

Breaking of the overall permutation symmetry in nonlinear optical susceptibilities of periodic systems

Mingzhong Xu

Department of Chemistry
New York University
New York, NY 10003

Shidong Jiang

Department of Mathematical Sciences
New Jersey Institute of Technology
Newark, NJ 07102

CAMS Report 0405-22, Spring 2005

Center for Applied Mathematics and Statistics

NJIT

Breaking of the overall permutation symmetry in nonlinear optical susceptibilities of periodic systems

Minzhong Xu*

Department of Chemistry, New York University, New York, NY 10003

Shidong Jiang

Department of Mathematical Sciences, New Jersey Institute of Technology, Newark, NJ 07102

(April 1, 2005)

Abstract

Based on infinite one-dimensional periodic chain models (Su-Shrieffer-Heeger and Takayama-Lin-Liu-Maki) of trans-polyacetylene, we show analytically that the overall permutation symmetry of nonlinear optical susceptibilities is, albeit preserved in the molecular systems with only bound states, no longer generally held for the periodic systems. Hence it breaks the Kleinman symmetry in the off-resonant regions. Our theory qualitatively explain the widely observed deviations of Kleinman symmetry in experiments. New nonlinear optical experiments are proposed to verify the overall symmetry break.

PACS: 78.66.Qn, 42.65.An, 72.20.Dp, 78.20.Bh

Typeset using REVTeX

* Author to whom correspondence should be addressed. Email: mx200@nyu.edu

The n th-order optical susceptibility is generally defined as a rank n tensor $\chi_{\mu\alpha_1\alpha_2\cdots\alpha_n}^{(n)}(-\omega_\sigma; \omega_1, \omega_2, \cdots, \omega_n)$, where $\omega_\sigma \equiv \sum_{i=1}^n \omega_i$. The intrinsic permutation symmetry, as described in Butcher and Cotter's book [1], implies that the n th-order susceptibility is invariant under all $n!$ permutations of pairs $(\alpha_1, \omega_1), (\alpha_2, \omega_2), \cdots, (\alpha_n, \omega_n)$. Intrinsic symmetry is a fundamental property of the nonlinear susceptibilities which arises from the principles of time invariance and causality, and applies universally. For the medium that is transparent in all the relevant frequencies, i.e., far away from all transition frequencies, the optical susceptibilities have one more interesting property, namely, the overall permutation symmetry, in which the susceptibilities are invariant when the permutation includes the additional pair $(\mu, -\omega_\sigma)$. Therefore, the n th-order susceptibility is invariant under all $(n+1)!$ permutations of the pairs $(\mu, -\omega_\sigma), (\alpha_1, \omega_1), \cdots, (\alpha_n, \omega_n)$ [2]. Furthermore, when the optical frequencies are much smaller than any of the transition frequencies, the dispersion of the medium at the relevant frequencies is negligible. And it follows that the susceptibility is invariant under all permutations of the subscripts $\mu, \alpha_1, \cdots, \alpha_n$. This property is known as Kleinman Symmetry [3]. Thus, it seems that Kleinman symmetry theoretically should be valid or preserved in the off-resonant regions for any systems. However, as pointed out by Simpson and his coauthors [4], the overwhelming majority of recent non-resonant optical experiments on various physical systems clearly showed the deviations from Kleinman symmetry even for off-resonant regions. In this letter, based on the theoretical framework developed in our previous work [5–9], we prove that the overall permutation symmetry in nonlinear optical susceptibilities is broken in periodic systems, and as a direct consequence, Kleinman symmetry is also broken. Finally, despite the wide acceptance of the overall permutation symmetry in the nonlinear optics [1,2], no direct measurement has been made to test the validity of the assertion. In this letter, a feasible experiment is suggested to test the overall permutation symmetry.

Indeed, the analytical derivations of nonlinear susceptibilities are rigorous and correct in

the molecular systems [1,2] where the position operator \mathbf{r} is well-defined in the whole real space. However, for periodic systems, the usual definition of \mathbf{r} is no longer valid for the whole space, instead the "saw-like" position operator must be introduced to maintain the periodic property of the systems [10,11]. If the periodic boundary condition is applied to a physical system, the average electronic position could be anywhere for delocalized states in periodic systems [10], while this is clearly not the case for most molecular systems with only bound states. For periodic systems, the position operator \mathbf{r} is often conveniently defined in the momentum space [12]:

$$\mathbf{r}_{nk,n'k'} = i\nabla_{\mathbf{k}}\zeta_{n,n'}(\mathbf{k}, \mathbf{k}') + \Omega_{n,n'}(\mathbf{k})\delta(\mathbf{k} - \mathbf{k}'), \quad (1)$$

and

$$\begin{aligned} \zeta_{n,n'}(\mathbf{k}, \mathbf{k}') &= \int_V \psi_{n,\mathbf{k}}^*(\mathbf{r})\psi_{n',\mathbf{k}'}(\mathbf{r})d\mathbf{r}, \\ \Omega_{n,n'}(\mathbf{k}) &= \frac{i}{v} \int_v u_{n,\mathbf{k}}^*(\mathbf{r})\nabla_{\mathbf{k}}u_{n',\mathbf{k}}(\mathbf{r})d\mathbf{r}, \end{aligned} \quad (2)$$

where V is the whole system volume, v is the unit cell volume, and $\psi_{n,\mathbf{k}}(\mathbf{r}) = u_{n,\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$ is the Bloch state with n and \mathbf{k} the band index and crystal momentum, respectively. The two terms in Eq.(1) correspond to the intra- and inter-band transitions, respectively [12].

On the other hand, the $\mathbf{p} \cdot \mathbf{A}$ (current-current correlation) instead of the $\mathbf{E} \cdot \mathbf{r}$ (dipole-dipole correlation) gauge is usually used and \mathbf{p} is treated as static [1,10]. Though quite successful in the linear case, the static current-current correlation is actually not equivalent to the dipole-dipole correlation or $\mathbf{E} \cdot \mathbf{r}$ gauge and gives wrong results in nonlinear optical studies in periodic systems [7,8]. To restore the equivalence between these two gauges, one needs to incorporate the proper gauge phase factor in the current-current correlation [7]. For convenience in studying nonlinear optical susceptibilities for periodic systems, we use the $\mathbf{E} \cdot \mathbf{r}$ gauge in this letter.

To demonstrate the symmetry breaking, we will focus on the two infinite one-dimensional(1D) single electronic periodic models - the SSH model [13] and its continuum sibling TLM model [14]. The models' successfulness in explaining optical properties of

trans-polyacetylene could be found in literature [15]. The advantage of choosing the single electronic periodic models as our examples is due to the analytically solvable feature for 1D simple bands and $\zeta_{n,n'}(\mathbf{k}, \mathbf{k}') = \delta_{n,n'}\delta(\mathbf{k} - \mathbf{k}')$ could be applied in Eq.(1) [16,17]. With the centro- or inversion symmetry applied on the system, it is straightforward to show that $\chi^{(2)}$ vanishes and the first non-zero nonlinear susceptibility should be $\chi^{(3)}$. The Hamiltonian of SSH model is described as follows [13]:

$$H_{SSH}^0 = - \sum_{l,s} \left[t_0 + (-1)^l \frac{\Delta}{2} \right] (\hat{C}_{l+1,s}^\dagger \hat{C}_{l,s} + \hat{C}_{l,s}^\dagger \hat{C}_{l+1,s}), \quad (3)$$

where t_0 is the transfer integral between the nearest-neighbor sites, Δ is the gap parameter and $\hat{C}_{l,s}^\dagger$ ($\hat{C}_{l,s}$) creates(annihilates) a π electron at site l with spin s .

Following the same procedure described in previous work [5–9], we consider the momentum space representation of the Hamiltonian given by Eq.(3). With the aid of the spinor description $\hat{\psi}_{k,s}^\dagger(t) = (\hat{a}_{k,s}^{\dagger c}(t), \hat{a}_{k,s}^{\dagger v}(t))$, where $\hat{a}_{k,s}^{\dagger c}(t)$ and $\hat{a}_{k,s}^{\dagger v}(t)$ are the excitations of electrons in the conduction band and the valence band with momentum k and spin s , we obtain the following formula:

$$\begin{aligned} \hat{H}_{SSH}(k, t) &= \hat{H}_{SSH}^0 + \hat{H}_{\mathbf{E},\mathbf{r}} \\ &= \sum_{-\frac{\pi}{2a} \leq k \leq \frac{\pi}{2a}, s} \varepsilon(k) \hat{\psi}_{k,s}^\dagger(t) \sigma_3 \hat{\psi}_{k,s}(t) - \hat{D} \cdot E_0 e^{i\omega t}, \end{aligned} \quad (4)$$

where

$$\hat{D} = e \sum_{-\frac{\pi}{2a} \leq k \leq \frac{\pi}{2a}, s} (\beta(k) \hat{\psi}_{k,s}^\dagger \sigma_2 \hat{\psi}_{k,s} + i \frac{\partial}{\partial k} \hat{\psi}_{k,s}^\dagger \hat{\psi}_{k,s}), \quad (5)$$

$\varepsilon(k) = \sqrt{[2t_0 \cos(ka)]^2 + [\Delta \sin(ka)]^2}$, σ_i ($i = 1, 2, 3$) are Pauli matrices, and $\beta(k) = -\Delta t_0 a / \varepsilon^2(k)$. $\beta(k)$ is the coefficient related to the interband transition between the conduction and valence bands in a unit cell of length $2a$, and the second term in Eq.(5) is related to the intraband transition [5–9].

By the field theory and Wick theorem [18], the general four-wave-mixing(FWM) can be expressed as [5–9]:

$$\begin{aligned}
\chi_{SSH}^{FWM}(-\Omega; \omega_1, \omega_2, \omega_3) &= \frac{2e^4 n_0}{\hbar^3} \frac{1}{3!L} \sum_{k, \mathcal{P}(\omega_1, \omega_2, \omega_3)} \int \frac{id\omega}{2\pi} Tr \left\{ (\beta(k)\sigma_2 + i\frac{\partial}{\partial k})G(k, \omega) \right. \\
&\quad (\beta(k)\sigma_2 + i\frac{\partial}{\partial k})G(k, \omega - \omega_1) (\beta(k)\sigma_2 + i\frac{\partial}{\partial k})G(k, \omega - \omega_1 - \omega_2) \\
&\quad \left. (\beta(k)\sigma_2 + i\frac{\partial}{\partial k})G(k, \omega - \omega_1 - \omega_2 - \omega_3) \right\}, \tag{6}
\end{aligned}$$

where $\Omega = \sum_i \omega_i$, L is the chain length, n_0 is the number of chains per unit cross area, and $\mathcal{P}(\omega_1, \omega_2, \omega_3)$ represents all permutations for ω_1, ω_2 and ω_3 . The polymer chains are assumed to be oriented, and Green's function $G(k, \omega)$ is defined as follows [5–7]:

$$G(k, \omega) = \frac{\omega + \omega_k \sigma_3}{\omega^2 - \omega_k^2 + i\epsilon}, \tag{7}$$

with $\omega_k \equiv \varepsilon(k)/\hbar$ and $\epsilon \equiv 0^+$.

The analytical expression for the general four-wave-mixing can be found in [5–9]. Here we consider $\chi_{TLM}^{(3)}(-3\omega; \omega, \omega, \omega)$ and $\chi_{TLM}^{(3)}(\omega; \omega, \omega, -3\omega)$ to demonstrate the break of the overall permutation symmetry. To do a simple comparison of the overall permutation symmetry, we only listed two cases under the TLM model - the continuum limit of the SSH model. Obviously, these two quantities should be equal if the overall permutation symmetry were preserved. However, our analysis shows that

$$\begin{aligned}
\chi_{TLM}^{(3)}(-3\omega; \omega, \omega, \omega) &= \chi_0^{(3)} \frac{45}{128} \left\{ -\frac{14}{3z^8} - \frac{4}{15z^4} + \frac{(37 - 24z^2)}{8z^8} f(z) + \frac{(1 - 8z^2)}{24z^8} f(3z) \right\} \tag{8} \\
&= \chi_0^{(3)} \left(\frac{5}{28} + \frac{80}{11} z^2 + \frac{98580}{1001} z^4 + O(z^6) \right) \quad (z \rightarrow 0),
\end{aligned}$$

and

$$\begin{aligned}
\chi_{TLM}^{(3)}(\omega; \omega, \omega, -3\omega) &= \chi_0^{(3)} \frac{5}{1024z^8} \left\{ \frac{5}{3} (40z^2 - 61) f(z) + \frac{16}{3} (4z^2 - 1) f(2z) \right. \\
&\quad \left. - \frac{1}{243} (1944z^2 - 241) f(3z) + \frac{32}{243} (27z^4 - 30z^2 + 805) \right\} \tag{9} \\
&= \chi_0^{(3)} \left(\frac{5}{28} + \frac{80}{33} z^2 + \frac{28500}{1001} z^4 + O(z^6) \right) \quad (z \rightarrow 0).
\end{aligned}$$

where $\chi_0^{(3)} \equiv \frac{8}{45} \frac{e^4 n_0 (2t_0 a)^3}{\pi \Delta^6}$, $z = \hbar\omega/2\Delta$, and the function f is defined by the formula

$$f(z) \equiv \begin{cases} \frac{\arcsin(z)}{z\sqrt{1-z^2}} & (z^2 < 1), \\ -\frac{\cosh^{-1}(z)}{z\sqrt{z^2-1}} + \frac{i\pi}{2z\sqrt{z^2-1}} & (z^2 > 1). \end{cases} \quad (10)$$

For polyacetylene, typical parameters are $t_0 = 2.5eV$, $\Delta = 0.9eV$, $n_0 = 3.2 \times 10^{14}cm^{-2}$ and $a = 1.22\text{\AA}$, and we have $\chi_0^{(3)} \approx 1.0 \times 10^{-10}$ esu [5–9]. In Fig.1 we have plotted $\chi_{TLM}^{(3)}(-3\omega; \omega, \omega, \omega)$ and $\chi_{TLM}^{(3)}(\omega; \omega, \omega, -3\omega)$ in the off-resonant region. And the graph shows that there is about 40% difference for $z = 1/6$ (about $0.3eV$ or $4.14\mu m$) between these two quantities. Subtracting two asymptotic expressions in Eq. (8) and (9), we observe that the difference between $\chi_{TLM}^{(3)}(-3\omega; \omega, \omega, \omega)$ and $\chi_{TLM}^{(3)}(\omega; \omega, \omega, -3\omega)$ in the off-resonant region satisfies the following relationship:

$$\delta\chi^{(3)}(\omega) \propto \frac{e^4 n_0 t_0^3 a^3 \hbar^2 \omega^2}{\Delta^8}. \quad (11)$$

Clearly, the overall permutation symmetry of $\chi^{(3)}$ is no longer held under the TLM model (and its discrete counterpart – the SSH model).

We have also computed nonlinear susceptibilities without the ∇_k or ∂_k terms in Eq.(5) [9]. The results preserve both the overall permutation and Kleinman symmetries. Excluding ∇_k terms is kind of kludge for molecular systems where polarization current is not present [19]. Therefore in periodic systems, the ∇_k terms break the overall permutation symmetry that should be maintained for molecular systems with only bound states [1,2].

Due to the similar formula between the overall permutation and Kleinman symmetry [1], Eq.(11) can be used to explain the deviation of Kleinman symmetry in recent off-resonant experiments qualitatively. Those experiments include the electric-field-induced second harmonic(EFISH) generation on some simple atom and molecular systems with periodic electrode array imposed in the gas cell [20–22], second harmonic generation (SHG) studies of oriented organic films [23–25] and inorganic crystals [26–28]. Eq.(11) shows that: (i). The break increases with decreasing band gap and proportional to ω^2 , it is consistent with the

previously reported experiment [28]; (ii). The break increases with t_0 (the hopping of π electrons between the nearest-neighbor atoms), it explains the experimental results that the deviation of Kleinman symmetry is favorable of (20~50%) the delocalized states such as aromatic molecules [22] and some polymers or crystals [23,24], while unfavorable of ($\leq 8\%$) the localized states such as molecular systems such as O_2 , N_2 , etc. [20,21]. On the other hand, the vanishing $\chi^{(2)}$ under the SSH or TLM model shows that some symmetries such as centro-symmetry, etc, can suppress the deviation from Kleinman symmetry even for periodic systems. It may explain the reason why Kleinman symmetry is still preserved in some $\chi^{(2)}$ experiments of crystals [29].

Regardless of the underlying structures, our results embed some successful theoretical models in explaining the deviations. For example, Eq.(11) gives Levine's model [30] that predicts the second order polarizability tensor $d^F/d^A \propto \omega^2$ where superscripts F and A mean forbidden and allowed respectively with the frequency ω . For a benzene ring structure, dipole contributions from two perpendicular directions should both influence the nonlinear susceptibilities due to the periodicity along the circle of ring. This fits the assumption of contributions of a low-lying electronic band with the transition dipole perpendicular to the symmetry axis [22].

In conclusion, the overall permutation symmetry for nonlinear susceptibilities is, albeit preserved in the molecular systems with only bound states, no longer generally held for the periodic systems having delocalized states, therefore it breaks the Kleinman symmetry. The break $\delta\chi^{(3)}$ is proportional to $\frac{e^4 n_0 t_0^3 a^3 \hbar^2 \omega^2}{\Delta^8}$ in the off-resonant regions. Our theoretical results qualitatively explain the widely observed deviation from Kleinman symmetry in experiments. Furthermore, we suggest experimentalists to perform the off-resonant $\chi^{(3)}$ measurements on some centro-symmetric 1D periodic polymer structures such as trans-polyacetylene, etc, to directly test the validity of overall permutation symmetry and our arguments above.

The authors would like to thank Dr. Xing Wei for very helpful discussions.

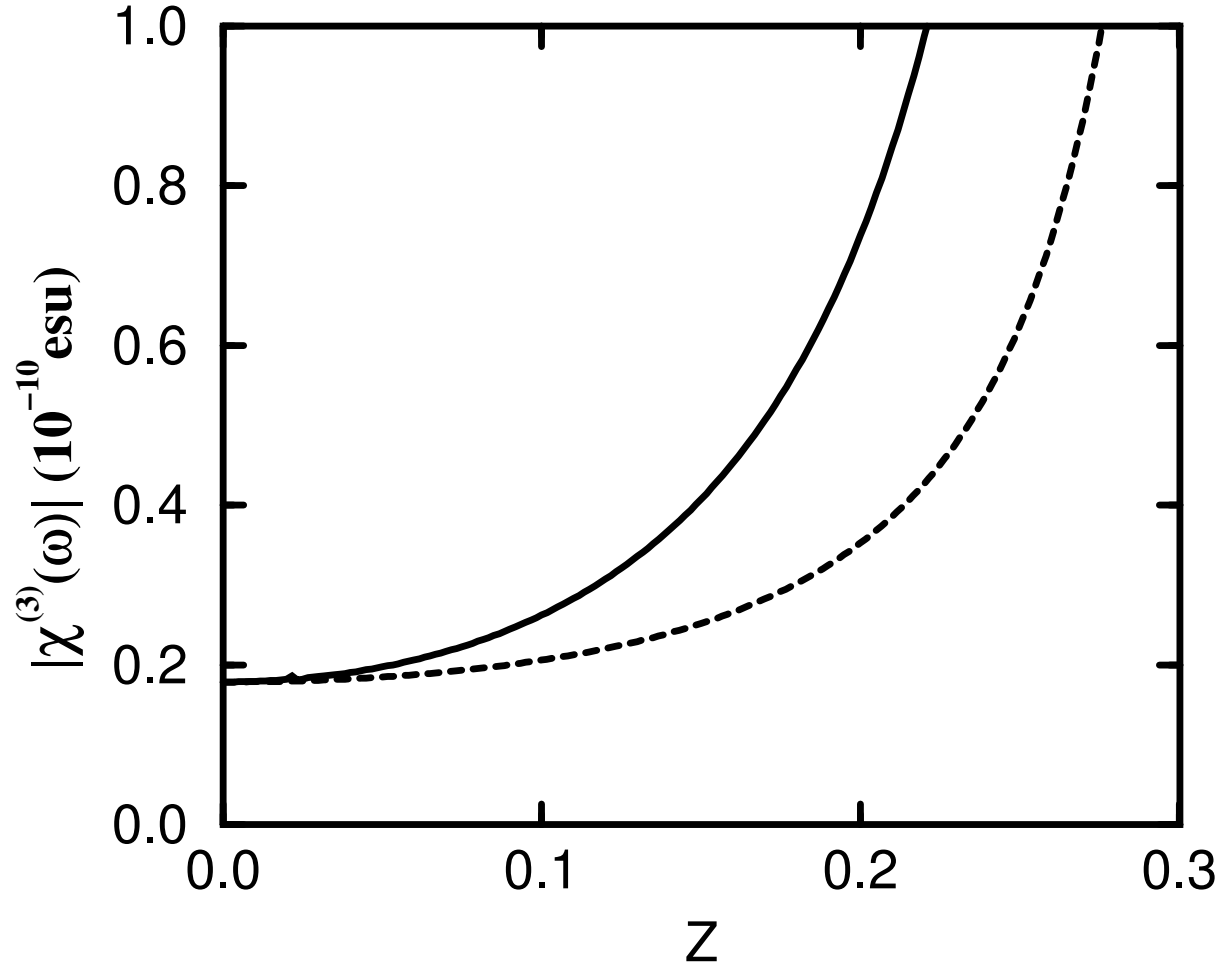


FIG. 1. The hyperpolarizabilities under the TLM model for non-resonant region: $\chi_{TLM}^{(3)}(-3\omega; \omega, \omega, \omega)$ (real line) versus $\chi_{TLM}^{(3)}(\omega; \omega, \omega, -3\omega)$ (long dashed line), where $Z \equiv \hbar\omega/2\Delta$.

REFERENCES

- [1] P.N. Butcher and D. Cotter, *The Elements of Nonlinear Optics* (Cambridge University Press, 1990).
- [2] P.N. Butcher and T.P. McLean, Proc. Phys. Soc. (London) **83** 579(1964).
- [3] D.A. Kleinman, Phys. Rev. **126**, 1977(1962).
- [4] C.A. Dailey, B.J. Burke and G.J. Simpson, Chem. Phys. Lett. **390**, 8(2004).
- [5] M.Z. Xu and X. Sun, Phys. Rev. B **61**, 15766 (2000).
- [6] M.Z. Xu and X. Sun, Phys. Lett. A **257**, 215 (1999); **259**, 502 (1999).
- [7] M.Z. Xu and X. Sun, J. Phys. Condens. Matter **11**, 9823 (1999).
- [8] M.Z. Xu and S.D. Jiang, to be submitted.
- [9] S.D. Jiang and M.Z. Xu, to be submitted.
- [10] F.M. Peeters, A Matulis, M. Helm, T. Fromhertz and W. Hilbert, Phys. Rev. B **48** 12008 (1993).
- [11] D. Vanderbilt, J. Phys. and Chem. of Solids **61**, 147 (2000).
- [12] E. I. Blount, in *Solid State Physics: Advances in Research and Applications*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1962), Vol. 13.
- [13] W.P. Su, J.R. Schrieffer, and A.J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979); Phys. Rev. B **22**, 2099 (1980).
- [14] H. Takayama, Y.R. Lin-Liu, and K. Maki, Phys. Rev. B **21**, 2388 (1980).
- [15] A.J. Heeger, S. Kivelson, J.R. Schrieffer, and W.P. Su, Rev. Mod. Phys. **60**, 781 (1988) and references there in.
- [16] W. Kohn, Phys. Rev. **115**, 809 (1959).

- [17] J. Zak, Phys. Rev. Lett. **54**, 1075 (1985).
- [18] G.D. Mahan, *Many-Particle Physics* (New York: Plenum, 1990).
- [19] C. Kittel, Quantentheorie der Festkörper, 1st ed. (Oldenburg, München-Wien, 1970).
- [20] V. Mizrahi and D.P. Shelton, Phys. Rev. A **31**, 3145(1985).
- [21] D.P. Shelton and Z. Lu, Phys. Rev. A **37**, 2231(1988).
- [22] R. Wortmann, P. Krämer, C. Glania, S. Lebus and N. Detzer, Chem. Phys. **173**, 99(1992).
- [23] C. López-Garabito, J.A. Campo, J.V. Heras, M. Cano, G. Rojo and F. Agulló-López, J. Phys. Chem. B **102**, 10698(1998).
- [24] N. Tsutsumi, T. Mizutani, W. Sakai, T. Watanabe and S. Miyata, J. Chem. Phys. **108**, 9839(1998).
- [25] N. Tsutsumi, Y. Okabe and W. Sakai, Macromolecules **32**, 3249(1999).
- [26] S. Singh, W.A. Bonner and L.G. Van Uitert, Phys. Lett. **38A**, 407(1972).
- [27] D.S. Chemla and J. Jerphagnon, Appl. Phys. Lett. **20**, 222(1972).
- [28] G.R. Crane and J.G. Bergman, J. Chem. Phys. **64**, 27(1976).
- [29] See for example: F.G. Parsens, E. Yi Chen, and R.K. Chang, Phys. Rev. Lett **27**, 1436(1971).
- [30] B.F. Levine, IEEE J. Quantum Electron. QE-**9**, 946(1973).