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Degenerate four wave mixing efficiency of organic materials (tetrathiafulvalene derivatives) exhibiting linear and saturable absorption

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We investigate the DFWM efficiency of molecules m_1 and m_2 belonging to two groups of analogues of tetrathiafulvalene (TTF): ethylenic TTF and hyper-TTF derivatives. The molecules m_1 and m_2 display respectively linear and saturable absorption (SA). The hyperpolarisability value is found 23 as large in hyper-TTF molecules m_2 than in the ethylenic TTF derivative m_1.

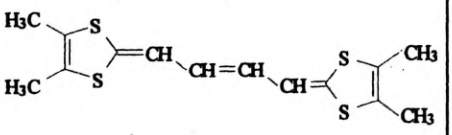
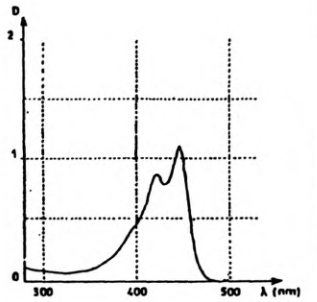
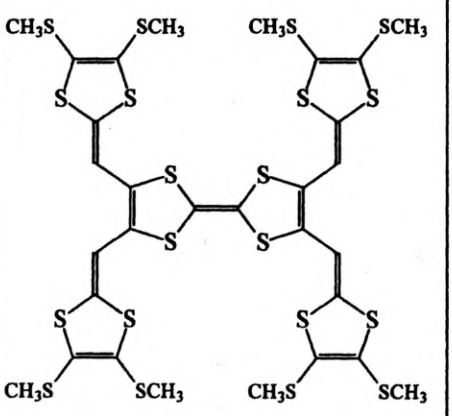
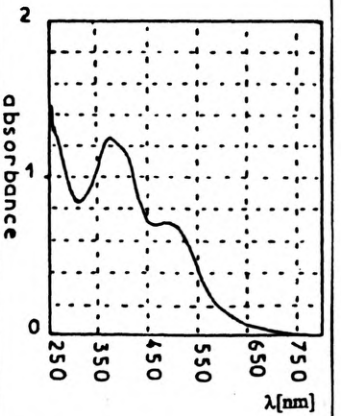
We study and compare the nonlinear optical properties of tetrathiafulvalene (TTF) analogues: ethylenic TTF and hyper-TTF derivatives. The structures of their representants m_1 and m_2 are shown in the Table. The tetrathiafulvalene derivatives are the base of organic metals and their charge-transfer salts present remarkable conducting or even superconducting properties [1], [2]. Due to their highly conjugated framework, they are expected to reveal large third-order nonlinear optical susceptibilities and they are suitable materials for nonlinear optics.

The excitation is provided by 30 ps light pulses ate 532 nm, which are generated by an amplified mode locked Quantel YAG laser. The pulses are nearly Fourier transform limited and the laser operates at the 1 Hz repetition rate.

The following experiments are performed:

– Pump transmission versus pump fluence: in this case only one beam is sent in the medium.

Table. The chemical structures of the molecules m_1 and m_2, their molar masse M and concentration optimum C_{opt}

Molecules	M [g]	C_{opt} [mg/cm^3]	Spectra
m_1 	312	9	
m_2 	1029	1	

– Degenerate four wave mixing measurements (DFWM): the signal beam intensity is measured as a function of the exciting beam intensities.

– Supplementary tests concerning self-focusing or defocusing effects and the changes in the polarization state of a single beam travelling through a nonlinear medium.

The DFWM experiment with the basic geometry illustrated in Fig. 1 is used to measure the third-order susceptibilities $\chi^{<3>}$ of the materials studied. In our experiment the incident wave intensities verify the relations: $I_1(z = 0) = I_2(z = l)$ and $I_3 = 10^{-2} I_1$. The angle θ between the beams <1> and <3> in air is 12° and the

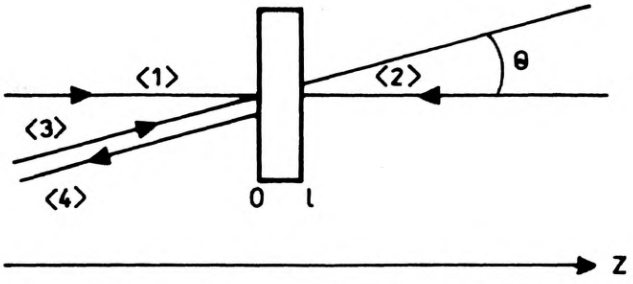


Fig. 1. Geometry of degenerate four wave mixing experiment

thickness of the cell containing the sample is $l = 1$ mm. The incident beams have linear polarization *xxx*.

For measurements of degenerate four wave mixing efficiency at 532 nm, high concentration is necessary ($\gg$0.01 g/l), leading to a strong absorption. The dependence of DFWM signal intensity $I^{\langle 4\rangle}$ upon the solution concentration shows that the compounds display the same kind of curves for a given pump intensity $I^{\langle 1\rangle}$: a single maximum of the reflectivity is obtained for an optimum concentration C_{opt}. For this reason the transmission of m_1 and m_2 is studied as a function of input intensity at their optimum concentration of 9 g/l and 1 g/l, respectively. The first material displays linear absorption and the other one a saturable absorption (SA), Fig. 2. This SA is well described by four level model [3]–[5], in which the pump intensity change along the propagation axis 0z is described by

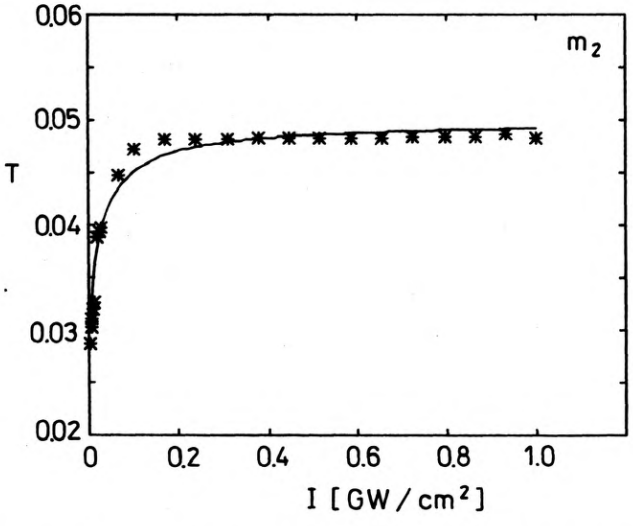


Fig. 2. Changes in the pump transmission versus pump fluence at zero delay for m_2. The sample thickness is $l = 1$ mm. The concentration in tetrahydrofuran is 1 g/l. Asterisk represents the experimental data and the solid curve represents a fit with the solution of Eq. (1)

$$\frac{dI}{dz} = -I\left[\frac{\alpha_{01}+\alpha_{02}(I/I_s)}{1+(I/I_s)}\right] \tag{1}$$

where I_s is the saturation intensity, α_{01} – the absorption coefficient at the ground state, and α_{02} – the absorption coefficient at the excited state. To extract the parameters we perform the best fir of the experimental data using formula (1) and we obtain $\alpha_{01} = 35.3\ \text{cm}^{-1}$, $\alpha_{02} = 29.9\ \text{cm}^{-1}$, $I_s = 3.9 \cdot 10^5\ \text{W/cm}^2$.

The DFWM efficiency $R = I_4(0)/I_3(0)$ is measured as a function of the pump intensity I_1 for the optimum concentration C_{opt}, Fig. 3a. The linearly absorbing material m_1 displays quadratic dependence of R on I_1 in all the range of excitation. Using the Maxwell nonlinear propagation equations (in slowly varying envelope approximation) for a linearly absorbing material, one can show that the DFWM reflectivity R can be written [6]

$$R = \frac{(k\chi^{<3>}I_1)^2\exp(-\alpha l)}{\left[p\coth(pl)+\frac{\alpha}{2}\right]^2} \tag{2}$$

where: $p = \left[\left(\frac{\alpha}{2}\right)^2 - (k\chi^{<3>}I_1)^2\exp(-\alpha l)\right]^{1/2}$, $k = \frac{48\pi^3}{n^2 c\lambda}$ (in esu system).

The parameters α, l, λ and n are respectively the linear absorption coefficient, the cell length, the wavelength of the laser and the linear refractive index of the material. In our experiment we have $\frac{\alpha}{2} \gg (k\chi^{<3>}I_1)\exp\left(-\frac{\alpha l}{2}\right)$. Therefore, $p \approx \frac{\alpha}{2}$ is independen of $I^{<1>}$ and R depends quadratically on $I^{<1>}$.

To extract the real part of third order susceptibility for m_1 we perform the best fit of the experimental data using Eq. (2) and we obtain $|\chi'^{<3>}| = 8 \cdot 10^{-20}\ \text{V}^2\text{m}^{-2}$, so the hyperpolarisability of m_1 is $\gamma = 1.1 \cdot 10^{-45}\text{m}^5\text{V}^{-2}$. The material m_2, exhibiting saturable absorption, displays quadratic increase of R only at high excitations $I_1 > 0.7\ \text{GW} \cdot \text{cm}^{-2}$, *i.e.*, when I_1 is far larger than the saturation intensity I_S. At low intensities ($I_1 < 0.3\ \text{GW cm}^{-2}$), a decrease of R with I_1 can be observed, in agreement with the predictions [7] made in the range of saturable absorption. In agreement with the model developed by ABRAMS and LIND [7] we can thus consider that the material m_2 has the same behaviour as linearly absorbing material when $I_1 \gg I_S$. Therefore the value of the real part $\chi'^{<3>}$ of the third order nonlinear susceptibility $\chi^{<3>}$ for $I \gg I_S$ can be deduced from the measured value of R using the classical formula (2), which leads to $|\chi'^{<3>}| = 6 \cdot 10^{-20}\ \text{V}^2\text{m}^{-2}$ for m_2. The respective value of γ for the molecule m_2 is equal to $2.5 \cdot 10^{-44}\ \text{m}^5\text{V}^{-2}$. We can see, from the shape of the $R = f(I_1)$ curve (Fig. 3b) in the range $0 < I_1 < 0.7\ \text{GWcm}^{-2}$ that the measured reflectivity values are larger than the values predicted by theoretical formula (2). This leads to the conclusion that in this range of intensities, the contributions of SA and of the correlated refraction index changes are important.

DFWM method allows to calculate only absolute values of $\chi'^{<3>}$. To deduce the sign of $\chi'^{<3>}$, we perform the supplementary tests concerning self-defocusing of a

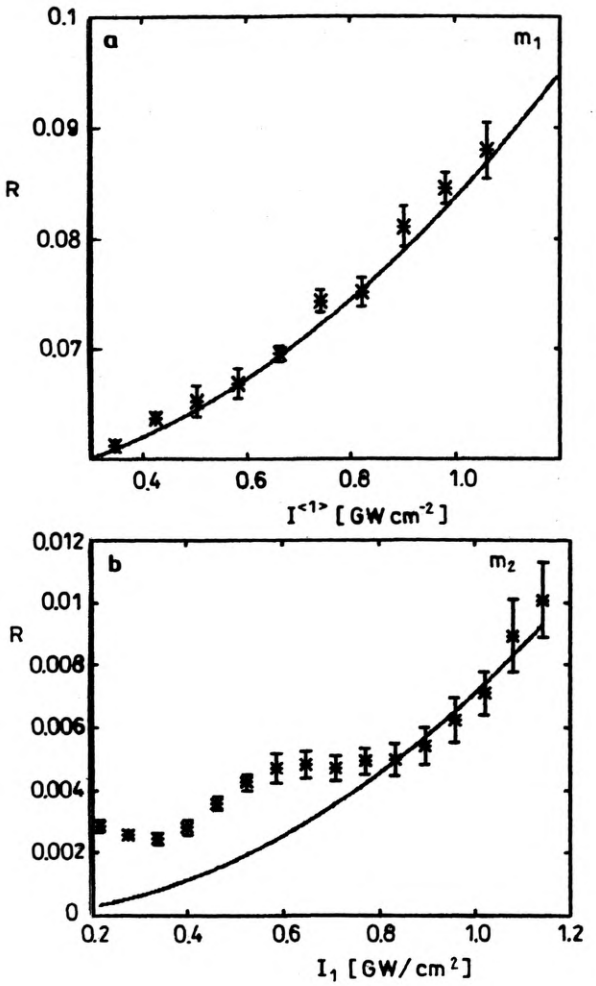


Fig. 3. Reflectivity R with respect to the pump intensity $I^{<1>}$ reference for: **a** — the compound m_1 at the optimum concentration $C_{opt} = 9$ gl^{-1}, **b** — the compound m_2 at the optimum concentration $C_{opt} = 1$ gl^{-1}. The linear polarization states of incident beams are the same. The smooth curve represents the theoretical curve obtained from Eq. (2)

single beam travelling through the samples [8]. The solutions of both materials studied present a self-defocusing effect of the exciting laser beam, which indicates that the sign of $\chi'^{<3>}$ is negative.

Ethylenic TTF analogue m_1 and hyper-TTF derivative m_2 display respectively linear and saturable absorption (SA). In agreement with the experimental results and the model [7] we can consider that for laser intensities much bigger than saturation intensity I_S, the material m_2 has the same behaviour as linearly absorbing materials. In the range of relatively small intensities, the measured reflectivity values are larger than the values predicted by theoretical formula for linearly absorbing materials,

which is caused by important contributions of SA. The hyperpolarisability is found larger in m_2 than in m_1 for two additive reasons: on the one hand, the electronic cloud deformation due to the light field is larger in the plane molecules m_2 than in the quasi-linear molecule m_1, on the other hand, a resonant refractive index change – connected with SA – is present in m_2.

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