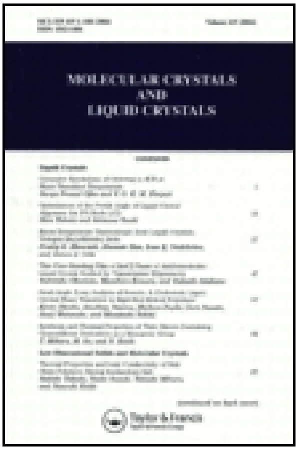

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Contribution of Intra- and Intermolecular Interaction to Nonlinear Optical Susceptibilities

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Contribution of Intra- and Intermolecular Interaction to Nonlinear Optical Susceptibilities

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We present a new model of intermolecular interactions taking into account the anharmonic coupling between the tunneling inter-conformation molecular mode and the long-range crystalline displacement. The coupling of the anharmonic phonon modes and local mode disordering causes the non-centrosymmetry in the electrostatic potential distribution. Symmetry of the molecular disorder has a point group C_3. The model is explained within a framework of tunneling soft mode conception and including molecular dynamics *ab initio* molecular dynamics simulations. The optical second harmonic generation (SHG) sensitive to local potential non-centrosymmetry is used as an experimental method for detection of manifestation the intermolecular disordering. The results are considered to be general importance for systems with electron-phonon anharmonic ordering, which is common to many organic materials.

Keywords: non-linear optics; SHG; molecular dynamics; geometry optimization; intermolecular interaction

INTRODUCTION

Traditionally an understanding of the structural transformations in organic materials (molecular crystals, polymers, ceramics etc)[1] was based on a model of the quantum tunneling introduced by Blinc [2]. In the disordered phase each molecule occupies several equilibrium positions appropriate to the total energy minimums of the particular molecular conformation. Inter-conformation tunneling between these positions suppresses molecular localization. With decreasing temperature inter-conformation barrier increases and the tunneling mode frequency decreases. This process analogously to the conception of the tunneling mode in the ferroelectrics or superconductors[2] is traditionally named as a mode softening[2].

From an analysis of the references concerning the organic materials[3] one can see essential disagreement both in the absolute values as well in a general behavior with temperature and pressure. In the present work we will show both theoretically as well experimentally that the main role in this case play the intermolecular coupling directly connected with a degree of crystalline long-range ordering.

Recent high-resolution neutron data on the benzene[5] as well the extended X-ray absorption fine structure (EXAFS) measurements[4] have provided additional evidence that at low temperatures (below 50 K) there appears structural changes depending on the inter-molecular order. One can guess that the conception of the low-temperature coupling between the tunneling modes and long-range displacement could be fruitful for this case[6, 7].

EXPERIMENTAL

The crystals with the different ordering degree $\mathbf{d_0}$ have been synthesized using a slow evaporation from the solution. Varying the evaporating rates crystals with the different $\mathbf{d_0}$ have been obtained. The quantitative classification of particular specimen was done using X-ray diffractometry. Ratios of (110) to (002) X-ray reflex intensities have been chosen as a degree of ordering $\mathbf{d_o}$. We have revealed that the minimal possible value of $\mathbf{d_o}$ is equal about 0.49 because for the lower $\mathbf{d_o}$ the crystalline structure is unstable.

Non-linear optical measurements have been done using the traditional optical second harmonic generation (SHG). The optimal angles for fulfilling of the phase matching conditions lie within the angle ranges 12 – 25 degree in respect to the optical axes and within the 24 – 37 degrees in the XY crystallographic plane. The specimens have been kept into the quartz cryostat to vary the temperature with an increment about 0.02 K. The YAG:Nd laser (λ=1.06 μm; W=25 MW; τ=18 – 45 ps) has been used for detection of the SHG as well for the control of the photoinduced absorption. The grating monochromator with resolution up to 2 nm/mm has been connected with the boxcar with a gate up to 420 ps allowing to monitor temporal SHG dependencies.

Experimental results

Varying geometry of the measured SHG tensor component we have revealed that the maximal value of the SHG tensor corresponds to the d_{222} component.

In the Fig. 1 are presented experimental dependencies of the SHG versus degree of molecular ordering $\mathbf{d_o}$ and temperature for the d_{222} tensor component. One can see an essential enhancement of the SHG from 0.098 pm/V up to 0.103 pm/V with decreasing temperature from 90 K to 10 K. Simultaneously with the increasing ordering parameter $\mathbf{d_o}$ from 0.5 to 0.78 the SHG increases and achieves its saturation. The SHG has a maximum value of about 0.103 pm/V below 30 K and for the $\mathbf{d_o}$ higher than 0.75.

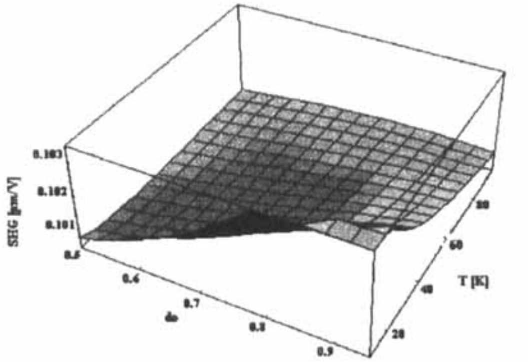

FIGURE 1 Dependence of the SHG d_{222} tensor component in the benzene crystals versus degree of ordering $\mathbf{d_o}$ and temperature.

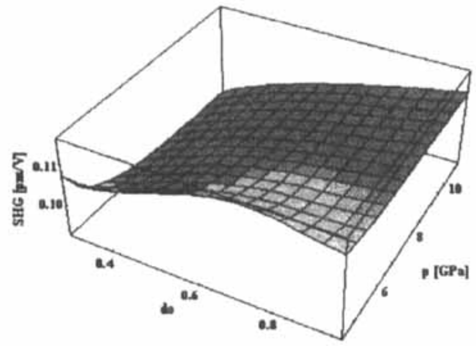

FIGURE 2 Dependence of the SHG d_{222} in the benzene crystals versus degree of ordering d_0 and hydrostatic pressure p.

The precision of the performed SHG measurements is better than 0.0002 pm/V. The obtained dependencies unambiguously show that there exist a limit of saturation for the total non-linear optical susceptibilities. The second reason for such increase is similar to a soft mode condensation[8] due to hybridization of the tunneling inter-conformation and simple acoustical modes[9].

The second important factor changing contributions of particular molecule to the SHG is hydrostatic pressure[10]. The corresponding dependencies for the different d_0 are presented in the Fig. 2. One can see that for the pressures within the range of 2 – 4 GPa there appears a SHG maximum at the d_0 about 0.6. With the next increase of the applied hydrostatic pressure this maximum decreases and disappears for pressures higher than 8 GPa. For these pressures only a smooth increase of the SHG is observed (up to $d_0 \cong 0.6$) with the next saturation. Such unusual pressure SHG dependence reflects complicated feature of the intermolecular disordering under the applied hydrostatic pressure. Lets consider temporary kinetics of the photoinduced absorption changes under the YAG:Nd doubled-frequency laser illumination.

From the Fig. 3 one can see a quasi-periodical dependence of the absorption changes D with a time period of about 8 ps. The latter one reflects a relaxation of the particular molecule after photopoling process. With increasing optical poled field power an increase of the optical response (photoinduced absorption) amplitudes is slightly enhanced.

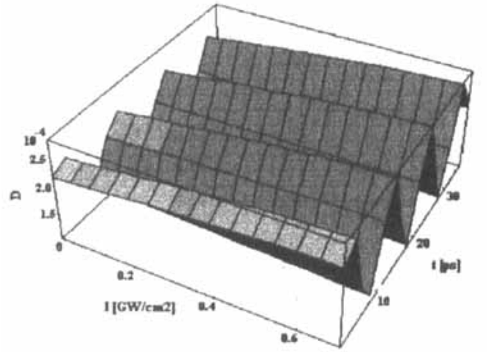

FIGURE 3 Temporary kinetics of additional optical density D versus photoinduced YAG:Nd laser beam intensity I and degree of ordering d_o.

Theoretical simulation and discussion

To obtain information concerning an origin of the observed SHG effects calculations of the electrostatic potential distribution determining the non-linear optical properties described by the third rank polar tensors have been performed. It is clearly that the observed non-centrosymmetry is a result of resonance-like interaction between the long-range acoustical displacement and order-disorder inter-conformational tunneling modes[6-8]. The resonance will appear at the definitive temperature or pressure. As a consequence, we perform the procedure for different temperature and pressure with taking into account of electron-phonon anharmonic interactions.

At the beginning calculations of the band energy structure have been carried out using *ab initio* norm-conserving pseudopotential method. The concrete details of the calculations are presented in the Ref.[10,11]. As a result the real electrostatic potential contours have been evaluated. Introducing of external parameter of intermolecular reorientation has included the ordering parameter d_0.

Within this approach we use long-range ordered crystalline approaches and inter-molecular reorientation with two different potentials, similarly as in the Ref.[10]. Calculation of the phonon modes has been performed at the beginning within harmonic approach:

$$d^2\Psi_k/dQ_k^2+[4\pi^2\mu_k h^{-2}E_k^2]\Psi_k=0 \tag{1}$$

where Ψ_k is a phonon-like wave function corresponding to k-th normal coordinate Q_k of the benzene molecule renormalized by the superimposed long-range potential; μ_k denotes a reduced mass of the interacted atoms for the k-th phonon mode.

An eigen-energy of the k-th phonon mode was written in a form:

$$E_k(\nu_k)=2E_{k0}(\nu_k+1/2)\,, \tag{2}$$

where $E_{k0}=(h/2\pi)(f_k/\mu_k)^{-1/2}/2$ is an eigen-energy for the k-th zero-point quasi-phonons and $\nu_k = 0, 1, 2, \ldots$ are phonon quantum numbers described by the appropriate expressions; spring constants f_k is evaluated as second space derivative of electrostatic potential calculated within a framework of the proposed models:

$$\Psi_k(Q_k)=(2E_{k0}/\pi)^{1/4}(2^{\nu_k}/\nu_k!)^{-1/2}\exp(-E_{k0}Q_k^2)H_\nu((2E_{k0})^{1/2}Q_k) \tag{3}$$

where $H_\nu(x)$ is a Hermit's polynomial.

In order to perform a modeling of the disorder influence the non-linear electron-phonon interactions have been considered as a low-frequency inter-conformational tunneling phonon modes that could be in frequency resonance with external displace acoustical phonon waves. The appropriate calculations have been done using molecular dynamics total energy potential barriers between the particular molecular fragments. Renormalized tunneling mode frequencies were calculated with inclusion of interactions possessing electron polarization (optical phonons) and acoustical displacements (acoustical phonons). In such a way the coupling constants responsible for the temperature and pressure-dependent soft-mode behaviors automatically have been taken into account. Calculation of the anharmonic electron-phonon interaction potential was carried out in a non-linear approximation similar as in the Ref.[11]:

$$V_{e\text{-}ph}(\mathbf{r}_i)=e^2\sum_{ms}M_{ms}^{-1/2}\Big[Z_{ms}(\mathbf{r}_s-\mathbf{u}_{ms})|\mathbf{r}_s-\mathbf{u}_{ms}|^{-3}-\sum_{m's'} Z_{m's'}(\mathbf{r}_{s'}-\mathbf{u}_{m's'})|\mathbf{r}_{s'}-\mathbf{u}_{m's'}|^{-3}\Big] \qquad (4)$$

where M_{ms} and eZ_{ms} are effective ionic mass and charge for the corresponding ions, numbered by m and s, respectively. Both intra- as well intermolecular interactions were considered. The corresponding spring constants were evaluated as the second and third space derivatives of the crystalline system. At the same time two effective wavevectors have been introduced. The first one corresponds to the perfect crystalline unit and the second one is built on the effective molecular sphere originating from the disordering background. Influence of the interface region (between the intramolecular and intermolecular backgrounds) has been evaluated by performing of a derivative procedure eliminating possible potential singularities on the boarders.

The $\mathbf{u}_{ms,m's'}$ vector is a relative displacement of two ions from their equilibrium positions $\mathbf{r}_s$ and $\mathbf{r}_{s'}$. A probability of a one-phonon transition induced by the phonon of a frequency Ω_k is equal to:

$$\Xi(\Omega_k)=4(h/2\pi)^{-2}c^{-3}H^{-1}g^{-1}(r_i)(E_{el}-\Omega_k)^2\,\Theta(\Omega_k) \qquad (5)$$

where H is a sum of the η and ξ levels widths, E_{el} is an inter-band electron transition energy, Ω_k denotes a phonon energy and $g(r_i)$ is a degeneration degree of the appropriate electron energy levels. The parameter $\Theta(\Omega_k)$ is equal to:

$$\Theta(\Omega_k)=\sum_{\eta}^{g(\eta)}\sum_{\xi}^{g(\xi)}\Big|\Big\{\sum_{\varphi}<\eta,\eta_{\Omega}|V_{e\text{-}ph}(\mathbf{r}_i)|\varphi,\eta_{\Omega+1}><\varphi|\mathbf{d}|\xi>(E_{\xi}-E_{\eta}+\Omega_k)^{-1}+\sum_{\varphi}<\eta|\mathbf{d}|\varphi><\varphi,\eta_{\Omega}|V_{e\text{-}ph}(\mathbf{r}_i)|\xi,\eta_{\Omega-1}>(E_{\xi}-E_{\eta}-\Omega_k)^{-1}\Big\}\Big|^2_{\theta} \qquad (6)$$

where η and the ξ are lower and upper electron energy levels, respectively; φ denotes a virtual electron state, **d** is an electric dipole moment for a given spectral transition. The summation is performed over all degenerated initial and final electron-phonon states. The symbol θ denotes an averaging over the occupied phonon states.

The normal coordinates are expressed as a linear combination of symmetric phonon vibrations included in the electron-phonon interaction (see Eq. 5):

$$\Theta\,(\Omega_k)=C_{\eta\xi}^{\gamma}(r_{\lambda}^{\Delta})C_{\eta\xi}^{\gamma'}(r_{\lambda'}^{\Delta'})\,\mathrm{Im}\,G_{\Delta\Delta'}^{\gamma\gamma'}(r_{\lambda}^{\Delta},\Omega_k^2) \qquad (7)$$

where $G_{\Delta\Delta'}^{\gamma\gamma'}(r_{\lambda}^{\Delta})$ is a Green function (γ and γ' are denote numbers of interacting coordination sphere) defined as:

$$G_{\Delta\Delta'}^{\gamma\gamma'}(r_{\lambda}^{\Delta})=\sum_{\varphi}\{<\eta|V_{e\text{-}ph}(\mathbf{r}_i)|\varphi><\varphi|\mathbf{d}|\xi>+<\eta|\mathbf{d}|\varphi><\varphi|V_{e\text{-}ph}(\mathbf{r}_i)|\xi>\}(E_{\xi}-E_{\eta})^{-1} \qquad (8)$$

The Green function calculations are carried out for an ideal lattice renormalized by a long-range disturbed potential with taking into account of the concrete intermolecular tunneling order-disorder phonon. The summation was done over the 125 **k**-points in the irreducible part of the Brillouin zone. The resulting expression is given below:

$$G_{\Delta\Delta'}^{\gamma\gamma'}(r_{\lambda}^{\Delta},\Omega_k^2)=\sum_{\Omega}K_{\Delta'}^{\gamma'}(r_{\lambda}^{\Delta})\,K_{\Delta}^{\gamma}(r_{\lambda}^{\Delta})(\Omega_k^2-\Omega^2-i\delta)^{-1} \qquad (9)$$

where the coordinates $K_{\Delta}^{\gamma}(r_{\lambda}^{\Delta})$ are obtained for a given phonon type after the static electron states averaging. The long-range lattice perturbation was included into the Green function formalism with taking into account a molecular deformation localization that allows us to use the Dyson relations:

$$G_{\Delta\Delta'}^{\gamma\gamma'}(1)=G_{\Delta\Delta'}^{\gamma\gamma'}(0)+G_{\Delta\Delta'}^{\gamma\gamma'}(0)\,U\,G_{\Delta\Delta'}^{\gamma\gamma'}(1) \qquad (10)$$

where $G_{\Delta\Delta'}^{\gamma\gamma'}(0)$ and $G_{\Delta\Delta'}^{\gamma\gamma'}(1)$ are the Green functions for ideal and disordering systems, respectively. From the mentioned equation we have obtained the modified electron-phonon wavefunction for calculation of the intra-the-cluster electrostatic potential and corresponding phonon modes with and without inclusion of the interconformation tunneling modes. The performed calculations have shown that the symmetry of these modes is C_3.

The superposition of the acoustical modes on the effective tunneling modes has been carried out similarly as in the Ref.[6, 8]. Therefore dependencies of electrostatic potential both versus temperature as well of the degree of the long-range orientation have been obtained.

In the Fig. 4a is presented a sequence of electrostatic potential space distribution for the particular benzene molecule in the case of the $\mathbf{d_0} \cong 0.55$ corresponding to the maximally possible reorientation of the molecule. One can see that the molecular structure for such degree of ordering is similar to the ones for an isolated molecule. Intermolecular long-range non-centrosymmetry defining the non-centrosymmetry is relatively slight. Calculation performed for the higher disorder shows that the degree of the electrostatic potential non-centrosymmetry is changed less than 1 %. Only taking into account of the electron-phonon anharmonic interactions within the framework of the Eqn(3-10) gives an opportunity to observe the appearance of essential non-centrosymmetry in the electrostatic potential contours (Fig. 4b).

One can clearly see that intermolecular phonon softening (due to close values of the acoustical and interconformation tunneling modes) stimulates relative shift of the electrostatic potential space distribution higher than 6%. It is necessary also to add that such non-centrosymmetry (point group symmetry C_3) is a result of resonance superposition of the low frequency acoustical modes (due to long-range intermolecular interaction) and the soft intermolecular tunneling modes. When the values of frequencies are close one can observe a static fixation ("pinning") of long-range non-centrosymmetry.

Similar effect is observed when an external hydrostatic pressure is applied (see Fig. 4c). The soft mode coupling favors an appearance of essential non-centrosymmetry. The observed behaviors are very similar to the non-centrosymmetry caused by crystalline ferroic domains[12] and one can expect an appearance of different critical phenomena.

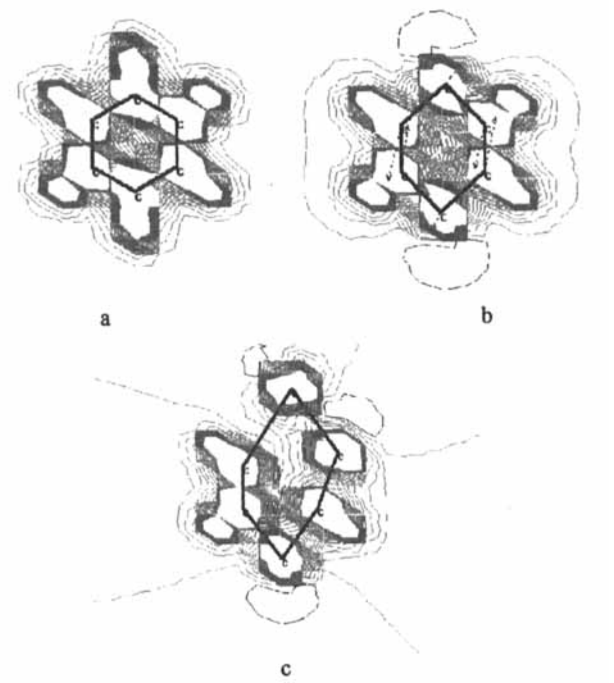

FIGURE 4 Typical electrostatic potential distribution in the benzene molecule: a) for degree of ordering d_0=0.7 without taking into account of electron-phonon anharmonic interactions; b) the same with the taking into account of the interactions and increase of ordering degree d_0 up to 0.85; c) the same with applying of external hydrostatic pressure.

CONCLUSIONS

The performed experimental and theoretical investigations show that competition between the intermolecular long-range crystalline ordering and intermolecular tunneling plays a chief role in the temperature and pressure behaviors of the SHG for organic materials. Varying the external temperature and pressure a non-centrosymmetry in electrostatic potential distribution is varied. The SHG shows essential sensitivity to such kinds of modes and could be used as a powerful tool for defining of the intra- as well of the intermolecular contributions to the second-order non-linear optical susceptibilities.

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