

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231629909>

# Temperature–Pressure Anomalies of Electrooptic Coefficients in C<sub>60</sub>–TTF Derivatives

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · JUNE 2001

Impact Factor: 3.3 · DOI: 10.1021/jp010593f

---

CITATIONS

29

---

READS

15

## 2 AUTHORS:



**Bouchta Sahraoui**

University of Angers

**384** PUBLICATIONS **2,978** CITATIONS

SEE PROFILE



**Iwan V Kityk**

Czestochowa University of Technology

**959** PUBLICATIONS **7,927** CITATIONS

SEE PROFILE

## ARTICLES

Temperature–Pressure Anomalies of Electrooptic Coefficients in C<sub>60</sub>–TTF Derivatives

B. Sahraoui and I. V. Kityk\*

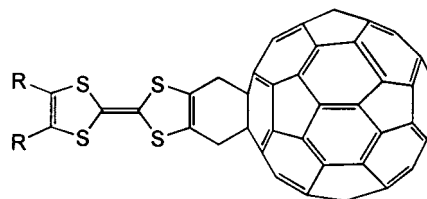
*Université d'Angers, Laboratoire POMA, EP CNRS 130, 2 Boulevard Lavoisier, UFR Sciences, 49045 Angers Cedex, France*

P. Hudhomme and A. Gorgues

*Laboratoire d'Ingénierie Moléculaire et Matériaux Organiques, UMR CNRS 6501, Université d'Angers, 2 Boulevard Lavoisier, 49045 Angers Cedex, France**Received: February 14, 2001; In Final Form: April 19, 2001*

A sharplike modulation of the linear electrooptic (LEO) coefficient with pressure ( $p$ ) and temperature ( $T$ ) has been observed for the first time. The modulation depth of the LEO ( $r_{222}$ ) tensor component in the C<sub>60</sub>–TTF (for the He–Ne laser,  $\lambda = 633$  nm) was equal to about 2.6%. By varying the applied hydrostatic pressure to up to 15 GPa and the temperature from 4.2 to 25 K, we have unambiguously demonstrated that the observed effect is caused by the incorporation of the TTF moiety. This effect is absent from the unsubstituted fullerenes when the applied hydrostatic pressure is increased to 19 GPa and the temperature varied from 4.2 to 150 K. Norm-conserving self-consistent pseudopotential and molecular dynamics simulations independently reproduce these modulations and attribute them to the electron–vibration interactions associated with the LEO coefficients. The contribution of the interconformational tunneling under the applied pressure and temperature is demonstrated. The data obtained give a possibility for using the discovered effect for contactless measurements of low temperatures and high pressures.

Systems that show changes in optical, electronic, dielectric, and mechanical 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.<sup>1–11</sup> To date, these materials are used as light frequency modulators, deflectors, and media for optical information storage. However, the linear electrooptic (LEO) effect (or Pockels effect) described by the polar tensor of the third ranks for such kinds of composites is rather purely studied. This effect refers to the substantial contribution of both the electronic and the vibrational subsystems to the output nonlinear optical susceptibility. These contributions may give additional possibilities for applications in different optoelectronic pressure and temperature sensors. More prominent candidates for these goals are fullerenes that have been chemically modified by incorporating different donating moieties, such as tetrathiafulvalene (TTF) derivatives.<sup>12</sup> The design of new materials with enhanced nonlinear optical (NLO) susceptibilities is usually restricted to  $\pi$ -conjugated compounds. In this case, the molecular engineering is directed prevalingly on the modification of the length of the methylenic chains or/and the substitution of the conjugated chains with electron-donating or electron-accepting substituted aromatic moieties.<sup>7</sup> Strongly-accepting fullerenes can be used for the elaboration of such materials. Thus, molecular systems incor-



**Figure 1.** Chemical structure of the investigated molecules: (a) R = S(CH<sub>2</sub>)<sub>4</sub>–CH<sub>3</sub>; (b) R = CH<sub>3</sub>.

porating a fullerene with an electron donor can exhibit strong charge transfer (CT) effects and electron–vibration interactions (EVIs). The latter factors play a central role in the total values of second-order susceptibility.

Fullerene molecules serve as acceptors for the added organic groups (Figure 1). Because of the relatively large sizes of such types of molecules, the intermolecular interactions may give essential contributions to the appropriate susceptibilities and will be sensitive to external hydrostatic pressure ( $p$ ) and temperature ( $T$ ). Hence, we propose to apply the LEO effect to the detection of pressure ( $p$ ) and temperature ( $T$ ).

Fullerenes possess a large third-order nonlinear optical response,<sup>12–15</sup> substantially stronger than that of the traditional  $\pi$ -conjugated polymers, which are usually one-dimensional. Appropriate use of different pressure- and temperature-dependent contributions may lead to an enhanced NLO response.<sup>11</sup>

The enhancement of the second-order nonlinear optical response is largely dependent on electrical and optical poling

\* Permanent address: Institute of Physics WSP, Al. Armii Krajowej 13/15, 42201 Czechochowa, Poland. E-mail: i.kityk@wsp.cze.pl.

procedures.<sup>16</sup> These procedures stimulate long range molecular orientation and determine the output of second-order susceptibility, which is allowed only in noncentrosymmetric media. In the case of the chemically modified fullerenes, there exist many molecular conformations with different potential (total energy) barriers.<sup>17–19</sup> As a consequence, one can expect the existence of the transformation of the molecule between the particular local total energy minima because of the application of external hydrostatic pressure and the variation of temperature.<sup>20</sup> This situation is quite similar to usual phase transitions.<sup>21,22</sup> However, in this case we have many thermodynamic 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 a probability that is inversely proportional to the mentioned total energy barriers. Thus, one can introduce an order parameter to describe the tunneling process as shown in refs 21 and 22. The frequency of the tunneling is usually called a “soft mode”, because its frequency drastically decreases for the external thermodynamic parameters close to the phase transitions. External pressure and temperature cause “freezing” (decrease of frequency) of the particular modes, favoring the appearance of corresponding phase transitions. Probably, new kinds of phase transitions, namely those formed by interconformation tunneling, should be considered. These transitions will be studied separately. In the present case, EVI plays a special role in NLO susceptibility.<sup>23,24</sup>

The intermolecular interactions give a relatively low contribution to the NLO response.<sup>24</sup> However, under 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 because of the above-mentioned reasons.

The electrical poling and optical poling of the fullerenes require essentially smaller poled fields compared to those for traditional organic materials. This is caused by the higher degree of freedom of fullerene-like molecules. This leads also to the possibility of effective CT in the fluorinated TTF derivatives incorporated into the appropriate polymer matrixes.

For the mechanical and chemical stabilization of fluorinated 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 the enhancement of the output nonlinear optical susceptibilities.<sup>12,24</sup> We also expect that the remarkable discrepancies observed in available experimental data for the fullerene-like materials indicate a critical role caused by the structural conformation rearrangement varying under external fields.

The main drawback of traditional NLO methods, such as two-photon absorption (TPA), degenerate fourth wave mixing (DFWM), optical second harmonic generation (SHG), and so forth, consists<sup>2,3,7</sup> of a relatively small sensitivity to the contribution of the EVI subsystems, which are responsible for the  $p$ – $T$  influence. Contrary to the above-mentioned effects, the linear electrooptic effect (LEO) allows us to detect contributions of the electronic effects as well as of the EVI effects.<sup>7,24</sup> Simultaneously, the LEO (Pockels) effect can be a nondestructive tool for  $p$ – $T$  measurements and is complementary to traditional methods of phase transition investigations (such as differential thermal analysis, differential scanning calorimetry, etc.).

In this paper, we describe the first results on the ( $p$ – $T$ )-induced interconformation transition in newly synthesized  $C_{60}$ –

TTF molecules detected by the LEO effect. Theoretical molecular dynamics simulations as well as experimental LEO data will be presented.

For the studied molecule, one can see essential changes of electronic CT as a consequence of both intra- and intermolecular contributions.<sup>20</sup> However, the main changes are only observed within the molecule, while negligible changes are seen in the intermolecular charge density distribution. The intermolecular interactions usually suppress the intramolecular hyperpolarizabilities.<sup>24</sup>

TTF– $C_{60}$  derivatives were prepared according to Diels–Alder cycloaddition of the transient diene generated in situ by 1,4 reductive elimination of the corresponding 2,3-bis(bromomethyl)TTF.<sup>26</sup>

The synthesized samples consisted of powderlike pieces of the chromophores with diameters ranging from 10 to 20  $\mu\text{m}$ . For technological applicability, such powderlike specimens were incorporated into the oligoetheracrylate photopolymer matrixes. A solidification process<sup>25</sup> was performed using a nitrogen laser ( $\lambda = 337 \text{ nm}$ ) with photon energy power of about 45  $\text{W}/\text{cm}^2$ . Specimen sizes were equal to about  $5 \times 5 \times 3 \text{ mm}^3$ . Specimen spatial nonuniformity did not exceed 1.2% over the composite surface. These matrixes allow a fitting of their parameters to the optical coefficients of the investigated fullerenes.

The measurements of the LEO coefficients were conducted using the traditional Senarmont method. A He–Ne laser beam ( $\lambda = 633 \text{ nm}$ ) with power of about 10 mW has been used as a light source. The diameter of the laser beam was equal to about 3.5 mm. The precision of birefringence evaluation was about  $10^{-5}$ . This allows us to measure the LEO coefficient with accuracy up to 0.005  $\text{pm}/\text{V}$ . By varying the experimental geometry, we have found that the LEO effect corresponds to the  $r_{222}$  tensor component.

For the LEO measurements under applied hydrostatic pressure, a special thermo–pressure chamber with sapphire windows was constructed. The pressure was changed within the 0.1–15 GPa range. Precision of the pressure stabilization was about  $\pm 0.2 \text{ GPa}$ . This chamber allowed us to perform measurements in a high-pressure atmosphere and with a temperature range of 4.2–300 K (with increments of 0.02 K), as it was described in ref 24. 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 a large number (100–160) of beam points through the specimen surfaces for each  $p$ – $T$  point. Afterward, a fitting procedure was done using a spline smoothing and  $\chi^2$  statistics with a parameter better than 0.02. A mixture of methanol/ethanol/liquid nitrogen or liquid argon in the proportions of 15:5:2 was used as a pressure medium. Ruby fluorescence was applied for a hydrostatic pressure determination of the pressure gradients.

To eliminate the elasto-optic contribution of the sapphire windows from the EOE coefficient, we have performed measurements of the pressure–temperature-dependent birefringence without the samples. Afterward, the corresponding corrections were introduced into the expression for the determination of the EOE coefficients.

Another important point consists of our 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 filmlike specimens of different thicknesses. Pressure–temperature variation stimulated the occurrence of many wavelength maxima and minima. As a consequence of resolving the set of equations,

we have determined the variation of film thickness with a precision of up to 0.02  $\mu\text{m}$  versus  $p$ – $T$ . The performed evaluations, taking into account the Clarius–Mosotti equations, have shown that the contribution of the effective changes of the specimen thickness gives about 3.6% of the 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 to the measurement background. Thus, the oligoetheracrylate matrixes are appropriate for evaluations of the EOC coefficients for the given composites.

The molecular dynamics geometry optimization was carried out for the isolated fullerene-like molecule using MM<sup>+</sup> method<sup>27</sup> and a derivative procedure of the Broyden–Fletcher–Goldfarb–Shanno type<sup>27</sup> with variable effective cluster cutoffs. An effective molecular cluster radius varied from 12 to 54 nm in increments of 0.5 nm. The Becke's molecular dynamics boundary conditions were taken into account.<sup>27</sup> An iteration convergence was achieved when the difference between two successive values of the optimized total energy minima was smaller than 0.02 eV. Afterward, the effective electrostatic intermolecular interactions of higher order (like the dipole–quadrupole one) between the oligoetheracrylate photopolymer (guest) matrix and chromophore as well as chromophore–chromophore interactions have been included, analogous to the procedure described in ref 30. A self-consistent iteration procedure (with continuously varying values of the total energies) was applied. To introduce partial contributions of the given conformation, appropriate weighting factors (proportional to the probability  $p_i$  of a given phase, similar to those in ref 34) were introduced.

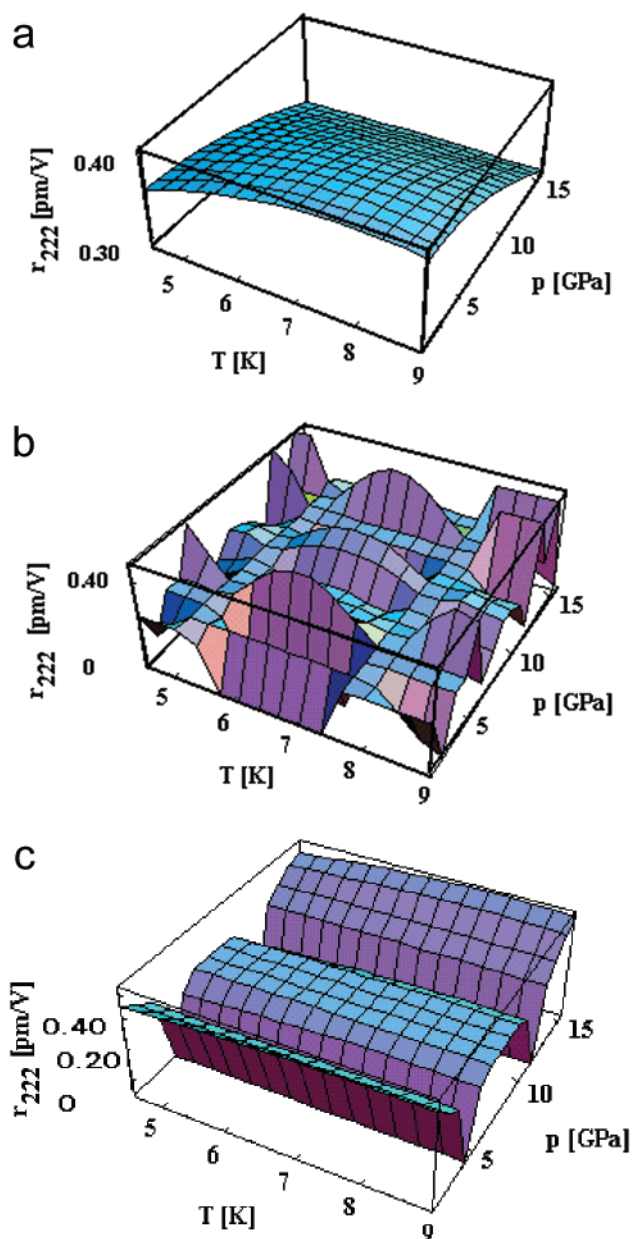
External scalar perturbations (such as pressure and temperature) have also been taken into account. The norm-conserving pseudopotential method of Bachelet, Hamann, and Schluter<sup>38</sup> has been applied within a framework of a local density approximation (LDA). This is especially important for the fullerenes with variable topological curvatures. All intermolecular interactions have been taken into account using a solid-state band energy approach developed in ref 29. For each  $p$ – $T$  point, EVIs have been included.

Acceleration of the iteration convergence was achieved by mixing the  $(m-1)$ -th iteration result with 85% of the output electron charge density  $\rho$  before its substitution into the next equation, using a method described in ref 29. Energy eigenvalues have been convergent within a range of 0.003 eV. The procedure of secular equation diagonalization was performed using a query limited Jacobi modified method.

The Hamiltonian has been diagonalized at 136 equally spaced points in the  $1/64$  part of the effective molecule to enhance a precise description of the electronic density of states. The numerical evaluations were done using a tetrahedral method. The effectiveness of these methods was controlled by the agreement between the experimental and theoretical values of the energy gaps and the electron density of states.

To simulate the behavior of the LEO coefficient versus  $p$ – $T$ , a contribution of the EVI to dipole moments (defining the second-order NLO response) has been included. The EVI contributions have been evaluated by Green functions in a standard approximation.<sup>30</sup> The Green functions were calculated by summation over 864 points within the effective molecule. The influence of neighboring molecules was renormalized by local Lorenz field factors. The precision of the LEO  $r_{222}$  tensor component determination was about 0.003 pm/V.

Calculated dependencies of the LEO coefficient  $r_{222}$  on  $p$  and  $T$  are presented in Figure 2 for the pure fullerene (Figure 2a).

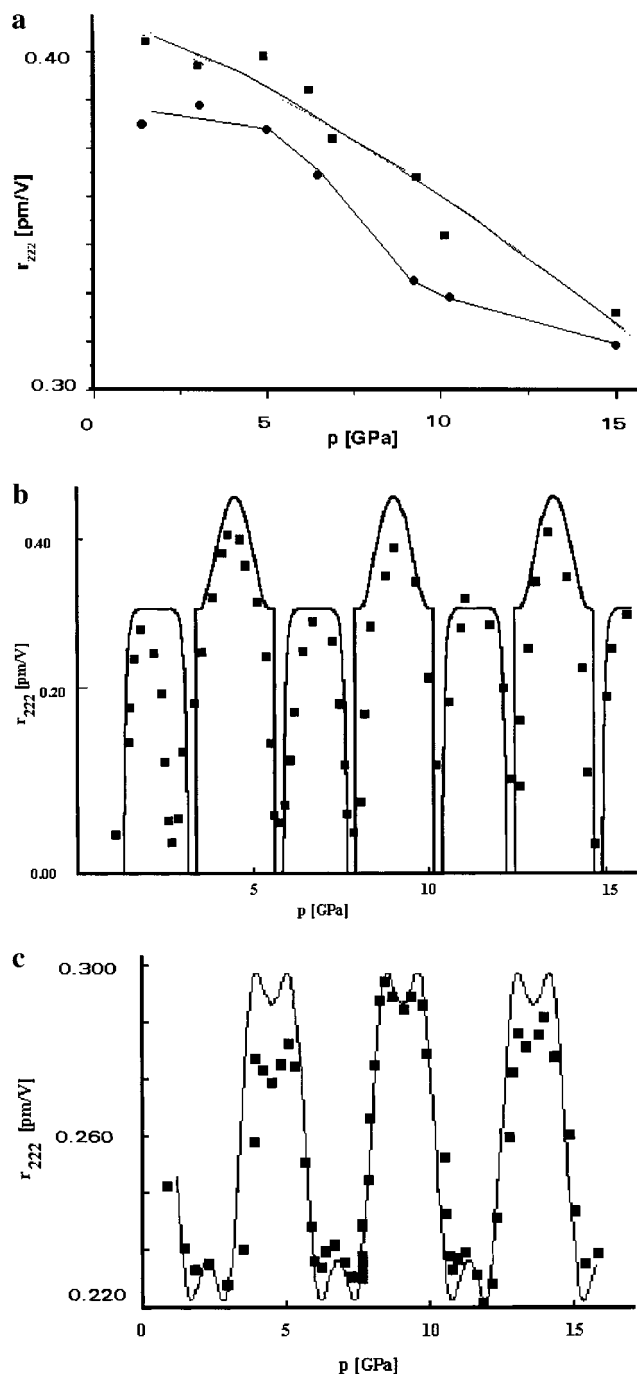


**Figure 2.** Calculated dependencies of the LEO tensor component  $r_{222}$  versus pressure and temperature: (a) pure fullerenes; (b) molecule a; (c) molecule b.

One can see only a smooth decrease of the  $r_{222}$  coefficient. More striking seems to be appearance of modulation in the LEO  $p$ – $T$  dependencies (see Figure 2b and c). A “softening” of the interconformation molecular tunneling causes the origin of the observed LEO’s modulation. This fact can be used in the detection of  $p$ – $T$  parameters using the LEO effect. With increasing temperature, even up to 12 K, we have observed a substantial decrease of the EOC. As an example, see Figure 2a. Similar behaviors are observed for fullerene derivatives.

The fullerenes with the added TTF show strong  $p$ – $T$  modulation of the corresponding LEO coefficient. The decrease of the TTF tail length (specimen b in Figure 2) (stronger intermolecular interactions) leads to the modulation of the LEO versus  $p$  as well as  $T$  (Figure 2b), with sharp-like LEO maxima possessing  $T$  and  $p$  half-widths at 45 K and 0.8 GPa, respectively. However, with increasing tail length (specimen a, Figure 2c), the LEO effect shows only the  $p$ -dependent modulation.

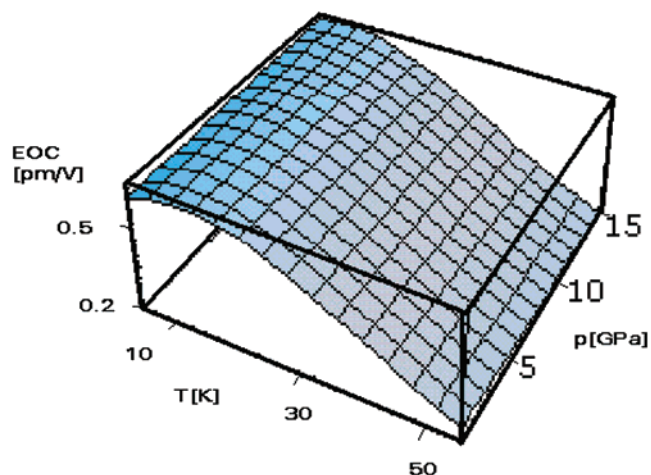




**Figure 3.** Measured pressure dependencies of the electrooptics coefficients  $r_{222}$ : (a) pure fullerene,  $T = 4.2$  K; (b) molecule **b**,  $T = 6.5$  K; (c) molecule **b**,  $T = 8.4$  K.

The calculations performed by us show that the EVIs contribute at least 65% to the observed EOE  $r_{222}$  coefficients. These confirm that an essential role in the observed  $p$ - $T$  EOE modulations comes from the contribution of the EVI (up to 92%). A major role is played by the anharmonic interconformational tunneling phonon modes within the 50–270  $\text{cm}^{-1}$  spectral range.

The measured pressure–temperature ( $p$ - $T$ ) dependencies of the  $r_{222}$  LEO coefficient for  $\text{C}_{60}$  and  $\text{C}_{60}$ -TTF are presented in Figure 3. One should notice an appearance of a clear modulation of the  $r_{222}$  with respect to  $p$  and  $T$  at temperatures below 25 K for the modified  $\text{C}_{60}$  (b specimen). A shift of temperature from 6 K up to 7.5 K leads to the occurrence of the strong pressure-dependent behavior of the LEO effect (compare Figure 3b and



**Figure 4.** Temperature and pressure dependences of the EOC.

c). It is necessary to add that the Pockels effect has been observed also without applied external hydrostatic pressure.

Comparing the obtained experimental data with those which are theoretically calculated, we observe a fairly good agreement (Figure 3). The main origin of such critical behavior reflects its soft mode appearance because of interconformational quasi-phonon modes.

Several discrepancies could be possibly caused by experimental errors as well as by limiting the DFA quantum chemical model during descriptions of mesoscopic effects or by the influence of higher order anharmonic EVI. At lower temperatures, the experimentally observed LEO effects for the pure  $\text{C}_{60}$  show a smooth decrease, analogous to the calculated results (Figure 2a and Figure 3a). In the case of the TTF-modified  $\text{C}_{60}$ , sharp-like LEO maxima (Figure 3b and c) with 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 45–300  $\text{cm}^{-1}$ , demonstrated a good correlation between the density of the low-frequency phonon modes and the observed  $p$ - $T$  LEO dependencies.<sup>31</sup> This fact confirms the theoretical prediction about a dominant role of the interconformational 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 a further increase of the pressure and temperature the EOC strongly decreases (see Figure 4). This fact reflects an occurrence of temperature reorientation of the fullerene-like derivatives.

It is important that for longer TTF chains (specimen b) we have observed the modulated dependence of  $r_{222}$  only on pressure. The observed modulated  $p$ - $T$  dependence of the LEO 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). In the result, one can shift the total energy minimum by applying the external  $p$  or varying  $T$ .

It is necessary to underline that, to date, the nature of nonlinear optics effects in fullerene is still not well understood. This fact is a focus of worldwide scientific discussion.<sup>21–27</sup> Both theoretical and experimental investigations have explained the discrepancies only within a framework of essential dependences of the optical nonlinearities on the mass of the investigated modified fullerene molecule.<sup>29,30</sup> We think that the results presented here will open a new view on the origin of the observed NLO effects. On the other hand, the discovered

sensitivity of the LEO coefficients to pressure and temperature can serve as a powerful tool for understanding the structural transformations in the fullerene-like molecule.<sup>23</sup>

All of the results presented reflect an essential role of multi-metastable molecular conformations (because of close values of the total minima for particular molecular conformations) in the observed dependencies of the LEO effect. Such behavior may reflect an interest in developing the low-temperature phase transitions in the organic materials with multiple order parameters. As a consequence, the well-known model of single-order parameters<sup>21</sup> should be extended to the multiorder ones, and the whole theory of the intermolecular (interconformational) tunneling should be a bit modified. The investigated fullerene-TTF derivatives may be a good model subject for the development of such multiordering models of phase transitions.

In summary, the modulated-like LEO dependencies with  $p$ - $T$  have been observed for the first time in the TTF-derivatized fullerenes. The results presented here provide unambiguous answers to the role played by EVIs in the measured LEO coefficients. Theoretical modeling of the pressure-temperature-dependent LEO effect is proposed, and the key features of the experimental results have been reproduced numerically. A new type of EVI manifestation of the multiconformational systems in the LEO phenomenon is shown. We have proved that induced fluctuations by the applied  $p$ - $T$  become important for the C<sub>60</sub>-TTF molecule, because such a system exhibits a delicate balance of the interconfiguration ( $p$ - $T$ -dependent) states. The LEO effect is unusual among the nonlinear optical ones, which are sensitive to such kinds of phase transitions.

## References and Notes

- (1) Dhenaut, C.; Ledoux, I.; Samuel, D. W.; Zyss, J.; Bourgault, M.; Bozec, L. *Nature* **1995**, 374, 339.
- (2) *Organic Thin Films for Waveguiding Nonlinear Optics*; Kajzar, F., Swalen, J. D., Eds.; Advances in Nonlinear Optics; Gordon and Breach: Amsterdam, 1996.
- (3) *Characterization Techniques and Tabulations for Organic Nonlinear Optical Materials*; Kuzyk, M. G., Dirk, C. W., Eds.; Marcel Dekker, Inc.: New York, 1998.
- (4) Lee, J. Y.; Kim, K. S. *J. Chem. Phys.* **1997**, 107, 6515.
- (5) Marder, S. R.; Perry, J. W.; Tiemann, B. G.; Gorman, C. B.; Biddle, S. L.; Bourhill, G. *J. Am. Chem. Soc.* **1993**, 115, 2524.
- (6) Bronold, F. X.; Bishop, A. R. *Phys. Rev.* **1996**, B53, 13456.
- (7) *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic: New York, 1987; Vols. I and II, p 8. *Nonlinear Optical and Electroactive Polymers*; Prasad, P. N., Ulrich, D. R., Eds.; Plenum: New York, 1988.
- (8) *Conjugated Polymers*; Bredas, J. L., Silbey, R., Eds.; Kluwer: London, 1991.
- (9) Tykewinski, R. R.; Gubler, U.; Martin, R. E.; Diederich, F.; Bosshard, C.; Gunter, P. *J. Phys. Chem. B* **1997**, 102, 4451.
- (10) Ahlheim, M.; Bazoukas, M.; Bedworth, P. V.; Blanchard-Desce, M.; Fort, A.; Hu, Z.-Y.; Marder, S. R.; Perry, J. W.; Runser, C.; Staehelin, M.; Zysset, B. *Science* **1996**, 271, 335.
- (11) Bosshard, C.; Gunter, P. In *Nonlinear Optics of Organic Molecules and Polymers*; Nalwa, H. S., Miyata, S., Eds.; CRC Press: Boca Raton, FL, 1997; Chapter 9, pp 391-399.
- (12) Sahraoui, B.; Nguyen Phu, X.; Kityk, I. V.; Hudhomme, P.; Gorgues, A. *J. Nonlinear Opt.* **1999**, 21, 543.
- (13) Blau, W. J.; Byrne, H. J.; Cardin, D. J.; Dennis, T. J.; Hare, J. P.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Phys. Rev. Lett.* **1991**, 67, 1423.
- (14) Xu, C. H.; Scuseria, G. E. *Phys. Rev. Lett.* **1995**, 75, 274.
- (15) Kajzar, F.; Taliani, C.; Zamboni, R.; Rossini, S.; Danieli, R. *Synth. Met.* **1996**, 77, 257; *Phys. Rev. Lett.* **1994**, 73, 1617.
- (16) Nunzi, J.-M.; Fiorini, C.; Etile, A. C.; Kajzar, F. *Pure Appl. Opt.* **1998**, 7, 14.
- (17) Hirsh, A. *The Chemistry of the Fullerenes*; Georg Thieme Verlag Stuttgart: New York, 1994.
- (18) Hirsh, A. *Synthesis* **1995**, 895-913.
- (19) Diederich, F.; Thilgen, C. *Science* **1996**, 271, 317.
- (20) Kityk, I. V.; Mervinski, R. I.; Yasinski, M. F.; Makowska-Janusik, M.; Kasperczyk, J.; Solecki, J. *Ferroelectrics* **1996**, 186, 259.
- (21) Blinc, R.; Zeks, B. *Adv. Phys.* **1972**, 21, 693.
- (22) Bussmann-Holder, A.; Buttner, H. *Nature* **1992**, 360, 541.
- (23) Dalal, N.; Klymachyov, A.; Bussmann-Holder, A. *Phys. Rev. Lett.* **1998**, 81, 5924.
- (24) Sahraoui, B.; Kityk, I. V.; Phu, X. N.; Hudhomme, P.; Gorgues, A. *Phys. Rev.* **1999**, B59, 9229.
- (25) Kityk, I. V.; Sahraoui, B.; Nguyen, P. X.; Rivoire, G.; Kasperczyk, J. *Nonlinear Opt.* **1997**, 18, 13.
- (26) Hudhomme, P.; Lin, S. G.; Kreher, D.; Caniou, M.; Gorgues, A. *Tetrahedron Lett.* **1999**, 40, 2927.
- (27) Broyden, C. G. *J. Inst. Math. Its Appl.* **1970**, 6, 222; Fletcher, R. *Comput. J.* **1970**, 317; Goldfarb, D. *Math. of Comput.* **1970**, 24, 23; Shanoo, D. F. *Math. of Comput.* **1970**, 24, 647; Becke, A. D. *J. Chem. Phys.* **1994**, 98, 1372; *J. Chem. Phys.* **1994**, 98, 5648; Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1993**, 98, 1358.
- (28) Bachelet, G. B.; Hamann, D. R.; Schluter, M. *Phys. Rev.* **1982**, 26B, 4199.
- (29) Kityk, I. V.; Kasperczyk, J.; Andrievskii, B. V. *Phys. Lett.* **1996**, 216A, 161.
- (30) Antonyak, O. T.; Kityk, I. V.; Pidzyrailo, N. S. *Opt. Spectrosc.* **1987**, 63, 683.
- (31) Sahraoui, B.; Kityk, I. V.; Bieleninik, J.; Hudhomme, P.; Gorgues, A. *Mater. Lett.* **1999**, 41, 164.