Nonlinear optical susceptibilities of new tetrathiofulvalene derivative molecules

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1. Introduction

Investigations of thiofulvalenes [1]−[3] seem to be very interesting in order to search and design new nonlinear optical materials. These materials show substantial changes of the nonlinear intensity-dependent refractive index, short response times and weak absorption losses. Due to their highly conjugated framework, they should fulfil some criteria which are necessary to posseses large third-order nonlinear optical susceptibilities.

A special structure of these molecules allows to change their chemical content in desirable manner. The most typical representative of these materials is presented in Fig. 1. It is well known that the double as well as the simple carbon bonds contribute to a total value of the nonlinear optical susceptibility. A continuous variation of these values can be obviously expected on the ground of the structure presented in Fig. 1.
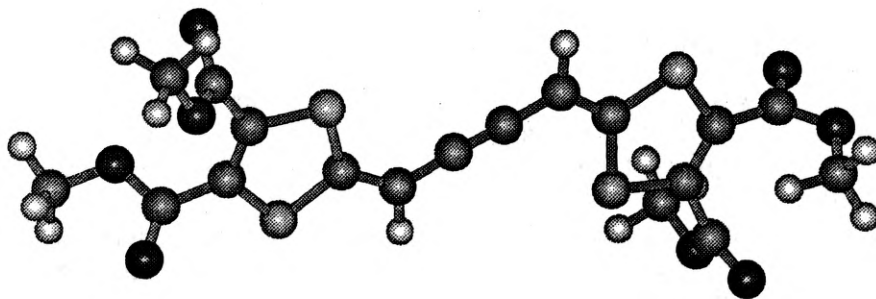

Fig. 1. Typical structure of thiofulvalene derivatives

2. Molecular geometry optimization

The structural optimization is usually carried out using standard molecular dynamics methods, such as MOPAC, GAUSSIAN [4], [5], *etc.* However, our special investigations of the hyperfine structure and comparison with the results of optical investigations have unambiguously shown that it was necessary to consider a superposition of different structural clusters which essentially contributed to the final values of nonlinear optical susceptibilities.

The main difference of our approach compared with traditional ones consists in taking into account many structural configurations and their mutual interactions. Therefore, we have considered the structural clusters with different values of the optimized potential energy. The potential energy of the considered molecular system was increased step by step to destabilize the system using a self-consistent precedure. Simultaneously, we have renormalized the effective potential using weighting factors p_i which are proportional to a probability of appearance of a given structural cluster

$$p_i = \exp(-U_i/k_B T) \tag{1}$$

where $\Sigma_i p_i = 1$. Necessary summations were stopped if the p_i values became less than 0.02.

To improve the calculations, an inter-cluster coupling was also taken into account. It is, in general, a very difficult problem. For simplicity, we have restricted ourselves to a linear coupling between the considered clusters and performed minimization of the corresponding energies. We have increased the number of coordination spheres up to 6 in order to approach the actual physical conditions as exactly as possible. The final step consisted in addition of an external potential created by the coordination sphere environment.

We have used a very great number of different structural configurations in the thiofulvalene derivatives. This number was ranging from 50 to 78 depending on a given chemical formula. It is very important to include proper boundary conditions for each cluster since the boundary conditions are very sensitive to the cluster sizes. To overcome this difficulty, we have performed a special calculational procedure to avoid a potential jump at the boundaries. We have calculated the interface potential gradients in such a way to ensure necessary continuity of the first and second partial derivatives of the potential.

3. Electronic charge density distribution

The electronic structure calculations were performed using our extended cluster approximation. A special computer program has optimized different possible structural configurations using both the molecular dynamics and the quantum chemical approach.

First of all, we have built all possible structural arrangements of the mentioned polymers. Each structural configuration arrangement was chosen with respect to a minimum of the total potential energy. All structural fragments of minimum cluster energies were found and then averaged using corresponding weighting factor.

The atom number in a given cluster was varying from 1420 to 1600 and even more, depending on the molecular size. All calculations were performed using *ab initio* methods. Therefore, we have taken into account all atomic orbitals starting from 1 s one. To calculate necessary dipole metrix elements, we have used a Green's function technique. Let the operator L act on a basis state wavefunction $|\varphi>$

$$\hat{L}/\varphi = E/\varphi>. \tag{2}$$

The operator solution of this equation is

$$|\varphi> = (\hat{L})^{-1}/\Psi> \tag{3}$$

where $(\hat{L})^{-1}$ is an inverse Green's operator that is associated with the L operator. The operator $\hat{L}$ is written as

$$(\hat{L})^{-1} = \int dx dy |x> \hat{G}(x,y) <y|. \tag{4}$$

For the operator $E - \hat{H}$, the inverse operator, *i.e.*, the Green's function is denoted as

$$(E - \hat{H})^{-1} = \hat{G}. \tag{5}$$

Considering the Hamiltonian $H = \dfrac{p^2}{2m} + V$, we pass to a coordination representation in which

$$\int d^3\vec{r}'' <\vec{r}|E - n|\vec{r}'' \times \vec{r}''|\hat{G}|\vec{r}'> = \delta(\vec{r} - \vec{r}'). \tag{6}$$

The corresponding differential equation for the Green function is

$$[\vec{\nabla}^2 + E - V(\vec{r})] G(\vec{r}, \vec{r}') = \delta(\vec{r} - \vec{r}'). \tag{7}$$

Taking the above expression into account, we may write

$$\hat{G}(\vec{r}, \vec{r}') = \sum_n \frac{<\vec{r}|n> <n|\vec{r}'>}{E = En}. \tag{8}$$

We have used more than 247 possible structural combinations and the probability of each configuration was determined by means of the total energy minimization.

To determine the Green's operator, we should introduce a small contribution to the denominator of Eq. (9). As a result, two new Green's operators are obtained:

$$G^+ = \frac{1}{E - \hat{H} + i\varepsilon}, \quad G^- = \frac{1}{E - \hat{H} - i\varepsilon}. \tag{9}$$

The introduction of $i\varepsilon$ contribution is caused by necessity to consider the boundary conditions. All these conditions were defined by the sizes of particular clusters.

The scattering problem is reduced to a determination of the Schrödinger equation solutions with the defined boundary conditions for a given eigenvalue E. For n tending to infinity, we may express the function $|\Psi>$ as a sum of two functions, *i.e.*, $|\varphi>$, which describes the incident wave

$$(E - \hat{H}_0)|\varphi> = 0 \tag{10}$$

and the function φ^+, which describes the scattered wave.

The final secular equation takes the usual form

$$\|\delta_{1i}t_i^{-1} - k^4 G^+\| = 0. \tag{11}$$

The temperature dependences were obtained due to Bose−Einstein distribution of quasi-phonons and they were included to the final formulae that are used in the calculations of the nonlinear optical susceptibilities.

To understand a contribution of the electron−phonon interaction and probably of the quasi-phonon anharmonicity, we have also included the operators of the electron−phonon interaction within the linear approximation. To calculate the Green functions, we have performed necessary summation over 450 points inside the efgfective sphere, where the atom positions were determined from the lattice dynamics matrices for the quasi-phonons at 8150 points inside the effective sphere. An influence of the neighbouring molecules was modelled by means of an effective local Lorentz field which actually renormalizes the eigenvalues and eigenvectors.

We have used Dyson equations with the electron−phonon perturbed potential that takes defect of charge and mass into account. A relation between the real and imaginary part of the Green function was determined by dispersion Kra-mers−Kronig relations. We have essentially improved the obtained results by introducing the electron−phonon perturbation.

4. Results and discussion

The electronic charge density of the "effective molecule" calculated in such a manner is presented in Fig. 2. One can clearly notice that the thiofulvalene system shows great gradients of the electronic charge density distribution. Higher order charge density perturbations can give better results for the nonlinear optical susceptibilities and better coincidence between the experiment data and our theory.

We have calculated a set of eigenvectors and eigenvalues based on the molecular structure. The eigenvalues are necessary in order to receive proper values of the matrix elements. The calculational results of the imaginary part of dielectric susceptibility are presented in Fig. 3 in the case with no electron-phonon interac-tions. The very complicated dependence should approximately correspond to the optical absorption spectra. Unfortunately, the shapes of these curves are quite different from the experimental spectra. Generally speaking, this essential difference points out that the electron−phonon interaction has to be taken into account in order to obtain a sufficient agreement between the experiment and theory.

We understand that such an improvement can be obtained due to the electron−phonon interaction, particularly of higher orders (for example, the electron−phonon anharmonicity). The experimental (absorption) and theoretical spectra are presented in Fig. 4 that shows a similarity of the mentioned spectra. Unfortunately, there exists a shift between the theoretical and experimental dependences. The observed discrepancies can be caused by natural lacks of the theoretical model as well as by the "non-purity" of the performed experiment (the
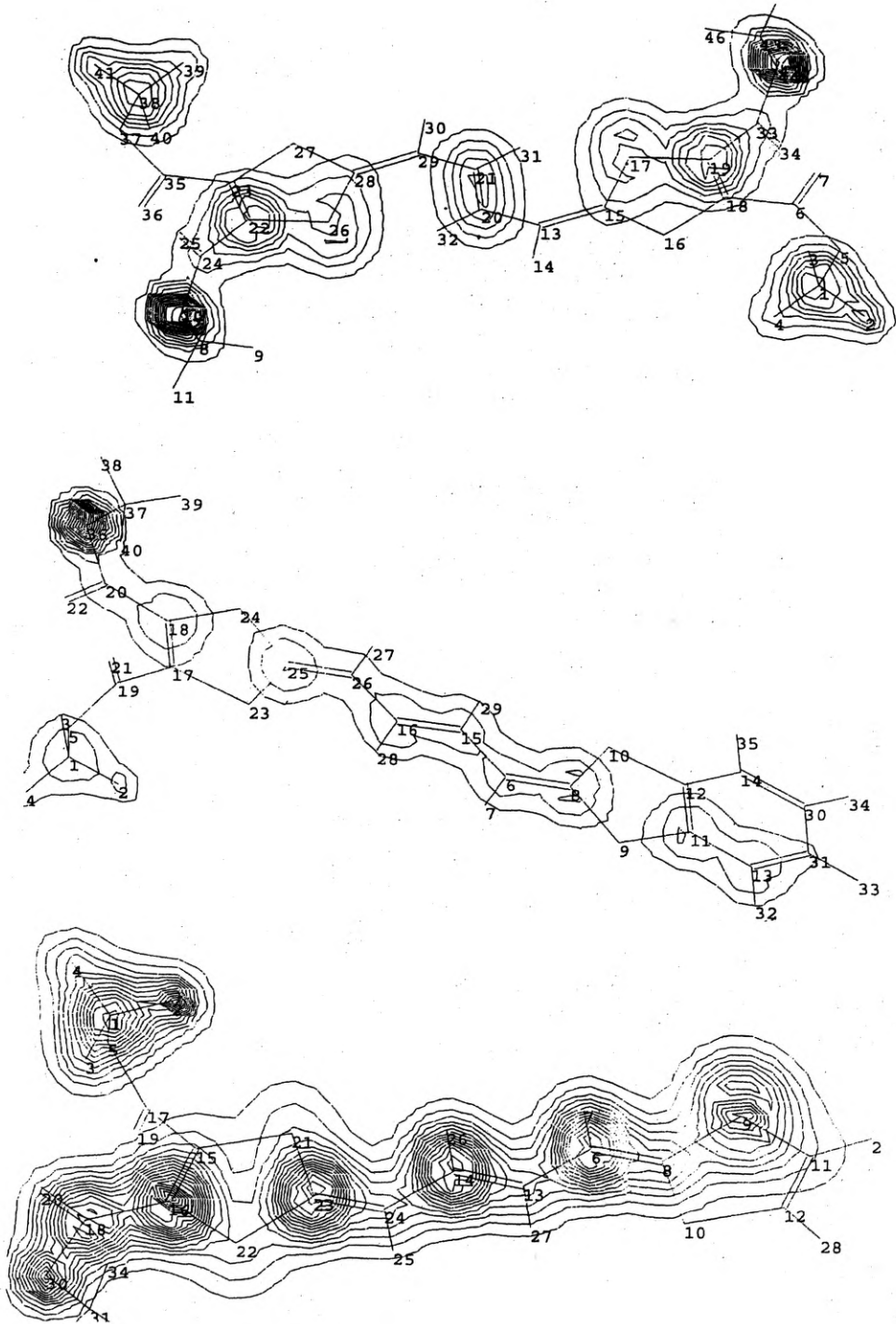
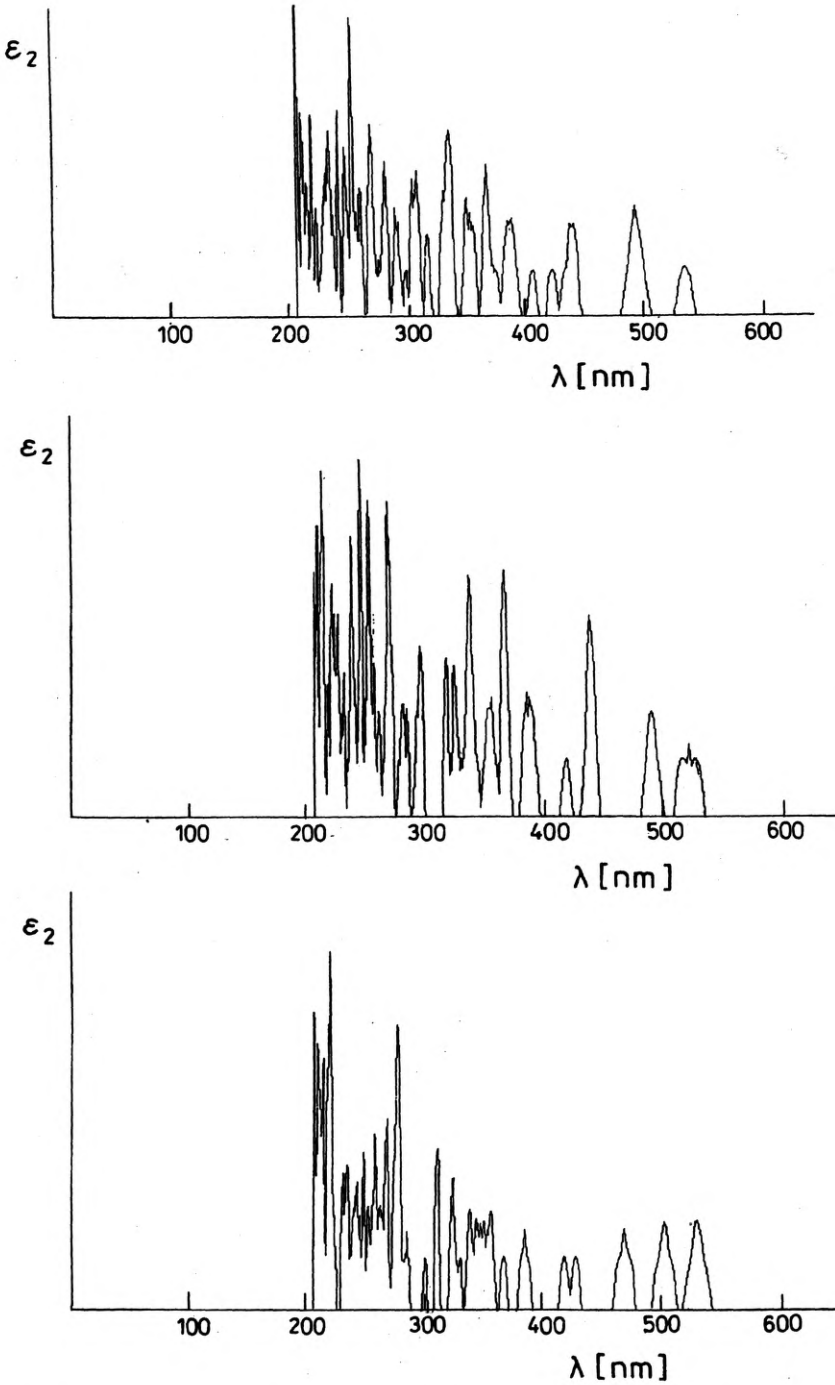Fig. 2. Electronic charge density distributions of typical thiofulvalene derivatives

Fig. 3. Imaginary part of dielectric susceptibility (in a.u.) for representatives of thiofulvalene materials
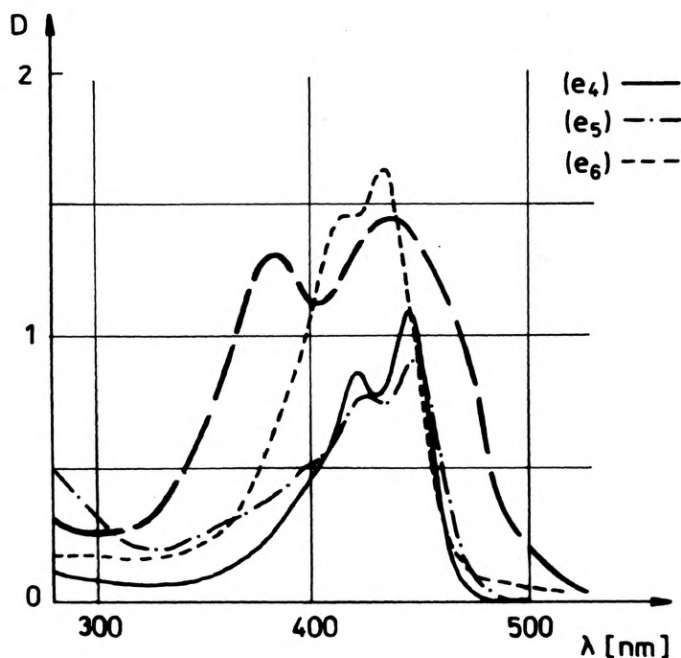
Fig. 4. Theoretical and measured optical spectra of example thiofulvalene derivatives. $(- - - -$ calculated)

systems are in solutions). The theoretical and experimental values of the χ_{xxxx} tensor components are presented in the Table.

Table. Nonlinear optical susceptibilities of thiofulvalene derivatives

Molecule	Experimental χ_{xxxx} [a.u.]	Calculated χ_{xxxx} [a.u.]
a_1	−4.59	−8.19
e_1	−4.51	−8.24
e_2	−6.47	−10.23
e_3	−10.82	−31.12
e_4	−13.15	−15.13
e_5	−2.36	−1.55
e_6	−13.74	−15.24

5. Conclusions

Besides some deviations, the good correlation between the experimental and theoretical data should be underlined in the case of the nonlinear optical susceptibilities of thiofulvalene derivatives. This comparison suggests a possibility to use the presented model as a basic one for prediction and design of the photopolymer

materials. Moreover, the obtained results can be very helpful for technologists in enhancement of the optical susceptibilities by substitution of the backbone radicals by NH_2 or NH_3 groups.

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