

Photoinduced Nonlinear Effects in C₆₀-2-thioxo-1,3-dithiole and C₆₀-TTF Derivatives

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Photoinduced effects in pure C₆₀: C₆₀-TTF and C₆₀-2-thioxo-1,3-dithiole cycloadducts are investigated using nonlinear optical techniques. We have studied photoinduced optical second harmonic generation, two-photon absorption, linear electro-optics, and quadratic electro-optic effect coefficient versus applied pressure (p) and temperature (T). We deduce the influence of the grafted substituents in pure C₆₀ on the observed photoinduced effects. The obtained results illustrate clearly that the photoinduced nonlinear optics can be used as a tool to detect structural changes at low temperature in modified C₆₀. We have unambiguously demonstrated that, under the applied hydrostatic pressure up to 19 GPa and the temperature from 4.2 up to 150 K, the observed effects are essentially caused by the grafted TTF derivatives.

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1. Introduction

Materials, which show changes in optical, electronic, dielectric and mechanic properties by applied hydrostatic pressure and temperature with high sensitivity

are very promising for material science. Among various candidates for such systems, nonlinear optical organic materials attract a lot of attention [1–11]. Up to date these materials are used as light frequency modulators, deflectors, and devices for optical information storage.

Chemical modifications of fullerenes are interesting owing to potential improvement of their stability and processability, as well as optical nonlinearity. This study concerns fullerenes functionalized with 2-thioxo-1,3-dithiole (CA) and tetrathiafulvalene (TTF) cycloadducts. More prominent for these goals are fullerenes chemically modified by incorporating different donating moieties, such as TTF derivatives [12]. The design of new materials with enhanced nonlinear optical susceptibilities (NLO) is usually restricted to π -conjugated compounds.

Fullerene molecules serve as acceptors for the added organic groups. Due to relatively large sizes of such types of molecules, the intermolecular interactions may give essential contribution to the appropriate susceptibilities and will be critical to external hydrostatic pressure (p) and temperature (T).

In this case the molecular engineering is directed prevalingly on modification of the length of the methylenic chains or/and substitution of the conjugated chains with electron-donating or electron-accepting substituted aromatic moieties [7]. Fullerene as strong acceptor, can be used for the elaboration of such materials. Thus, molecular systems incorporating fullerene with an electron donor can exhibit strong charge transfer (CT) effects and electron-vibration interactions (EVI). The latter factors play a central role in the total values of second-order susceptibility. Hence, we propose to study photoinduced optical second harmonic generation (PISHG), linear electro-optics (LEO), two-photon absorption (TPA) under pressure and temperature in order to found some correlation between these photoinduced effect and structural changes under p and T .

We choose the C_{60} -TTF because pure C_{60} possess a large third-order nonlinear optical response [12–15], substantially stronger than for the traditional π -conjugated polymers, which are usually one-dimensional ones. The TTF derivatives added to C_{60} lead to an increase in dipole moment of studied compound which could enhance NLO response [11] under the applied pressure and temperature.

The enhancement of second-order nonlinear optical response is largely dependent on electro-poling and optical poling procedure [16]. This stimulates long-range molecular orientation and determines the output of second-order susceptibility, which is allowed only in non-centrosymmetric media. In the case of the chemically modified fullerenes, there exist many molecular conformations with different potential (total energy) barriers [17–19]. As a consequence, one can expect the existence of transformation of the molecule between the particular local total energy minima due to applying of external hydrostatic pressure and variation of temperature [20]. This situation is quite similar to usual phase transitions [21]. However, in this case we have many thermodynamical states, contrary to the case of traditional phase transformations where there are only two. A tunneling process

between the particular molecular pressure–temperature (p – T) dependent conformations is possible with probability inversely proportional to the mentioned total energy barriers. Thus one can introduce an order parameter to describe the tunneling process as in Ref. [21]. The frequency of the tunneling is usually called soft mode, because its frequency drastically decreases for the external thermodynamic parameters close to the phase transitions. External pressure and temperature cause “freezing” (decrease in frequency) of the particular modes favoring appearance of corresponding phase transitions. Probably, new kind of phase transitions, namely by inter-conformation tunneling should be considered. These transitions will be studied separately. In the present case, EVI plays special role in NLO susceptibility.

The intermolecular interactions give relatively low contribution to the NLO response. However, under the applied external fields (particularly electromagnetic, hydrostatic pressure, temperature etc.) as well as with varying temperature, the contribution of the intermolecular interactions to the NLO drastically increases due to the above-mentioned reasons.

The electrical and optical poling of the fullerenes require essentially smaller poled fields comparing to traditional organic materials. This is caused by higher degree of freedom of fullerene-like molecule. This one leads also to possibility of effective CT in the fluorine-TTF derivatives incorporated into the appropriate polymer matrices.

For mechanical and chemical stabilization of fluorine derivatives a guest–host photopolymerization technique is applied. We also used the optically induced NLO effects in our previous investigations. The obtained results showed that operation by the intermolecular and intramolecular CT may lead to enhancement of the output nonlinear optical susceptibilities [12]. We also expect that the remarkable discrepancies observed in available experimental data for the fullerene-like materials indicate on critical role caused by the structural conformation rearrangement varying under external fields.

Main drawback of traditional NLO methods, such as TPA, degenerate fourth wave-mixing (DFWM), optical second harmonic generation (SHG) etc., consists [2, 3, 7] in a relatively small sensitivity to contribution of the EVI subsystems, which are responsible to p – T influence. Contrary to the above-mentioned effects, the linear electro-optics effect allows us to detect contributions of the electronic as well as of the EVI ones [7]. Simultaneously the LEO (Pockels) effect can be a nondestructive tool for p – T measurements and is complementary to traditional methods of phase transition’s investigations (like differential thermal analysis, differential scanning calorimeters etc.).

In this work we study photoinduced effects in mentioned compounds using nonlinear optical techniques such as PISHG, LEO and TPA. Measurements were carried out on C_{60} -TTF and C_{60} -2-thioxo-1,3-dithiole cycloadducts (see Fig. 1). We measure photoinduced optical second harmonic generation versus temperature (T).

The existence of large PISHG signal is due to the contribution arising from high asymmetry of charge density distribution in the case of fullerene derivatives.

We give correlation between differential scanning calorimetry (DSC) on one hand and PISHG, LEO, and TPA on the other hand. The comparison shows clearly that those effects can be used as a sensitive tool for detecting phase transitions in fullerene derivatives at low temperature.

2. Experimental methods and theoretical simulations

The chemical structure of investigated compounds are presented in Fig. 1. C_{60} -TTF derivatives and C_{60} -2-thioxo-1,3-dithiole were prepared according to Diels–Alder cycloaddition between the transient diene generated *in situ* by 1,4-reductive elimination of corresponding 2,3-bis [bromomethyl] TTF.

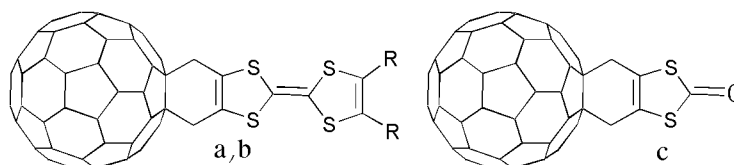


Fig. 1. Chemical structure of molecules: **a** — $R = S(CH_2)_4-CH_3$; **b** — $R = CH_3$, **c** — C_{60} -2-thioxo-1,3-dithiole.

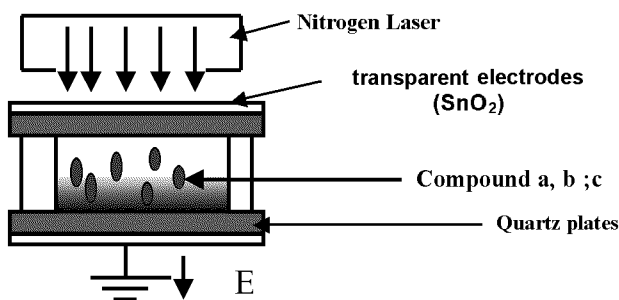


Fig. 2. The process of photopolymerization was carried out under applied electric field (E was varying from 300 to 800 kV). Solidification of the liquid composition was obtained using UV-light generated by nitrogen laser for about 3 min ($\lambda = 337$ nm and the used power was about 35 W/cm²).

The synthesized samples consisted of powder-like pieces of the chromophores with diameters ranging from 10 to 20 μ m. For technological applicability such powder-like specimens were incorporated into the oligoetheracrylate photopolymer matrices. A solidification process was performed using a nitrogen laser ($\lambda = 337$ nm) with photon energy power of about 45 W/cm² (see Fig. 2). Specimen's sizes were equal to about $5 \times 5 \times 3$ mm. Specimen's spatial non-uniformity did

not exceed 1.2% over the composite surface. These matrices allow fitting their parameters to the optical coefficients of the investigated fullerenes. The experimental setup of PISHG is presented by Fig. 3. We use Q -switched nitrogen laser as a pump beam ($\lambda = 337$ nm, $t = 5$ – 45 ps; power was varied up to 1.2 GW/cm²) and Nd:YAG laser as probe beam ($\lambda = 1.06$ μ m; $t = 30$ ps; power of probe beam (I_s) 30 MW). F is used in order to cut the $\lambda = 1.06$ μ m. The measurements were performed for polarized light beam.

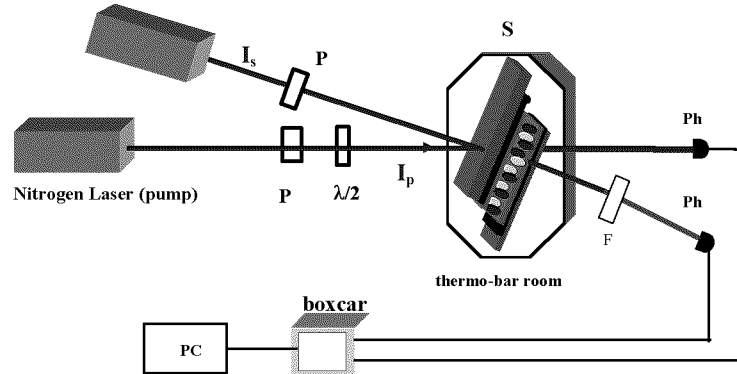


Fig. 3. The principal scheme of experimental setup used for the measurements of photoinduced second harmonic generation PISHG. P — polarizer, Ph — photodetector, F — filter, S — sample, I_p — pump beam, I_s — probe beam.

The measurements of the LEO coefficients were conducted using the traditional Senarmont method. A He–Ne laser beam (wavelength $\lambda = 0.633$ nm) with power of about 10 mW was used as a light source. Diameter of the used laser beam was equal to about 3.5 mm. Precision of birefringence evaluation was about 10^{-5} . This one allows us to measure the LEO coefficient with accuracy up to 0.005 pm/V. Varying the experimental geometry we found that LEO corresponds to the r_{222} tensor component. For the LEO measurements under applied hydrostatic pressure, a special thermopressure chamber with sapphire windows was constructed. Pressure was changed within the 0.1–15 GPa range. Precision of the pressure stabilization was about ± 0.2 GPa. The Mao and Bell type diamond anvil cell supplied with diamond optical windows was used for these measurements. All measured optical parameters were then statistically averaged using large number (100–160) of beam points through the specimen surfaces for each p – T point. Afterwards, a fitting procedure was done using a spline smoothing and χ^2 statistics with parameter better than 0.02. A mixture of methanol/ethanol/liquid nitrogen or liquid argon in proportion of 15:5:2 was used as a pressure medium. Ruby fluorescence was applied for a hydrostatic pressure determination of pressure gradients. To eliminate elasto-optic contribution of sapphire windows into the electro-optic coefficient (EOC) we have performed measurements of the pressure–temperature dependent

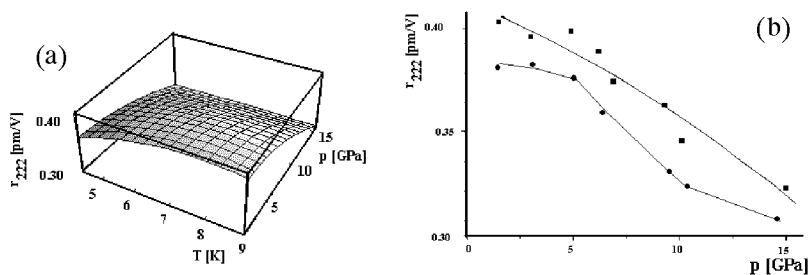


Fig. 4. (a) Calculated dependencies of the LEO tensor component r_{222} versus pressure and temperature: for pure fullerenes; (b) calculated dependencies and measured data of the LEO tensor component r_{222} versus pressure and temperature: for compound **b** for two different temperatures (\bullet) $T = 12$ K, (\blacksquare) $T = 4.2$ K.

birefringence without the samples. Afterwards the corresponding corrections were introduced into the expression for determination of EOC coefficients. The obtained experimental and theoretical data are presented in Fig. 4. One can observe good agreement between experimental and theoretical data. The used theoretical model can be found in Ref. [12].

Another important point consists in the evaluation of the thickness variations under applied hydrostatic pressures. The corresponding coefficients were determined using the interferometric measurements from the same p – T points for film-like specimens of different thickness. Pressure–temperature variation stimulated occurrence of many wavelength maxima–minima. As a consequence resolving the set of equations we determined variation of film thickness with precision up to $0.02 \mu\text{m}$ versus p – T . The performed evaluations with taking Clausius–Mosotti equations into account showed that contribution of the effective changes of the specimen thickness gives about 3.6% of contribution. The measurements performed for the pure oligoetheracrylates indicate that the EOC values are approximately equal to about 0.02 pm/V and are comparable with the measurement background. Thus the oligoetheracrylate matrices are appropriate for evaluations of the EOC coefficients for the given composites.

Experimental data concerning the photoinduced effects in pure C_{60} , C_{60} -TTF and C_{60} -2-thioxo-1,3-dithiole cycloadducts such as linear electro-optic effect are presented in Figs. 4 and 5; nonlinear photoquadratic electro-optic effect (QEOE) — in Fig. 6, two-photon absorption — in Fig. 7 and photoinduced optical second harmonic generation in Fig. 8. All photoinduced effects were measured versus applied pressure (p) and temperature (T).

We can easily observe the influence of the grafted substituents in pure C_{60} on the studied photoinduced effects. The correlation between DSC thermodynamics detection of phase transition (see Fig. 9) and obtained results concerning PISHG, QEOE illustrate clearly that the photoinduced nonlinear optics can be used as a tool to detect structural changes at low temperature in modified C_{60} .

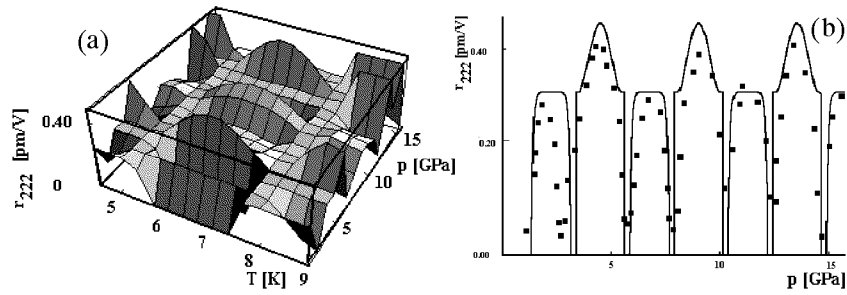


Fig. 5. (a) Calculated dependencies of the LEO tensor component r_{222} versus pressure and temperature; (b) comparison of the experimentally measured r_{222} with the calculated for compound C_{60} -TTF at $T = 6.5$ K.

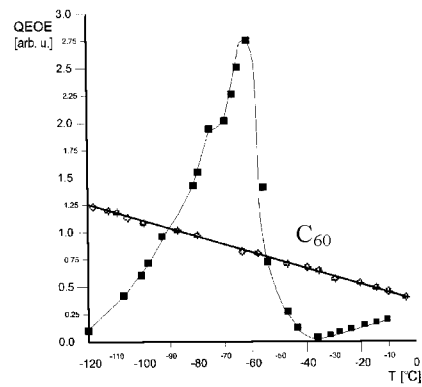


Fig. 6. Photoinduced quadratic electro-optic effect versus temperature T for compound **c**.

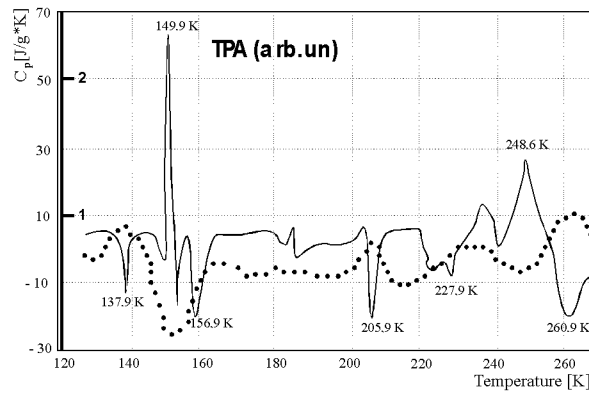


Fig. 7. Influence of increasing derivatives tails length on the changes of phase transitions. (●) TPA, (continued line) C_p differential scanning calorimetry thermodynamics detection of phase transition.

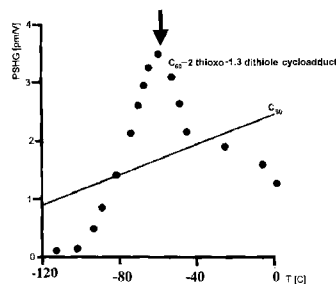


Fig. 8. Photoinduced optical second harmonic generation versus T .

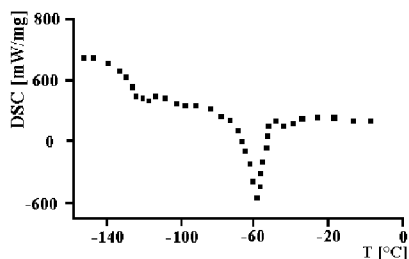


Fig. 9. Differential scanning calorimetry for compound **c**.

The measured pressure–temperature (p – T) dependencies of the r_{222} LEO coefficient for C_{60} and C_{60} -TTF are presented in Figs. 4 and 5. One should notice an appearance of clear modulation of the r_{222} versus p and T at temperatures below 25 K for the modified C_{60} (**b** specimen). A shift of temperature from 6 K up to 7.5 K leads to occurrence of the strong pressure-dependent behavior of the LEO (compare Fig. 3). It is necessary to add that the Pockels effect was observed also without applied external hydrostatic pressure. Comparing the obtained experimental data with theoretically calculated a fairly good agreement is observed. Main origin of such critical behavior reflects soft mode appearance due to inter-conformation quasi-phonon modes. Several discrepancies could be possibly due to limiting of the used quantum-chemical model during descriptions of mesoscopic effects or by influence of higher order anharmonic EVI. At lower temperatures, the experimentally observed LEO effects for the pure C_{60} show a smooth decrease analogously to the calculated results (Fig. 4a). In the case of the modified C_{60} , sharp-like LEO maxima (Fig. 5) with the half-widths of 45 K and 0.8 GPa are observed in agreement with the theoretical simulations. The Raman measurements versus applied p – T parameters, which were performed by us within the spectral range of 45–300 cm^{-1} demonstrated a good correlation between the density of the low-frequency phonon modes and the observed p – T LEO dependencies. This fact confirms the theoretical prediction about a dominant role of the inter-conformation tunneling modes in the observed LEO effects. We should also underline that the

optical SHG as well as TPA (performed in the same specimens under similar p - T conditions) did not show any p - T -dependent modulation.

It is important that with further increase in the pressure and temperature the EOC strongly decreases. This fact reflects an occurrence of temperature reorientation of the fullerene-like derivatives.

It is important that for longer TTF's chains (specimen **b**) we have observed the modulated dependence of r_{222} versus pressure p only. The observed modulated p - T dependence of the LEO effect is closely connected with the existing total energy minima separated by low total energy potential barriers between the total energy valleys (up to 0.24 eV), one can shift total energy minimum, applying the external p or varying T .

The molecular dynamics geometry optimization was carried out for the isolated fullerene-like molecule using a MM⁺ method and a derivative procedure of Broyden-Fletcher-Goldfarb-Shanno type with variable effective cluster cut-offs.

Calculations of the electronic structure were done using the semi-empirical AM1 method within the HYPERCHEM 7.0 program. The hyperpolarizabilities of the electro-optics were calculated using a method described in Ref. [12].

3. Conclusions

In summary, the modulated-like LEO dependences versus p - T have been observed in the TTF-derivatives fullerenes. The experimental results presented here provide unambiguous answers to the role played by EVI in the measured LEO coefficients. A new type of EVI manifestation of the multiconformational systems in the LEO phenomenon is shown. We show a good agreement between experimental and theoretical data of QEOE (Kerr effect). TTF cycloadduct favors the appearance of noncentrosymmetry of electron charge density which leads to an increase in photoinduced SHG signal. We should underline that PISHG, LEO (Pockels), QEOE (Kerr) shows high sensitivity to detection of phase transition in the modified C₆₀-TTF. We have demonstrated that the photoinduced fluctuations under the applied p - T are larger for the C₆₀-TTF molecule since such system exhibits a delicate balance of the interconfiguration (p - T -dependent) states and larger dipole moment than in the case of C₆₀.

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