



First and second derivative analysis of electroabsorption spectra in conjugated molecules and polymers: Stark shift and Stark broadening

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Abstract

Second-order Stark effect is analysed in terms of the third-order non-linear susceptibility $\chi^{(3)}(\omega; \omega, 0, 0)$ within a centrosymmetric one-dimensional three-level model. The Stark effect manifests itself in the electroabsorption spectrum mainly as the first or the second derivative of the unperturbed absorption spectrum that corresponds to either Stark shift or Stark broadening, respectively. Domination of the first or the second derivative in the electroabsorption lineshape depends on the energy gap between the first dipole-allowed state and a nearby excited dipole-forbidden state. The model takes into account inhomogeneous broadening and vibronic sidebands of both excited states. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Electroabsorption (EA) spectroscopy is a highly informative and sensitive tool for studying the excited state spectrum of condensed media in inorganic semiconductors [1,2], organic dyes in matrices [3], molecular crystals [4], conjugated molecules [5] and polymers [6,7]. The EA signal at probe energy $\hbar\omega$ is a change of the sample transmission in the presence of an applied electric field. This change can carry information about excited electronic states with ener-

gies near $\hbar\omega$. Electronic states of centrosymmetric materials are classified as dipole-allowed $|B_u\rangle$ and dipole-forbidden $|A_g\rangle$. The latter are invisible in linear absorption but play an important role in the non-linear-optical (NLO) response and relaxation processes. In particular, the EA intensity and lineshape strongly depend on the energies of the excited A_g and B_u states.

In many cases, the EA spectrum closely follows a derivative of the unperturbed absorption spectrum. The well-known case is a quadratic Stark shift for which an EA signal follows the first derivative (FD). The FD-like EA implies that an excited A_g state is near the $1B_u$ state and these two states are strongly dipole-coupled. The FD dominates the EA spectra of many conjugated polymers [6]. An EA spectrum

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following the second derivative (SD) was observed in various types of polyacetylenes [8–11] while an EA spectrum following a mix of SD and FD was reported for β -carotene [5]. The SD-like EA spectrum in polyacetylene was explained earlier as a field-induced broadening of defect [12] or excitonic states [9]. Recent interpretations of the SD-like EA involve the linear Stark effect appearing as a result of disorder-induced inversion symmetry breaking in the π -conjugated chain [7,13]. In this Letter we show that the SD-like EA can be interpreted as a quadratic Stark broadening.

If EA demonstrates a quadratic field dependence, it can be properly analysed in terms of the third-order NLO susceptibility $\chi^{(3)}(\omega; \omega, 0, 0)$, which can be calculated from a sum-over-state (SOS) model. The relationship between the absorption spectrum derivative and the EA spectrum seems to be first established by Aspnes and Rowe [14] for inorganic semiconductors. It was found that the EA follows the third derivative in a SOS $\chi^{(3)}$ model for extended states. For centrosymmetric materials with a discrete spectrum of states the derivative analysis of EA spectra was recently performed by Soos and co-authors [15] on the basis of a three-level model using Taylor expansion of the unperturbed absorption line-shape. The importance of the SD was shown in the case of overlapping B_u and A_g excited states. Petelenz analysed a simple dimer model for a pair of charge-transfer states in polyacenes [16]. He found that the quasi-degenerate pair of dipole-allowed and dipole-forbidden states corresponds to SD-like EA, whereas the well-separated pair corresponds to FD-like EA.

This Letter presents a systematic derivative analysis of the quadratic EA in terms of $\chi^{(3)}$ calculated within a centrosymmetric three-level SOS model. We show that the SD-like EA corresponds to quadratic Stark broadening and originates from the overlapping excited A_g and $1B_u$ states. The main parameter of the model is the ratio of the energy gap Δ between $|A_g\rangle$ and $|1B_u\rangle$ to the homogeneous line broadening parameter Γ . If $\Delta/\Gamma < 1$, then the SD dominates the EA profile (Stark broadening), if $\Delta/\Gamma > 1$, then the FD dominates the EA profile (Stark shift). Our model takes into account inhomogeneous broadening and vibronic sidebands of both excited states.

2. Derivative analysis in a three-level model

Assume that EA scales quadratically with the applied static electric field F . We do not consider here electrostriction and orientation contributions, which give EA signals following the absorption line-shape, i.e. the zero derivative [3].

We begin with an ideal one-dimensional case supposing that linear centrosymmetric non-interacting molecules with N electrons per unit volume are in vacuum. Consider a molecule with three states dominating the resonant optical response: the ground state $|G\rangle \equiv |1A_g\rangle$, the first dipole-allowed state $|1B_u\rangle$ and an excited dipole-forbidden state $|A_g\rangle$. According to Orr and Ward [17], the main contribution to F -induced optical polarization is given by the resonant term of $\chi^{(3)}$

$$\begin{aligned} \chi^{(3)}(\omega; \omega, 0, 0) &= \frac{2N}{\hbar^3} |\mu_0|^2 |\mu_1|^2 \frac{1}{(\omega_0 - \omega - i\Gamma)^2} \\ &\times \frac{1}{\omega_0 + \Delta - \omega - i\Gamma}, \end{aligned} \quad (1)$$

where ω_0 is the frequency of the dipole-allowed transition $|G\rangle \rightarrow |1B_u\rangle$ characterized by the matrix element μ_0 and $\Delta = \omega_{A_g} - \omega_0$ is the gap between $|A_g\rangle$ and $|1B_u\rangle$, which are coupled by the matrix element μ_1 .

The quadratic EA spectrum is given by a change in the absorption spectrum $\delta\alpha(\omega) = 4\pi\omega/(n(\omega)c) \text{Im}\chi^{(3)}(\omega)F^2$, where c is the light velocity and $n(\omega)$ is the refractive index. From Eq. (1) we have

$$\begin{aligned} \text{Im}\chi^{(3)}(\omega) &= \frac{2N}{\hbar^3} |\mu_0|^2 |\mu_1|^2 \Gamma \frac{1}{\left[(\omega_0 - \omega)^2 + \Gamma^2\right]^2} \\ &\times \frac{3(\omega_0 - \omega)^2 + 2(\omega_0 - \omega)\Delta - \Gamma^2}{(\omega_0 - \omega)^2 + 2(\omega_0 - \omega)\Delta + \Delta^2 + \Gamma^2}. \end{aligned} \quad (2)$$

2.1. Second derivative

Assume that $|1B_u\rangle$ and $|A_g\rangle$ are nearly degenerate, i.e. $|\Delta| \ll \Gamma$. Then Eq. (2) in the region of the

$|G\rangle \rightarrow |1B_u\rangle$ transition ($|\omega - \omega_0| \sim \Gamma$) can be expressed via the SD of the absorption lineshape¹

$$\begin{aligned} \text{Im} \chi^{(3)}(\omega) &= \frac{N}{\hbar^3} |\mu_0|^2 |\mu_1|^2 \frac{\partial^2}{\partial \omega^2} \frac{\Gamma}{(\omega - \omega_0)^2 + \Gamma^2} \\ &= |\mu_1|^2 \frac{\partial^2 \text{Im} \chi^{(1)}(\omega)}{\partial (\hbar \omega)^2}. \end{aligned} \quad (3)$$

$\text{Im} \chi^{(3)}(\omega)$ is negative near the absorption peak, when $|\omega - \omega_0| < \Gamma/\sqrt{3}$, and positive on the absorption edges. This can be considered as an F -induced broadening of the absorption lineshape. However, we note that this broadening is not an increase of Γ by a *constant* value that would mean a violation of the oscillator strength sum rule. Fig. 1a demonstrates that the EA lineshape is similar to the SD for $|\Delta| \leq \Gamma$. The EA peaks at ω_0 where it strongly depends on the linewidth, as Γ^{-3} , because of the triple resonance in Eq. (3). Note that from the SD-like EA one can directly obtain the transition dipole moment μ_1 (Eq. (3)).

2.2. First derivative

In the case of well-separated $|A_g\rangle$ and $|1B_u\rangle$, i.e. when $|\Delta| \gg \Gamma$, Eq. (2) gives in the region of the $|G\rangle \rightarrow |1B_u\rangle$ transition ($|\omega - \omega_0| \sim \Gamma$)

$$\begin{aligned} \text{Im} \chi^{(3)}(\omega) &= \frac{2N}{\hbar^3} |\mu_0|^2 |\mu_1|^2 \frac{1}{\Delta} \frac{\partial}{\partial \omega} \frac{\Gamma}{(\omega - \omega_0)^2 + \Gamma^2} \\ &= 2 |\mu_1|^2 \frac{1}{\hbar \Delta} \frac{\partial \text{Im} \chi^{(1)}(\omega)}{\partial (\hbar \omega)}. \end{aligned} \quad (4)$$

Thus, the perturbation of the absorption lineshape can be expressed through its FD and the Stark shift $\Delta_S(F)$

$$\begin{aligned} \delta \text{Im} \chi^{(1)}(\omega) &= \text{Im} \chi^{(3)}(\omega) F^2 \\ &= \frac{\partial \text{Im} \chi^{(1)}(\omega)}{\partial (\hbar \omega)} \Delta_S(F), \\ \Delta_S(F) &= 2 \frac{|\mu_1|^2 F^2}{\hbar \Delta}. \end{aligned} \quad (5)$$

¹ The FD and SD of $\alpha(\omega)$ near its resonances are proportional to the corresponding derivatives of $\text{Im} \chi^{(1)}(\omega)$ for soluble polymers and molecules in matrices [18].

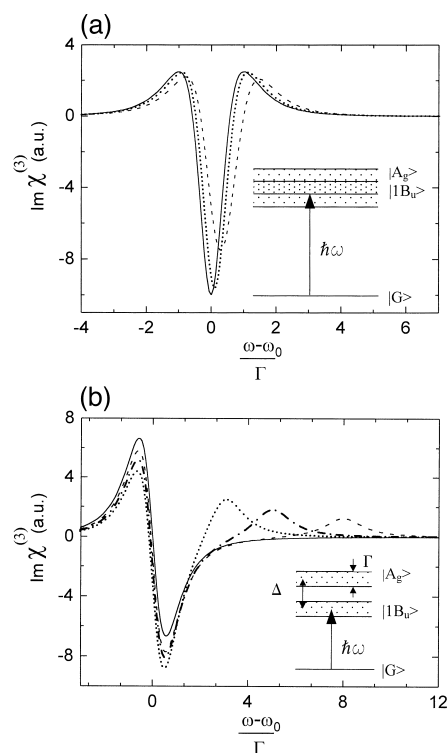


Fig. 1. EA spectra calculated from Eq. (2) and derivatives of the absorption spectrum. (a) Overlapping excited states: SD (solid line), $\Delta/\Gamma = 1/3$ (dotted line), $\Delta/\Gamma = 1$ (dashed line). (b) Non-overlapping excited states: FD (solid line), $\Delta/\Gamma = 3$ (dotted line), $\Delta/\Gamma = 5$ (dash-dotted line), $\Delta/\Gamma = 8$ (dashed line). Insets illustrate the energy diagram for the SD and FD cases.

Fig. 1b illustrates the EA closely following the FD near the $1B_u$ level for $\Delta \geq 3\Gamma$. Note that the larger the difference between $|\Delta|$ and Γ , the better the EA spectrum follows either the FD or the SD (Fig. 1). However, in the intermediate case, $\Gamma \leq |\Delta| \leq 3\Gamma$, $\text{Im} \chi^{(3)}$ can not be analytically expressed via a linear combination of the FD and the SD. The FD-like EA peaks at $\omega_0 \pm \Gamma/\sqrt{3}$ where it scales as $\mp (\Delta/\Gamma^2)^{-1}$ because of the double resonance in Eq. (4). As follows from Eqs. (3) and (4), the peak EA in the case of the degenerate excited states (Fig. 1a) is higher than that of the well-separated ones (Fig. 1b) by a factor $\approx 1.5\Delta/\Gamma$.

2.3. A_g lineshape

There is another contribution to EA for the well-separated $|A_g\rangle$ and $|1B_u\rangle$ ($|\Delta| > 3\Gamma$) that is not

described by the derivatives of the absorption lineshape. It corresponds to the dipole-forbidden transition $|G\rangle\text{--}|A_g\rangle$ at $\omega_0 + \Delta$, which becomes allowed in the presence of the electric field F (Fig. 1b). The lineshape of this weakly allowed transition is given by Eq. (2), which in the region $|\omega - \omega_0 - \Delta| \sim \Gamma$ can be rewritten as

$$\begin{aligned} \text{Im} \chi^{(3)}(\omega) &= \frac{2N}{\hbar^3 \Delta^2} |\mu_0|^2 |\mu_1|^2 \frac{\Gamma}{(\omega - \omega_0 - \Delta)^2 + \Gamma^2}. \quad (6) \end{aligned}$$

The peak EA for the dipole-forbidden transition ($|G\rangle\text{--}|A_g\rangle$) at $\omega_0 + \Delta$ is lower than that for the dipole-allowed transition ($|G\rangle\text{--}|1B_u\rangle$) at ω_0 by a factor $\approx 1.5\Gamma/\Delta$ (Fig. 1b). It should be stressed that in addition to the dominant term in $\chi^{(3)}(\omega)$ given by Eq. (1) there are other resonant terms in the full SOS $\chi^{(3)}(\omega; \omega, 0, 0)$ expression with peaks at ω_0 , $\omega_0 + \Delta$, and Δ [17,19]. We evaluated these terms and found that they can be neglected for $|\Delta| \ll \omega_0$.

3. Inhomogeneous broadening and derivatives

Inhomogeneous broadening in linear absorption can be described via a convolution of the homogeneous absorption lineshape $\text{Im} \chi_H^{(1)}(\omega)$ with the distribution $W_1(\omega_0)$ around the mean value $\bar{\omega}_0$ [20]

$$\text{Im} \chi^{(1)}(\omega; \bar{\omega}_0) = \int W_1(\omega_0) \text{Im} \chi_H^{(1)}(\omega; \omega_0) d\omega_0. \quad (7)$$

We take inhomogeneous broadening into account in our model as a convolution of the homogeneous EA lineshape $\delta \text{Im} \chi_H^{(1)}(\omega)$ with the factorized distribution of transition frequencies $W(\omega_0, \Delta) = W_1(\omega_0)W_2(\Delta)$ around the mean values $\bar{\omega}_0$ and $\bar{\Delta}$. If the distribution $W_2(\Delta)$ is within the homogeneous lineshape, $|1B_u\rangle$ and $|A_g\rangle$ are degenerate and therefore we have the SD case (Section 2.1). The inhomogeneously broadened EA lineshape reproduces the

SD shape of the inhomogeneously broadened unperturbed absorption

$$\begin{aligned} \delta \text{Im} \chi^{(1)}(\omega; \bar{\omega}_0) &= \int W_1(\omega_0) |\mu_1|^2 F^2 \frac{\partial^2 \text{Im} \chi_H^{(1)}(\omega; \omega_0)}{\partial(\hbar\omega)^2} d\omega_0 \\ &= |\mu_1|^2 F^2 \frac{\partial^2 \text{Im} \chi^{(1)}(\omega; \bar{\omega}_0)}{\partial(\hbar\omega)^2}. \quad (8) \end{aligned}$$

If the excited states gaps Δ given by $W_2(\Delta)$ exceed a few homogeneous widths Γ , we have the FD approximation (Section 2.2). In this case the inhomogeneously broadened EA follows the FD of the inhomogeneously broadened absorption lineshape

$$\begin{aligned} \delta \text{Im} \chi^{(1)}(\omega; \bar{\omega}_0) &= \int \int W_1(\omega_0) W_2(\Delta) \frac{2|\mu_1|^2 F^2}{\hbar \Delta} \\ &\quad \times \frac{\partial \text{Im} \chi_H^{(1)}(\omega; \omega_0)}{\partial(\hbar\omega)} d\omega_0 d\Delta \\ &= 2|\mu_1|^2 F^2 \frac{\partial \text{Im} \chi^{(1)}(\omega; \bar{\omega}_0)}{\partial(\hbar\omega)} \int \frac{W_2(\Delta)}{\hbar \Delta} d\Delta. \quad (9) \end{aligned}$$

Thus, in the above model inhomogeneous broadening does not break the correlation between the EA and the derivatives. This correlation holds if the conjugated chains forming an inhomogeneously broadened lineshape can be characterized by the same polarisability. If this is not the case, for instance if longer conjugated chains have higher transition dipole moments, the correlation between the EA and the derivatives decreases. In this case the response of the longest chains dominates the EA and therefore it should be red shifted relative to the derivatives. Such a red shift was observed in FD-like EA of MEH-PPV films [6] and in SD-like electroreflectance of directly synthesized *trans*-polyacetylene films [11].

4. Vibronic structure and derivative analysis

Both EA and absorption spectra of conjugated molecules and polymers demonstrate vibronic struc-

ture, i.e. each electronic transition has a series of vibronic replicas. The vibronic structure in EA of conjugated materials was analysed in Refs. [15,21] in the adiabatic, the Condon and the displaced harmonic oscillators approximations. In this section we include vibronic structure in the derivative analysis of EA spectra.

For simplicity we take into account the single backbone normal vibration which is the most strongly coupled with the π electrons. According to Ref. [15] and Eq. (1), vibronic sidebands in the above three-level model are readily taken into account. Each pair of vibronic sublevels (p, q) (p and q correspond to $|1B_u\rangle$ and $|A_g\rangle$, respectively) gives an additive contribution to $\chi^{(3)}(\omega)$, which depends on the appropriate Franck–Condon factors F_{pq}

$$\chi^{(3)}(\omega) = \frac{2N}{\hbar^3} |\mu_0|^2 |\mu_1|^2 \sum_{p,q} \frac{F_{0p}^2(b) F_{pq}^2(a)}{(\omega_0 + p\Omega_B - \omega - i\Gamma_p)^2} \times \frac{1}{\omega_0 + \Delta + q\Omega_A - \omega - i\Gamma_{pq}}, \quad (10)$$

where Ω_B and Ω_A are the vibrational frequencies of $|1B_u\rangle$ and $|A_g\rangle$, respectively, in which the corresponding broadening parameters are Γ_p and Γ_{pq} . b denotes the difference in the normal coordinate between the potential surfaces minima of $|G\rangle$ and $|1B_u\rangle$, a denotes the corresponding difference between $|1B_u\rangle$ and $|A_g\rangle$, $p, q = 0, 1, \dots$. As follows from the above model (Section 2) and Eq. (10), each overlapping pair of vibronic sublevels (p, q) (a pair for which the gap $|\Delta_{pq}| = |\Delta - p\Omega_B + q\Omega_A| < \Gamma_{pq}$) gives a dominant contribution to EA as the SD while each well-separated pair ($|\Delta_{pq}| > 3\Gamma_{pq}$) contributes to EA mainly as the FD.

To illustrate the effect of overlapping vibronic sidebands, we have calculated² the EA spectrum for a negative gap $\Delta = -2\Omega$ (Fig. 2). Such a case of negative Δ may correspond to polyenes [22] and some non-luminescent polymers for which $E_{A_g} <$

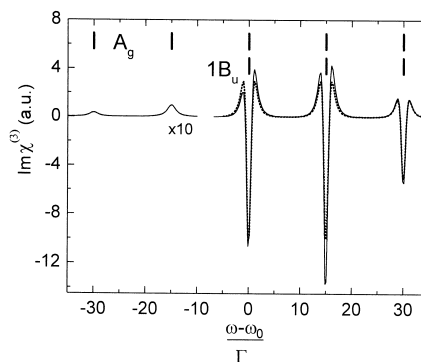


Fig. 2. EA calculated from Eq. (10) for the following parameters: $\Delta = -2\Omega$, $\Omega = 1500 \text{ cm}^{-1}$, $\Gamma = 100 \text{ cm}^{-1}$, $a = b = 1.41$, $\hbar\omega_0 \sim 2 \text{ eV}$. The lowest five vibronic levels of $|1B_u\rangle$ and $|A_g\rangle$ (bars) are taken into account. The dotted line shows the SD.

E_{1B_u} [23]. As seen in Fig. 2, the SD-like contributions to the EA dominate in the region of the overlapping vibronic sidebands. These SD-like lineshapes are somewhat asymmetric due to small FD-like contributions from the well-separated vibronic sidebands. The ratio of the SD contribution from (p, q) to the FD one from ($p, q \pm 1$) is estimated as Ω/Γ , with the Franck–Condon factors omitted (Section 2.2). In addition to the FD- and SD-like contributions to EA in the region of the $|1B_u\rangle$ vibronic sidebands, the $|A_g\rangle$ vibronic sidebands can be resolved in the EA spectrum (Fig. 2). Inhomogeneous broadening can be readily included in the model according to Section 3. As was mentioned above, SD-like EA is observed in various polyacetylenes. In particular, we observed the SD-like EA spectrum for both isomers of nanopolyacetylene [10]. This is in agreement with the EA spectrum in Fig. 2. The energy diagram in Fig. 2 reflects the non-luminescent nature of polyacetylenes.

5. Conclusions

The above three-level model establishes relations between the quadratic EA spectrum and the derivatives of the absorption spectrum for centrosymmetric molecules and polymers. In addition to the well-studied Stark shift effect associated with the FD, the model gives a natural explanation for the SD-like EA as a manifestation of the Stark broadening. From the

² We consider here the simplest case in which the broadening parameter $\Gamma = \Gamma_p = \Gamma_{pq}$ is a constant and the normal mode frequency $\Omega = \Omega_B = \Omega_A$ is the same in the electronic states involved.

SD-like EA one can directly obtain the transition dipole moment between the electronic excited states. The model gives relative intensities of the FD EA, the SD EA, and the EA in the region of the dipole-forbidden transition $|G\rangle \rightarrow |A_g\rangle$ weakly allowed in the presence of the electric field. Inhomogeneous broadening and vibronic sidebands have been included in the model. Thus, the model gives a very useful and comprehensive tool for analysing EA spectra of conjugated molecules and polymers.

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References

- [1] M. Cardona, *Modulation Spectroscopy*, Academic Press, New York, 1969.
- [2] D.E. Aspnes, *Surf. Sci.* 37 (1973) 418.
- [3] C. Poga, T.M. Brown, M.G. Kuzyk, C.W. Dirk, *J. Opt. Soc. Am. B* 12 (1995) 531.
- [4] A. Elschner, G. Weiser, *Chem. Phys.* 98 (1985) 465.
- [5] F. Rohlfing, D.D.C. Bradley, *Chem. Phys. Lett.* 277 (1997) 406.
- [6] I.M. Liess, S. Jeglinski, Z.V. Vardeny, M. Ozaki, K. Yoshino, Y. Ding, T. Barton, *Phys. Rev. B* 56 (1997) 15712.
- [7] G. Weiser, A. Horvath, *Chem. Phys.* 227 (1998) 153.
- [8] J. Orenstein, G.L. Baker, Z. Vardeny, *J. Phys. (Paris) Colloq.* 44 (1983) 403.
- [9] G. Lanzani, G. Kanner, S. Jeglinski, Z.V. Vardeny, *Synth. Met.* 50 (1992) 461.
- [10] D.Yu. Paraschuk, T.A. Kulakov, R.I. Rokitskii, V.M. Kobryanskii, *Synth. Met.* 84 (1997) 949.
- [11] T. Nishioka, T. Yamada, S. Shibahara, K. Ishikawa, H. Takezoe, A. Fukuda, *Jpn. J. Appl. Phys. Pt. 1/36* (1997) 1099.
- [12] S.D. Phillips, R. Worland, G. Yu, T. Hagler, R. Freedman, Y. Cao, V. Yoon, J. Chiang, W.C. Walker, A.J. Heeger, *Phys. Rev. B* 40 (1989) 9751.
- [13] A. Horvath, G. Weiser, G.L. Baker, S. Etemad, *Phys. Rev. B* 51 (1995) 2751.
- [14] D.E. Aspnes, J.E. Rowe, *Phys. Rev. B* 5 (1972) 4022.
- [15] Z.G. Soos, D. Mukhopadhyay, M.H. Hennessy, *Chem. Phys.* 210 (1996) 249.
- [16] P. Petelenz, *Chem. Phys.* 171 (1993) 397.
- [17] B.J. Orr, J.F. Ward, *Mol. Phys.* 20 (1971) 513.
- [18] T.A. Kulakov, Ph.D. Thesis, Faculty of Physics, Moscow State University, Moscow, Russia, 1997.
- [19] N. Bloembergen, H. Lotem, R.T. Lynch, *Indian J. Pure Appl. Phys.* 16 (1978) 151.
- [20] S. Mukamel, *Principles of non-linear optical spectroscopy*, Oxford University Press, New York, 1995.
- [21] D. Mukhopadhyay, Z.G. Soos, *J. Chem. Phys.* 104 (1996) 1600.
- [22] B.E. Kohler, C. Spangler, C. Westerfield, *J. Chem. Phys.* 89 (1988) 5422.
- [23] M. Ozaki, E. Ehrenfreund, R.E. Benner, T.J. Barton, K. Yoshino, Z.V. Vardeny, *Phys. Rev. Lett.* 79 (1997) 1762.