



First hyperpolarizability of the molecular excited states: Calculations for *p*-nitroaniline and comparison with experiments

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Abstract

We calculated the first hyperpolarizability of the molecules with some fraction of both ground and excited state populations. We used a numerical procedure employed widely known software. The comparison with experimental data for para-nitroaniline molecule obtained by the Hyper-Rayleigh technique is done.

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1. Introduction

Many applications in photonics are based on non-resonant second- and third-order optical nonlinear processes. They occur due to virtual electronic transitions and are described by the first $\beta(-\omega_3; \omega_1, \omega_2)$ and second $\gamma(-\omega_4; \omega_1, \omega_2, \omega_3)$ hyperpolarizabilities, respectively. Such processes, as they involve only virtual electronic excitations, are essentially instantaneous, and avoid attenuation of optical signals. Magnitudes and signs of β and γ are determined by the electronic structure of molecule and by the frequency of optical waves ω_i participating in a given nonlinear process.

Usually hyperpolarizabilities are studied for molecules in their ground state. However the real population of the initial state for the virtual elec-

tronic excitations can include not only the ground state but also excited states populated owing to an external source. As is shown in [1–3] non-resonant optical nonlinear processes can be changed if the excited states are populated. This effect is mainly due to the incorporation of new energy levels allowed to the virtual transitions responsible for the nonlinear process.

Experimental and theoretical studies of the excited-state hyperpolarizabilities were done mainly for second hyperpolarizabilities $\gamma(-\omega_4; \omega_1, \omega_2, \omega_3)$ [1–9].

The first hyperpolarizability $\beta(-\omega_3; \omega_1, \omega_2)$ of molecules with excited states has been more sparsely investigated. Theoretical calculations of $\beta(-2\omega; \omega, \omega)$ for 1,1-dicyano-8-dimethylamino-octatetraene and trans-octatetraene were done in [3]. The hyper-Rayleigh Scattering (HRS) measurements in solution of *p*-nitroaniline (PNA) in methanol showed that β increases upon 10 ns pulse

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excitation at 464 nm. By *CW* excitation (457.9 nm) of the PNA an increase of the HRS signal was also observed [10–12]. From the time dependence of HRS intensity the life time of the excited state (9.3 ns) and the value of β at the excited state (2.05×10^{-27} esu) were found [10]. First hyperpolarizabilities for several twisted intramolecular charge transfer molecules including PNA at the ground and excited states have been calculated in [13] using CNDO/S method. For PNA the enhancement of the β -values for the excited states by 10–30 times was predicted. In our recent paper [14] we reported results on the HRS measurements in the PNA by pulse excitation at 355 nm. We observed that the contribution of optically pumped excited states to the total first hyperpolarizability depends of the energy of pump photons: in contrast to [10–12] we found a decrease of the first hyperpolarizability for the excited molecules.

In this Letter we report results of numerical calculations of the first hyperpolarizability $\beta(-2\omega; \omega, \omega)$ of PNA in excited states. We choose this molecule for the following reasons. The nonlinear properties of the molecule in the ground state are well studied experimentally and theoretically [15–18]. It is important also to have a good knowledge of the photo-physical properties of the molecule studied, in particular to know the ways of energy transformation of the molecule after excitation. Some properties of the PNA molecule with excited states have been investigated by different techniques [19–21]. Also the nonlinear properties of the molecule in excited states can be calculated with reasonable accuracy due to its relative small size and comparisons with experiments [10–12, 14] can be done.

Unlike [13] we suppose that two states (the ground state and an excited state) are populated. We applied directly the standard perturbation theory and by calculations of the dipole moments, transitions dipole moments and transitions energies we used widely known software.

2. Theory

We suppose that a molecule is initially at the excited state such as two energy levels – the ground

state *g* and the first electronic excited state *e* – are populated and the populations of the both states are stationary. We suppose that a source of excitation produces the distribution of population such as the ground and excited states are coherent during the time needed for nonlinear polarization measurements. A non-resonant monochromatic probe beam with frequency ω induces nonlinear optical processes at frequencies different from the resonant frequencies for transitions between the ground state and excited states, i.e., both the fundamental probe and output signals fall in the transparency regions, experiencing no optical loss (Fig. 1).

We calculated the nonlinear response of the excited molecule using standard time-dependent perturbation theory [22]. We express the wave function of our system Ψ as a superposition of wave functions of the ground Ψ_g and excited states Ψ_e : $\Psi = a\Psi_g + b\Psi_e$, where a and b vary between 0 and 1. The second-order contribution to the induced nonlinear polarization $p_i^{(2)}$ generated by the fundamental field $E_j(\omega)$ contains following components:

$$p_i^{(2)} = \{ \beta_{ijk}(-2\omega; \omega, \omega) + R_{ijk}(-2\omega - \omega_{eg}; \omega, \omega, \omega_{eg}) + R_{ijk}(-2\omega + \omega_{eg}; \omega, \omega, \omega_{eg}) \} E_j(\omega) E_k(\omega).$$

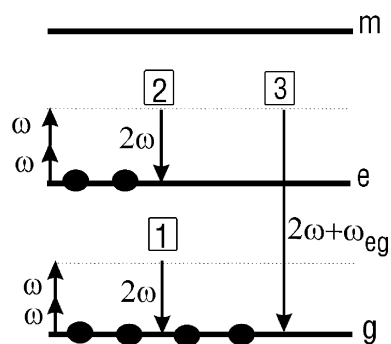


Fig. 1. Two energy levels (the ground state *g* and first electronic excited state *e*) are occupied. There are several contributions into the first hyperpolarizability at the frequency 2ω (for example, 1 and 2) and different contributions (for example, 3) with frequency $2\omega + \omega_{eg}$ due to the Raman-type processes. Here ω_{eg} is the frequency of transition between the ground state and first excited state, and *m* is the second excited state.

Here $\beta_{ijk}(-2\omega; \omega, \omega)$ is the first hyperpolarizability, $R(-2\omega \pm \omega_{eg}; \omega, \omega, \omega_{eg})$ are the Stokes and anti-Stokes Raman components of the nonlinear polarization emitted by the molecule at the frequencies $2\omega - \omega_{eg}$ and $2\omega + \omega_{eg}$, respectively. These signals are due to the presence of the populated excited state. However, all nonlinear measurements use filters to select the desired wavelength, and therefore by HRS measurements at the frequency 2ω the first term only should be included. The expression for $\beta_{ijk}(-2\omega; \omega, \omega)$ is given by

$$\beta(-2\omega; \omega, \omega) = \left[\rho_{gg} \Pi_{gg}^{ijk} + \rho_{ee} \Pi_{ee}^{ijk} + \rho_{eg} \Pi_{eg}^{ijk} + \rho_{ge} \Pi_{ge}^{ijk} \right],$$

where

$$\Pi_{\alpha\alpha}^{ijk} = \frac{1}{8\hbar^2} P_1 \sum_{m,n} \left\{ \frac{\mu_{\alpha n}^i \mu_{nm}^j \mu_{m\alpha}^k}{(\omega_{n\alpha} - 2\omega)(\omega_{m\alpha} - \omega)} + \frac{\mu_{m\alpha}^i \mu_{mn}^j \mu_{n\alpha}^k}{(\omega_{m\alpha} - \omega)(\omega_{n\alpha} - \omega)} + \frac{\mu_{m\alpha}^i \mu_{nm}^j \mu_{\alpha n}^k}{(\omega_{m\alpha} - 2\omega)(\omega_{m\alpha} - \omega)} \right\},$$

if $\alpha = \beta$,

and

$$\Pi_{\alpha\beta}^{ijk} = \frac{1}{8\hbar^2} P_1 \sum_{m,n} \left\{ \frac{\mu_{m\alpha}^i \mu_{mn}^j \mu_{n\beta}^k}{(\omega_{m\alpha} - \omega)(\omega_{n\beta} - \omega)} \right\},$$

if $\alpha \neq \beta$.

Here $\mu_{m\alpha}^i$ is the matrix element of the dipole moment operator along the i th molecular axis between the electronic states m and α , P_1 is the full permutation operator, $\rho_{gg} = |a|^2$, $\rho_{ee} = |b|^2$, and $\rho_{ge} = ab$ [22]. As seen, the total value of nonlinear response of the molecules that have some fraction of both ground and excited state populations includes also two terms proportional to the product of the populations of the ground and excited states.

Calculations of the dipole moments, transitions dipole moments $\mu_{m\alpha}^i$ and transition energies $\omega_{m\alpha}$ were performed using the semi-empirical Intermediate Neglect of Differential Overlap (INDO) Hamiltonian [23,24] implemented within ZINDO

program [25]. The configuration interaction technique with single excitations (INDO/S-CI) was used. The geometry of the PNA molecule was obtained using the AM1 (Austin model 1) Hamiltonian [26], implemented in the MOPAC93r2 program [27], which shows an excellent performance in predicting of the structures of organic molecules [28].

Below we present all calculated values of the first hyperpolarizability in terms of the total intrinsic first hyperpolarizability [29] $\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$, where $\beta_i = \beta_{iii} + \frac{1}{3} \sum_{i \neq j} (\beta_{ijj} + \beta_{jij} + \beta_{jji})$.

3. Results

Before proceeding with calculations of the first hyperpolarizability we compare the experimental and calculated spectra of linear absorption (Fig. 2). At least in terms of the band gap energy the experimental and theoretical results are in good agreement. These spectra have been thoroughly investigated [15,18,21,30,31]. Their most striking feature is the appearance of a partial electron migration in the molecule. Because of this migration there are two bands in the spectra in the range 200–420 nm. The band near 380 nm is due to the transition $n_{\text{NH}_2} \rightarrow n_{\text{NO}_2}^*$ with charge transfer from the nitrogen nonbonding orbital of the amino group to vacant orbital of the nitro group. The experiments [10–12] were done at the pump ener-

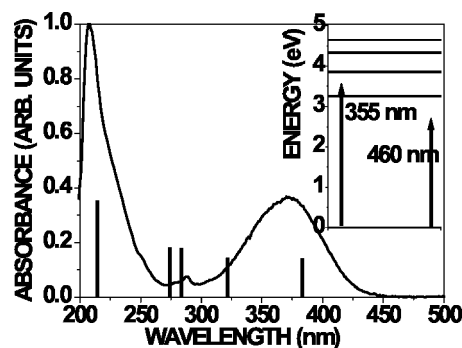


Fig. 2. Experimental (solid line) absorption spectra of the PNA molecule [14]. Vertical solid lines indicate the relative oscillator strength calculated at the energies for electronic transitions between ground and excited states.

gies of 464 nm (pulse excitation) and 457.9 nm (CW excitation) that are lower than the energy of maximal absorption. The pump energy in our experiment (355 nm) [14] is higher than the energy of maximal absorption. One can explain the absorption of the PNA by considering a possible electronic-state diagram [20,21]. The absorption band is due to the transition from the ground state S_0 to an excited singlet state S_1 (the transition energy $E_{S_0S_1} = 3.25$ eV). The fluorescence spectrum obtained with the pump energy $E_{\text{pump}} = 3.49$ eV shows one very weak band near 409 nm (3.03 eV) which is due to the fluorescence from the S_1 state with a short (picosecond) mainly radiationless decay life-time. The rapid decay of the S_1 state of PNA is due to very rapid intersystem crossing to a triplet state T_1 . The T_1 life-time determined from the decay of the time-resolved-microwave conductivity measurements was found to be 54 ns for PNA in benzene [21]. This unusual short time for T_1 to S_0 was ascribed to substantial mixing between T_1 and S_1 states, resulting in considerable singlet character of T_1 and enhanced efficiency for intersystem crossing to S_0 . This strong $T_1 \leftrightarrow S_1$ mixing indicates that S_1 and T_1 are close in energy and probably of different electronic configurations, i.e., ${}^1n\pi^*$ and ${}^1\pi\pi^*$. The lowest ${}^1n\pi^*$ and ${}^3\pi\pi^*$ are also close in energy and both contribute to the first absorption band of PNA [19,20,32]. The general conclusion is therefore that all of the lowest $n\pi^*$ and $\pi\pi^*$ singlet and triplet states of PNA are very close to each other.

It should be pointed out that within the limits of our simple model we could not include triplet excited states and hence the effect of strong $T_1 \leftrightarrow S_1$ mixing. This may be responsible for distinctions between the experimental spectrum and calculated energies of electronic transitions.

Supposing the population of the ground state ρ_{gg} or excited state ρ_{ee} to be equal to zero we calculated separately the first hyperpolarizabilities of the ground state β_g and excited state β_e . The dispersion behavior of these values is shown in Fig. 3. The calculated values of β_g and β_e correlate well with results published previously [13,29]. Throughout the entire energy range β_e is larger than β_g . The enhanced magnitude of β_g can be explained from the following reasons. Most chro-

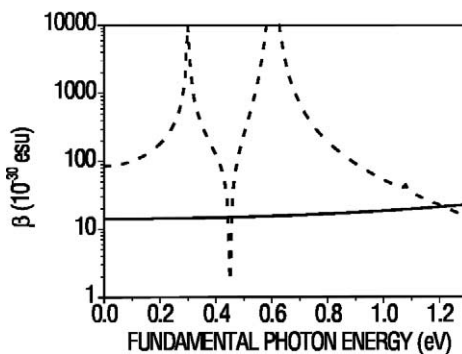


Fig. 3. Calculated dispersion curves of β_g (solid line) and β_e (dash line).

mophoric structures possess only one highly-allowed electronic transition in the visible or near-UV spectral region; that is, if μ_{ge} is large, μ_{gm} must be small. It means that the two-level contribution $\mu_{ge}\mu_{ee}\mu_{eg}$ must be larger than the three-level contribution $\mu_{ge}\mu_{em}\mu_{mg}$. Let us compare now the two-level contributions for the ground state hyperpolarizability and for the excited state hyperpolarizability. β_g is mainly proportional to $\mu_{ge}\mu_{ee}\mu_{eg} = |\mu_{eg}|^2\mu_{ee}$, however β_e is proportional to $\mu_{eg}\mu_{gg}\mu_{ge} = |\mu_{eg}|^2\mu_{gg}$. Usually [29] $\mu_{gg} \gg \mu_{ee}$, therefore we can expect that $\beta_e > \beta_g$.

An important result of our analysis is that the total first hyperpolarizability as a function of the population of the excited state can have a non-monotonic behavior. In fact, Fig. 4 shows an example of such a behavior obtained for the fun-

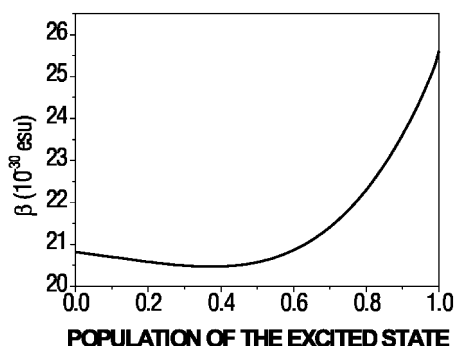


Fig. 4. Total first hyperpolarizability of the PNA molecule versus the population of the excited state. The fundamental photon energy is 1.17 eV (1064 nm).

damental photon energy of 1.17 eV that is the same as in the experiments [10–12,14]. In fact we observe a slight decrease of the total hyperpolarizability if the population of the excited state increases. By further increase of the population the total hyperpolarizability increases also. As the expression for $\beta(-2\omega; \omega, \omega)$ suggests the total value of first hyperpolarizability includes also the terms that are proportional to the product of the population of the ground and excited states. Since β_g and β_e have almost the same values at the 1.17 eV (see Fig. 3) the contribution of these terms becomes important. The β_e -spectrum has several infinitely sharp resonances. They are due to two-photon resonances by optical transitions between the ground state and excited states.

As indicated in Fig. 3, the enhancement of first hyperpolarizability is much higher at lower fundamental photon energies. In particular, for practical applications in fiber optics communications optical signals at 1550 nm ($\hbar\omega = 0.8$ eV) are of importance. For this fundamental photon energy the enhancement comprises more than one order of magnitude.

The experimental studies [10–12,14] showed that the contribution of optically pumped excited states to the total first hyperpolarizability depends of the energy of pump photons. To explain this difference we note first that the energy of pump photon of 355 nm is higher than the energy gap between the ground state and first excited state, whereas the energy of pump photon (460 nm) is below this gap. Hence, these two pump photons create different distribution of population of the excited state. Probably the population of the excited states by the 355 nm pump is lower than by the 460 nm pump due to the best coupling with triplet states. Following the Fig. 4 this can result to decreasing of the first hyperpolarizability. Of course, full understanding of such experimental facts should include additional experimental and theoretical studies, in particular the strong and rapid intersystem crossing to a triplet state T_1 must be included.

In conclusion, in this Letter we proposed a simple numerical procedure employed well-known software in order to calculate the first hyperpolarizability of the molecules with populated excited

states. The procedure may be improved for instance by including damping of excited states, vibrational states, optimization of the molecule geometry at the excited state both for singlet and triplet states, etc. The important result of our analysis is that the total first hyperpolarizability as a function of the population of excited state may have a nonmonotonic behavior.

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