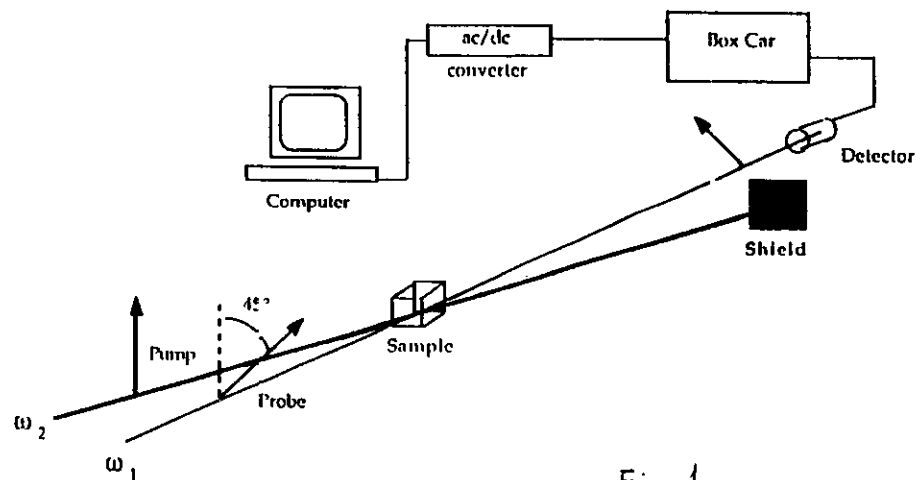


Fig. 1

Transient OKE Set-up

Fig 1 bis

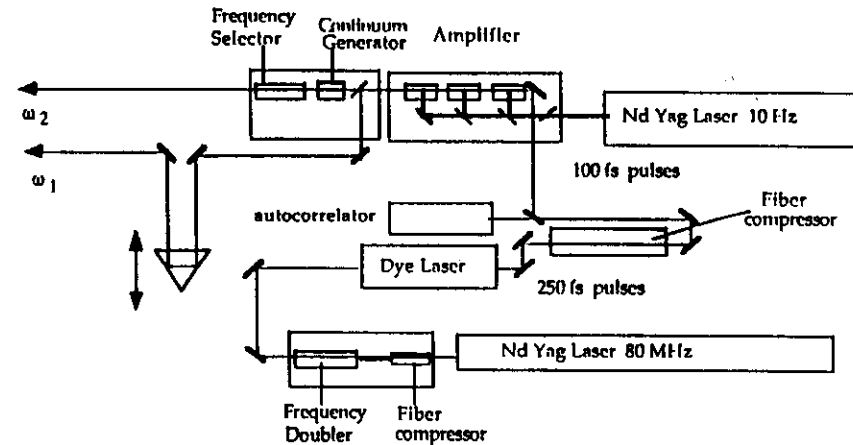
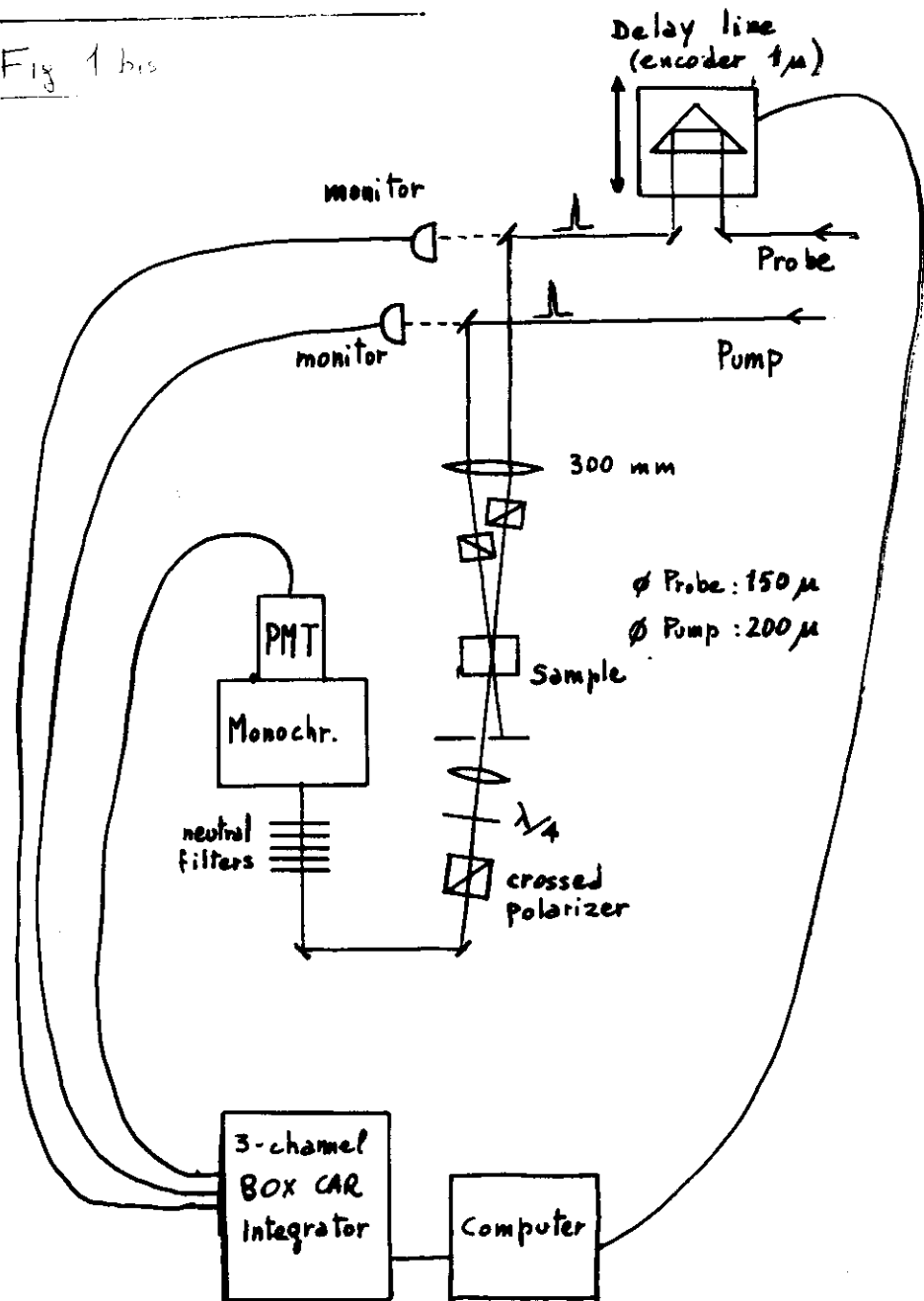


Fig. 2

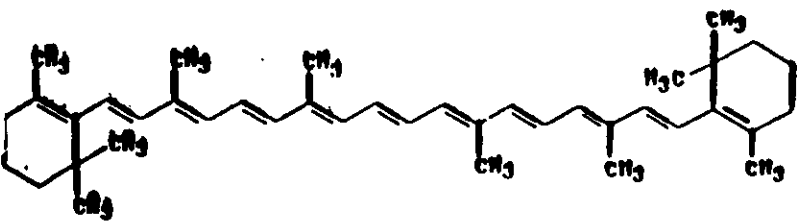


Fig. 3

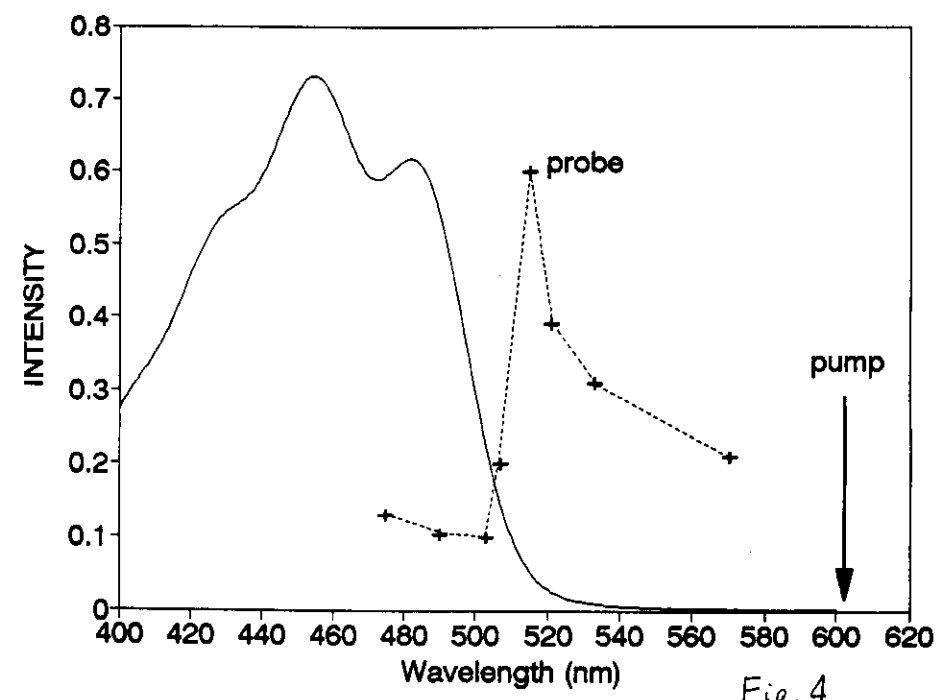


Fig. 4

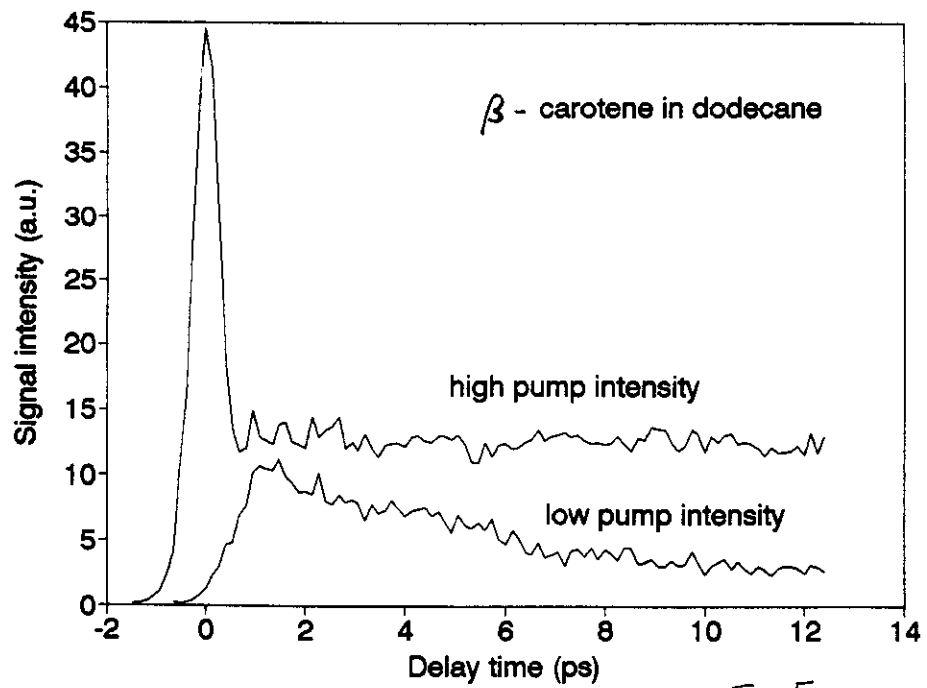


Fig 5

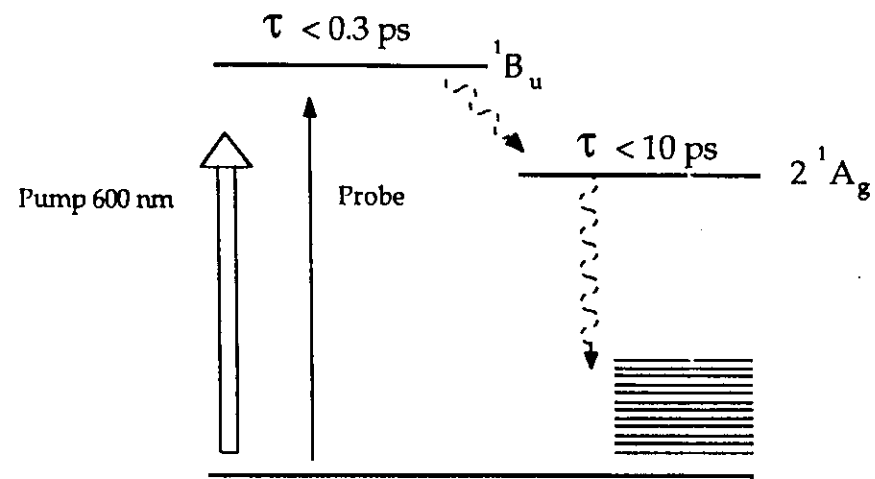


Fig. 6

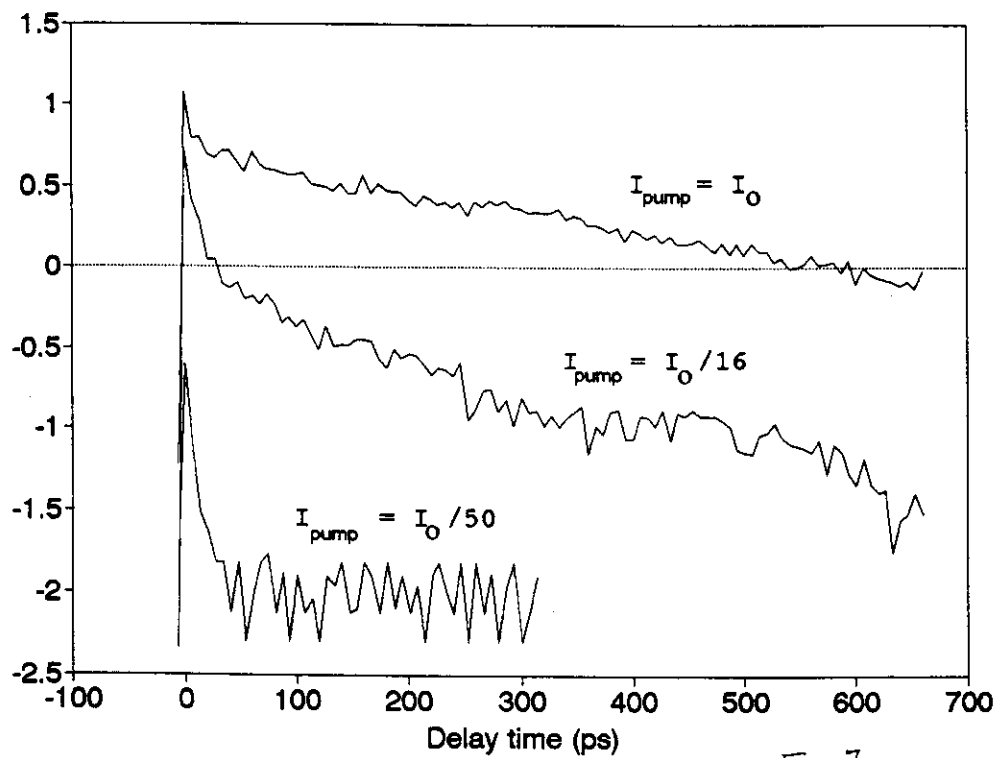


Fig 7

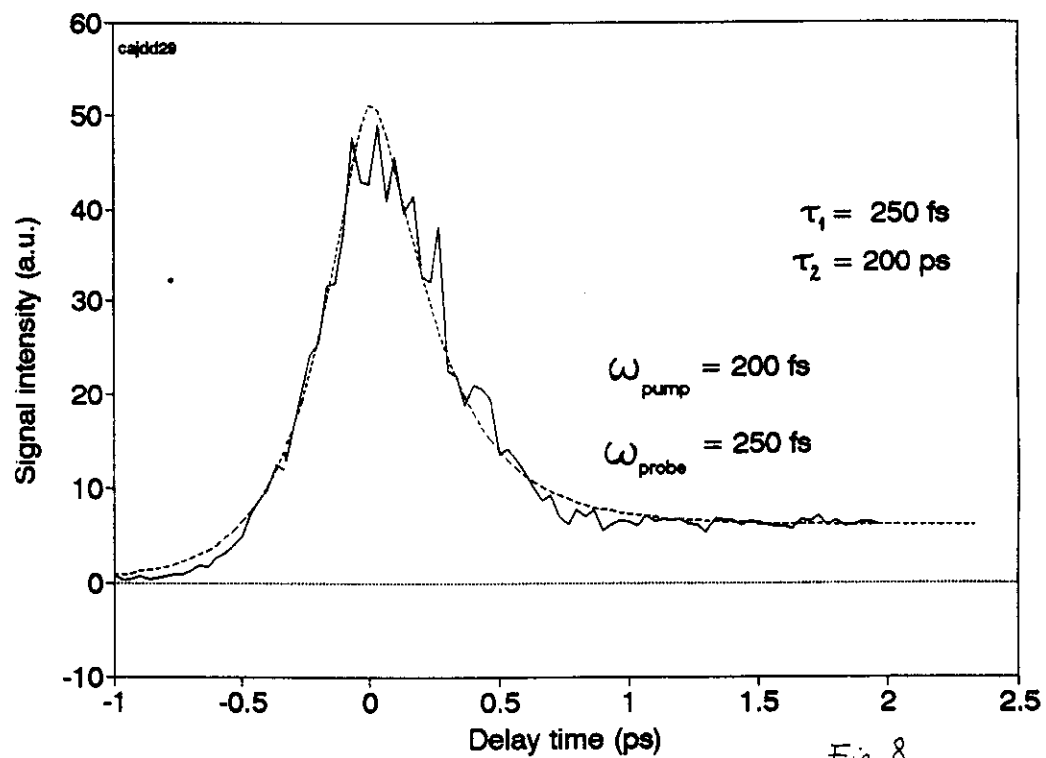


Fig 8

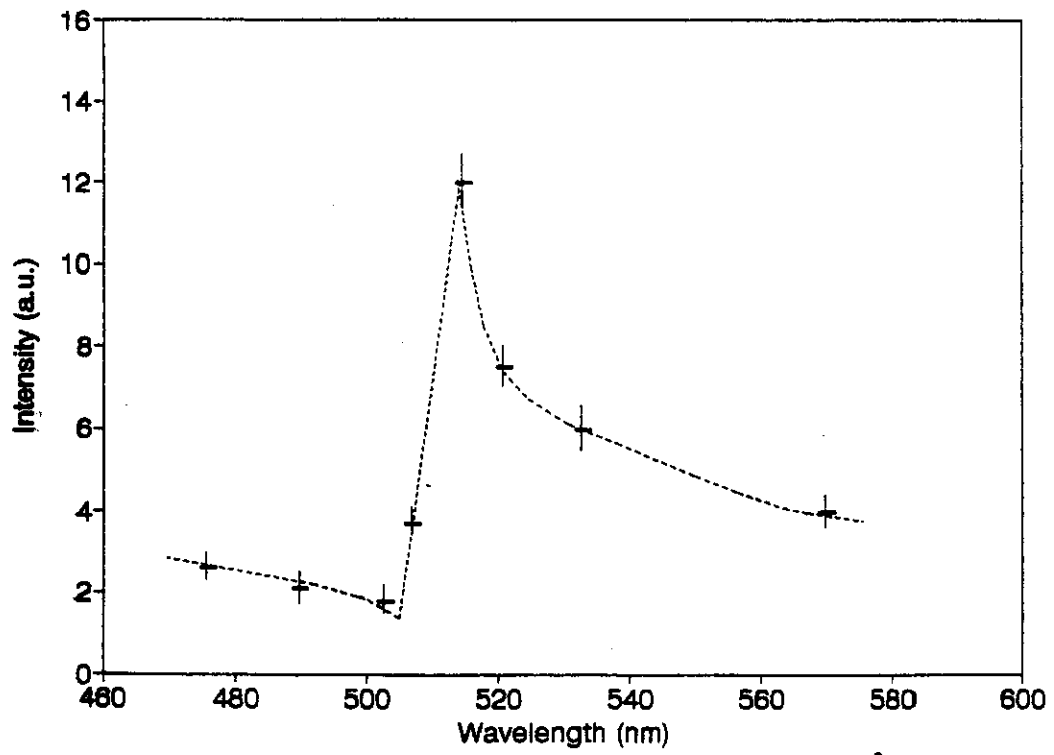


Fig 9