Large third-order optical nonlinearity of the organic metal α-[bis(ethylenedithio) tetrathiofulvalene] triiodide

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The organic metal α-[bis(ethylenedithio) tetrathiofulvalene]$_2$I$_3$ shows a large third-order optical nonlinearity around 650 nm, as observed by forward degenerate four-wave mixing. Nonlinear susceptibilities of $|\chi^{(3)}| \sim 5 \times 10^{-8}$ esu are observed along the direction of maximum conductivity. The frequency dispersion of the nonlinearity points to a plasma effect due to the conduction electrons.

Third-order optical nonlinearities have received much attention over the past years due to their considerable potential in optical signal processing, optical computing, and phase conjugation.[1] Among the organic materials which possess large nonlinearities the most promising ones seem to be conducting polymers,[2] such as polydiacetylenes, polyacetylenes, and polyphenylenes. In these polymers the conductivity stems from a delocalized π-electron system which also gives rise to the optical nonlinearity.

In organic metals, the conductivity is usually due to a partially filled conduction band formed by π-orbital overlap in stacked molecular structures. Thus organic metals are frequently one dimensional. In contrast, radical salts of BEDT-TTF [bis(ethylenedithio) tetrathiofulvalene] often show two-dimensional electrical conductivity due to the somewhat nonplanar donor structure. This results in strong intermolecular contacts and exchanges in more than one direction,[3] distantly reminiscent of semiconductor multiquantum well structures. Typical examples are the α and β phases of (BEDT-TTF)$_2$I$_3$ of which the β modification has attracted considerable interest recently as it is a superconductor at ambient pressure.[4] Thin platelets of the electrochemically prepared α modification show a brown color under the microscope which corresponds to an optical transmission window from 550 nm into the infrared, part of which is depicted in Fig. 3. An absorption minimum between 1.3 and 2.3 eV can be observed in most organic metals[5] and is attributed to the plasma edge and charge transfer excitations on the low energy and the onset of intramolecular absorption in the high-energy side. Both carrier density and delocalization are high in organic metals which have led us to investigate the third-order optical nonlinearity in α-(BEDT-TTF)$_2$I$_3$ in analogy to our recent studies in polydiacetylenes.[6] If a nonlinearity is caused by the conduction electrons it will relax with the collision time of the free carriers, i.e., $\sim 10^{-14}$–10^{-15} s. To the best of our knowledge this is the first report of optical nonlinearity in an organic metal.

The experimental setup for forward degenerate four-wave mixing is similar to the one described in Ref. 7. A DCM dye laser (PRA LN107 pumped by a LN 1000 N$_2$ laser) produced 500 ps pulses of 0.5 Å spectral width and 80 μJ typical energy. The laser output was split into two equally strong beams, sent through variable delay lines to ensure temporal overlap, and then focused through a 50-cm focal length convex lens into the sample. At the sample each beam had a nearly Gaussian cross section with a ~ 200-μm radius. The angle between the beams was kept small (<2°). The two beams interfere in the sample and set up a laser-induced grating from which the remaining parts of the beams are diffracted off.

The input and diffracted energies were measured with calibrated photodetectors. The samples used were thin crystalline platelets of 3 μm thickness, mounted on a rotation stage. The c^* axis was oriented parallel to the incident beam direction. From the diffraction efficiency η of the input pulse intensity I, the nonlinear susceptibility $\chi^{(3)}$ may be calculated[7]

$$\chi^{(3)} = \frac{8c^2 n^2 \epsilon_0 \alpha \sqrt{\eta}}{3\omega I (1 - T)} .\qquad(1)$$

Here n is the refractive index (1.9 ± 0.3 nearly constant over the wavelength range of interest, along the b axis), α the absorption coefficient [see Fig. 3(a)], T the sample transmission, and ω the laser angular frequency.

Equation (1) predicts a square dependence of the diffraction efficiency on the laser intensity for a material-dependent constant nonlinear susceptibility. This has been verified for various excitation wavelengths as shown in Fig. 1. There is no deviation from the square law indicating the presence of a Kerr-like susceptibility. Sample damage is observed at intensities $\geqslant 50$ MW/cm^2.

The maximum absorption in the visible is found for light polarized parallel to the a axis, i.e., the stacking direction.[8] The electrical conductivity is maximum along the b axis, however. By linearly polarizing the dye laser output and rotating the crystal around the c^* axis, the dependence of the diffraction efficiency on the laser polarization was studied. In contrast to the electrically nearly isotropic behavior a strong unidirectionality is found as depicted in Fig. 2. The maximum diffraction occurs along the b axis which indicates a direct relation of the nonlinearity to the electrical conductivity—similar to the results obtained in single crystalline polydiacetylenes.[9] The optical nonlinearities along the stack axis were found to be in the range of 5×10^{-8} esu depending
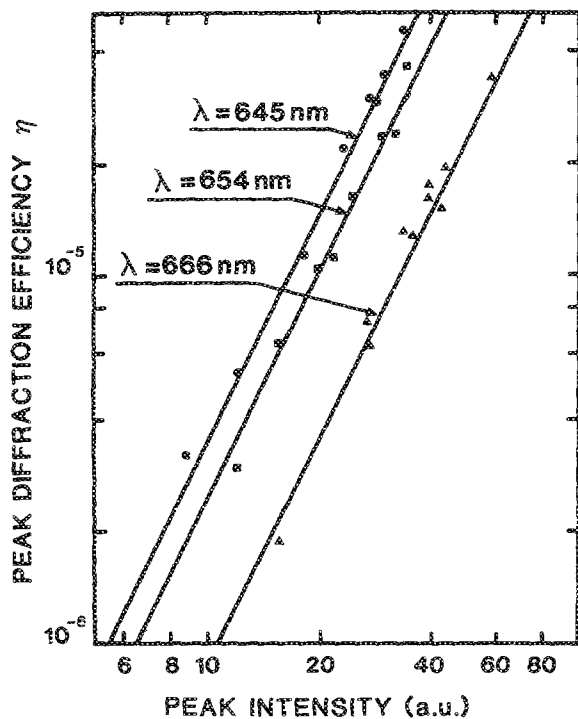
FIG. 1. Laser-induced grating diffraction efficiency vs incident pump pulse intensity for three different wavelengths. Sample thickness 3 μm.

on the laser wavelength as shown below. In the direction perpendicular to b, i.e., the a direction, the nonlinearity was a factor of > 3 less. This dependence allows us also to rule out thermal effects which are proportional to the absorption coefficient and should hence show the opposite behavior.

Figure 3 depicts the dependence of the third-order optical nonlinearity on the incident laser wavelength together with the linear absorption coefficient $\alpha(\lambda)$ of the sample, for polarization parallel to the b axis. The frequency dispersion of the nonlinearity is rather weak with some relation to the absorption coefficient. Ujihara[10] has derived an expression of $\chi^{(3)}$ for an electron plasma in a metal. Inserting Eq. (4)
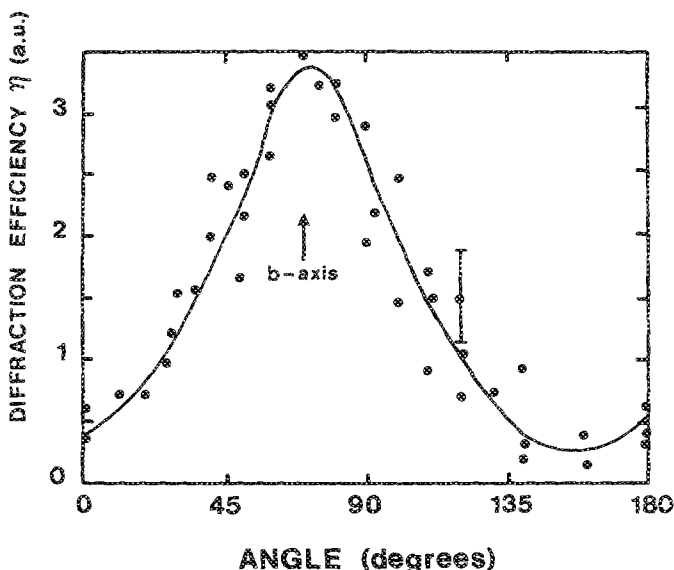

FIG. 2. Variation of the diffraction efficiency with crystal orientation relative to the direction of polarization. An angle of 70° corresponds to the direction of the b axis. Laser wavelength $\lambda = 660$ nm.
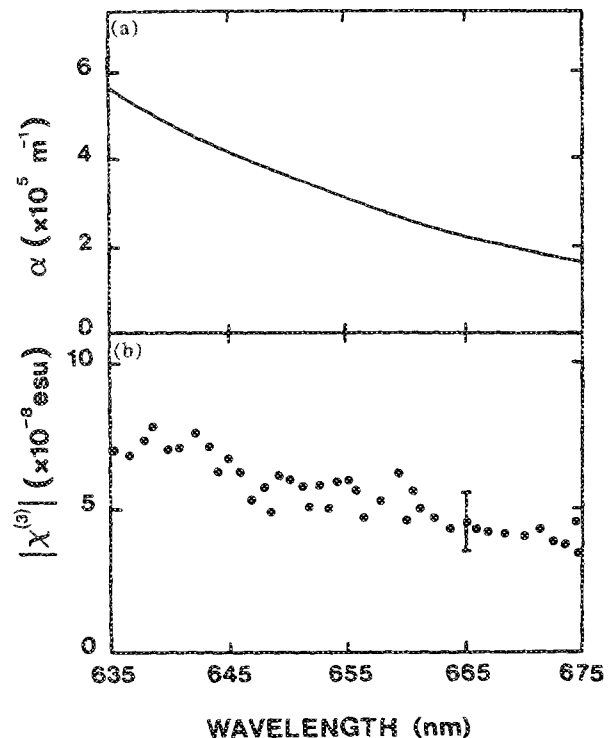

FIG. 3. (a) Wavelength dependence of the crystal absorption coefficient α. (b) Wavelength dependence of third-order optical nonlinearity $\chi^{(3)}$. Incident light polarized along the b axis.

from Ref. 10 into the expression of degenerate four wave mixing derived in Ref. 11 gives an expression for the nonlinear susceptibility (in esu)

$$|\chi^{(3)}| = \frac{2\pi^3 n^4 \lambda^2}{c^4} \omega_p^2 \tau^2 \left(\frac{e}{m^*}\right)^2 \frac{n^2 + 1}{n^2 - 1}. \quad (2)$$

Here ω_p is the plasma frequency of the metal ($\sim 6 \times 10^{16}$ s^{-1}), τ the collision time of the free carriers, and m^* the effective electron mass.

Using the values for τ and m^* given in Ref. 8 yields a value of $\chi^{(3)} = 3 \times 10^{-8}$ esu in the wavelength range studied. This is in remarkable agreement with the measured values. Equation (2) also predicts a wavelength dependence of $\chi^{(3)}$ which under the experimental conditions is dominated by the λ^2 term. Over the small tuning range of the dye laser this predicts a nearly constant susceptibility as observed. Furthermore, it should be noted that Eq. (2) also predicts the observed polarization dependence (Fig. 2) originating in the anisotropy of the effective mass tensor m^*.[8]

In this letter we have reported a large optical nonlinearity in an organic metal α-(BEDT-TTF)$_2$I$_3$. This nonlinearity has features similar to those of conducting single crystalline polymers, originating however from the electron plasma of the metal. In order to determine the temporal response of the nonlinearity precisely further experiments will be necessary, e.g., measuring the decay time of the laser-induced grating using femtosecond lasers. Further interesting directions of study may be the metal-semiconductor transition around 135 K in the material, the influence of crystal modifications and of other anions such as ClO$_4$, ReO$_4$, NO$_3$, Br$_2$I, I$_2$B,[12] and the influence of applied electric and magnetic fields. The phase transition from the α to the β modification

by annealing at 350 K may also be investigated directly. Finally, it should be noted that (BEDT-TTF) is electrochemically deposited. This opens the way to electrical preparation of active integrated optical devices by using suitably prepared conducting substrates and indicates the great promise this and similar materials may have in high-speed nonlinear optical applications.

[1]Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1985).

[2]D. J. Williams, ed., *Nonlinear Optical Properties of Organic and Polymeric Materials* (American Chemical Society, Washington D.C., 1983).

[3]K. Bender, I. Henning, D. Schweitzer, K. Dietz, H. Endres, and H. J. Keller, Mol. Cryst. Liq. Cryst. **108**, 359 (1984); **107**, 45 (1984).

[4]E. B. Yagubskii, I. F. Shchegolev, V. N. Laukin, P. A. Kononovich, M. B. Kartsovnik, A. V. Zvarykina, and L. I. Buravov, JETP Lett. **39**, 12 (1984); J. M. Williams, T. J. Emge, H. H. Wang, M. A. Beno, P. T. Copps, L. N. Hall, K. D. Carlson, and G. W. Crabtree, Inorg. Chem. **23**, 2558 (1984); H. Schwenk, C. P. Heidmann, F. Gross, E. Hess, K. Andres, D. Schweitzer, and H. J. Keller, Phys. Rev. B **31**, 3138 (1985).

[5]J. B. Torrance, J. E. Vazquez, J. J. Mayerle, and V. Y. Lee, Phys. Rev. Lett. **46**, 253 (1981).

[6]W. M. Dennis, W. Blau, and D. J. Bradley, Appl. Phys. Lett. **47**, 200 (1985).

[7]P. Horan and W. Blau, Semicond. Sci. Technol. **2**, 382 (1987).

[8]B. Koch, H. P. Geserich, W. Ruppel, D. Schweitzer, K. H. Dietz, and H. J. Keller, Mol. Cryst. Liq. Cryst. **119**, 343 (1985).

[9]G. Sauteret, J. P. Hermann, R. Frey, F. Pradere, J. Ducuing, R. H. Baughman, and R. R. Chance, Phys. Rev. Lett. **36**, 16 (1976).

[10]K. Ujihara, Opt. Commun. **43**, 225 (1982).

[11]A. Yariv and D. M. Pepper, Opt. Lett. **1**, 16 (1977).

[12]H. Endres, M. Hiller, H. J. Keller, K. Bender, E. Gogu, I. Heinen, and D. Schweitzer, Z. Naturforsch. **40b**, 1664 (1985).