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Giant Dipole Moment in a Triad System. Mechanisms of Anisotropic Photoresponse in the Transient dc Conductivity of Dipolar Solutes

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A transient dc conductivity method was used to observe formation of a giant dipole moment for the triad molecule MA-ANI-NI (methoxyaniline-aminonaphthalimide-dimethylphenyl-naphthalenediimide-octyl) in toluene. The independence of the dipole moment on excitation wavelength indicates high efficiency of intramolecular energy or (and) electron transfer. The effect of light polarization on the DC conductivity signal caused by a photoinduced increase in solute dipole moment is considered in detail. It is shown that the time variation of the signal includes information about structural anomalies in the angular distribution function of molecular dipoles and depends on light polarization even for zero ground state dipole moment. Nonzero ground state dipole moment and (or) electric field dependence of the charge transfer rate constants give an additional source for an anisotropic photoresponse signal. Analysis of the photoresponse and its anisotropy for the triad gives ground (μ_g), first (μ_1), and second (μ_2) excited state dipole moments as follows: $\mu_g = 12 \pm 5$ D, $\mu_1 = 35 \pm 10$, and $\mu_2 = 87 \pm 6$ D. The lifetime of the giant dipole state is $\tau = 290 \pm 10$ ns, and the molecule's rotational time is $\tau_r = 1.6 \pm 0.15$ ns.

Introduction

The main goal in mimicking photosynthesis is to use light to separate charges for chemical energy storage, *i.e.*, to separate charges by distances as large as possible for times as long as possible. Other important features are a broad spectrum of photoactivity and low energy loss between excitation and charge separation.

In this paper we study a very promising system: methoxyaniline-aminonaphthalimide-dimethylphenyl-naphthalenediimide-octyl (which we abbreviate as MA-ANI-NI, see Figure 1) in toluene solution. According to transient absorption measurements,¹ this triad molecule with ANI as a chromophore, MA as an electron donor, and NI as the acceptor undergoes multistep electron transfer. Excitation at wavelengths longer than 415 nm (primarily of the aminonaphthalimide (ANI) moiety) leads in 8 ps to an electron transfer from the methoxyaniline (MA) group to ANI with >99% yield. In the second step, an electron transfer from ANI⁻ to the naphthalene-diimide (NI) group competes with relaxation to the ground state (5.3 ns) and takes some 0.43 ns in toluene at room temperature. The resultant long range charge separated state is formed with a quantum yield of 0.92 and lasts for about 300 ns.

The transient dc conductivity method has been successful in studies of photoinduced dipole moments in a variety of systems including intramolecular^{2–5} and intermolecular⁶ charge transfer. In this paper we use the transient dc conductivity technique to study charge separation in MA-ANI-NI. For this complicated system, we also had to improve theoretical understanding of the technique.

In the previously developed theory of this method,³ we assumed that the angular distribution function of the dipoles deviated only slightly from equilibrium, hence only first order

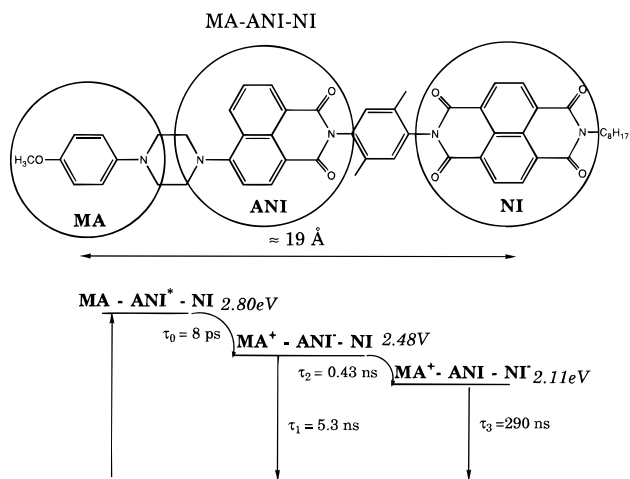


Figure 1. MA-ANI-NI molecule used in this study and diagram of three step charge separation with characteristic times measured by transient absorption in toluene¹.

Legendre polynomials were included. If new dipoles are created with substantial anisotropy, then the general case of an anisotropic angular distribution should be considered. Here we consider the general solution for small electric fields in detail and the experimentally relevant case of dipoles formed by linearly polarized light.

The anisotropy of the initial distribution is caused by three factors: the light polarization, a nonzero dipole moment of the ground state molecules, and any electric field dependence of the electron transfer. The latter is distinguishable only if the electron transfer occurs within the time scale of molecular rotation. All three factors affect the polarized-light dependence of the photoresponse. The difference between the signals for two perpendicular light polarizations (called the depolarization signal) reflects this anisotropy. As we will see, the depolar-

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ization signal exists even for molecules with a zero ground state dipole moment. The theoretical treatment was applied to MA-ANI-NI in toluene. All three mechanisms which can produce signal anisotropy were evaluated.

The analysis of the photoresponse signal gave ground (μ_g), first (μ_1), and second (μ_2) excited state dipole moments of $\mu_g = 12 \pm 5$ D, $\mu_1 = 35 \pm 10$ D, and $\mu_2 = 87 \pm 6$ D. The lifetime of the giant dipole state is $\tau = 290 \pm 10$ ns, and the molecule's rotational time is $\tau_r = 1.6 \pm 0.15$ ns. The moment μ_2 agrees with the expected distance of about 19 Å (4.8 D/Å) between the donor and acceptor centers. The yield of giant dipole formation was found to be independent of the excitation wavelength in a range over which the incident radiation varies from being absorbed virtually exclusively by chromophore (ANI) to over two-thirds being absorbed by acceptor (NI). This indicates the existence of an efficient intramolecular energy transfer from acceptor to chromophore or (and) an alternative electron transfer to the excited state of the acceptor.

Theory

As already discussed,^{3,4} a transient photoconductivity (photodisplacement) signal v measures the voltage variation across a load resistor R

$$v + \tau_{RC} \frac{dv}{dt} = \frac{R}{d} \frac{dP}{dt} \quad (1)$$

where τ_{RC} is the RC time of the circuit and d is the gap between cell electrodes.

We consider the problem of the time variation of the polarization P in a system of dipolar species in a condensed medium where the concentrations of the dipoles can vary in time. First, we introduce an angular distribution function $f_i(\Theta_i)$ for dipoles of type i . Retaining only linear terms in the Taylor series expansion with respect to the external electric field E , the concentration of the i th sort of dipole (with dipole moment μ_i) in a solid angle $d\Omega_i$ will vary in time according³ to eq 2

$$\frac{\partial f_i n_i}{\partial t} = \frac{n_i}{2\tau_r \partial \xi} \left(\left(\frac{\partial f}{\partial \xi} - \gamma_i E \right) (1 - \xi^2) \right) + \sum_{j \neq i} (f_j k_{ji} n_j - f_i k_{ij} n_i) \quad (2)$$

where n_i is the concentration of the i th dipoles; k_{ij} is the rate constant with which dipole moment μ_i transforms into dipole moment μ_j ; τ_r is the rotational time (assumed to be the same for all the dipoles), $\xi_i = \cos \Theta_i$ with Θ_i the angle between the dipole moment μ_i and the external electric field E . The coefficient γ_i depends on the dipole moment, the molecular shape, and the dielectric constant ϵ of the surrounding solvent:³

$$\gamma_i = \frac{f_c \mu_i}{k_B T} = \frac{\epsilon}{\epsilon + (1 - \epsilon) A k_B T} \mu_i \quad (3)$$

here f_c is called the local field factor, and A describes the degree of molecular nonsphericity.^{3,7,8} For a spherical molecular cavity, A equals 1/3.

The general solution of eq 2 may be written as an expansion in Legendre polynomials. The distribution function (averaged over polar angles) may be written as

$$f_i(\xi_i) = \frac{1}{2} \left(1 + \sum_{l \geq 1} a_l^i P_l(\xi_i) \right) \quad (4)$$

where $P_l(\xi_i)$ is the Legendre polynomial of order l . At equilibrium, the high order coefficients a_l^i are of order $(\mu_i E / k_B T)^l$. After substitution of eq 4 into eq 2, we have

$$l = 0: \frac{dn_i}{dt} = \sum_{j \neq i} (k_{ji} n_j - k_{ij} n_i) \quad (5)$$

$$l \geq 1: \sum_{l \geq 1} P_l \frac{d(a_l^i n_i)}{dt} = -\frac{n_i}{\tau_r} E \xi + \sum_{l \geq 1} \left(\frac{n_i}{\tau_r} \left\{ -\frac{l(l+1)}{2} P_l a_l^i + A_l a_l^i \right\} + \sum_{j \neq i} P_l \{ k_{ji} n_j a_j^l \beta_{ji}^l - k_{ij} n_i a_i^l \} \right) \quad (6)$$

where

$$A_l = \xi P_l - \frac{1 - \xi^2}{2} \frac{\partial P_l}{\partial \xi} = \frac{(l+1)(l+2)P_{l+1} - 2(l-1)P_{l-1}}{2l+1}$$

The dipole moments of i and j might not be collinear, and so factors β_{ij}^l are introduced. They represent the degree of overlap between corresponding Legendre polynomials for dipoles i and j . Specifically, if these dipoles are mismatched by the angle Θ_{ij} , then

$$\beta_{ij}^l = P_l(\cos \Theta_{ij}) \quad (7)$$

As seen from eq 7, the correlation factor for transformation of dipole i into dipole j is the same as for the reverse case, i.e., $\beta_{ij}^l = \beta_{ji}^l$.

The electric polarization equals

$$P = -\sum n_i \int \mu_i f_i \xi_i d\xi_i = \sum \frac{1}{3} n_i \mu_i a_i^1 \quad (8)$$

To calculate P in the vicinity of equilibrium, one needs only an equation for the first Legendre polynomial ($l = 1$). The only reason that we need second order polynomial ($l = 2$) is that the initial distribution function f_i after excitation with light is far from the equilibrium one, and a_i^2 is of order unity (instead of order E^2 as at equilibrium). It is worthwhile mentioning that even if one creates dipoles in an initial state with $a_i^1 \sim 1$ for any higher order of l , it is not necessary to include equations for them in calculation of the electrical polarization. Indeed, in the linear by electric field approximation, a_i^1 does not depend on any order of a_i^l higher than a_i^2 . Thus we need to consider in eq 6 only terms with $l = 1$ and 2. After defining $y_i = n_i a_i^1$ and $z_i = n_i a_i^2$ we arrive at the following equations:

$$\begin{aligned} \frac{dy_i}{dt} &= \frac{1}{\tau_r} \left(-y_i + \gamma_i E \left(n_i - \frac{2}{5} z_i \right) \right) + \sum_{j \neq i} \{ k_{ji} y_j \beta_{ji} - k_{ij} y_i \} \\ \frac{dz_i}{dt} &= -\frac{3z_i}{\tau_r} + \sum_{j \neq i} \left\{ k_{ji} z_j \frac{3\beta_{ji}^2 - 1}{2} - k_{ij} z_i \right\} \end{aligned} \quad (9)$$

As an example we consider a two state model. For simplicity assume that the excited state with dipole moment μ_s has a very long lifetime. Then eqs 9 and 1 lead to the following solution for the photodisplacement signal (see Appendix A):

$$v = B \left(\frac{(\mu_s^2 - \mu_g^2)}{\tau_r} \left(e^{-\frac{t}{\tau_r}} + \frac{\chi 3\beta^2 - 1}{2} \left(e^{-\frac{t}{\tau_r}} - 3e^{-\frac{3t}{\tau_r}} \right) \right) + \left(1 + \frac{2\chi}{5} \right) \beta \mu_s (\mu_s - \mu_g) \left(\delta(0) - \frac{e^{-\frac{t}{\tau_r}}}{\tau_r} \right) \right) \quad (10)$$

where β is the cosine of the angle between the directions of μ_s

and μ_g in the molecular frame. The transition dipole moment for excitation is assumed to be parallel to μ_s . The parameter χ depends on the angle ψ between the direction of light polarization and the applied electric field:

$$\chi = 3\cos^2\psi - 1 \quad (11)$$

The first term in eq 10 (independent of χ) corresponds to the difference in the equilibrium electric polarizations between the two states. The other terms have zero integrals and are responsible for changes in shape of the signal for different light polarizations. As one can see from eqs 10 and 11, at a certain "magic" angle of 54.7° ($\cos^2\psi = 1/3$), χ equals zero, and the signal behaves as if the excitation resulted in a uniform expansion of all the dipoles from μ_g to μ_s , independent of the orientation of ground state dipole with respect to the field. This magic angle has the same origin (and value) as the magic spinning angle used in the NMR spectroscopy of solids.

The straightforward way to extract polarization dependent terms from the signal is to subtract signals at two different light polarizations, say, parallel and perpendicular to the electric field, $\Delta\nu = \nu_{||} - \nu_{\perp}$:

$$\Delta\nu = \frac{3}{5}B \left(2\beta\mu_g(\mu_s - \mu_g) \left(\delta(0) - \frac{e^{-t/\tau_r}}{\tau_r} \right) + \frac{(\mu_s^2 - \mu_g^2)3\beta^2 - 1}{\tau_r} \left(e^{-t/\tau_r} - 3e^{-3t/\tau_r} \right) \right) \quad (12)$$

This signal $\Delta\nu$, which we call the "depolarization" signal is analogous to the depolarization signal in fluorescence kinetics and allows measurement of rotational times of molecules.^{3,5} Since $\Delta\nu$ has a term directly proportional to the ground state dipole moment, measurement of $\Delta\nu$ allows one to determine μ_g as well.^{3,5} Figure 2A shows a sketch of the depolarization signal and each of its two terms separately. The two terms are comparable in amplitude. The first term would prevail if $\beta \approx 1/3$, i.e., the angle between the ground and excited state dipoles is close to 60° . In contrast, when the ground state dipole moment is near zero, the depolarization signal is caused solely by the second term. If the rotational time is very long, only an instantaneous sharp signal, described by the delta function in eqs 10 and 12, will be seen.

Before applying this model to experimental data, we need to consider one more possible complication, namely an electric field dependence of the charge transfer rate constant.⁹ It is well-known that the charge transfer rate constant depends on the energy difference between the initial and the final state.¹⁰ The energy of a dipole in an external electric field is $-\mu f_c E \cos\Theta$. Thus, the free energy difference between states i and j : $\Delta G_{ij} = \Delta G_{ij}^0 + f_c E(\mu_i \cos\Theta_i - \mu_j \cos\Theta_j)$ could be significantly altered by the electric field if the dipole moment changes substantially. The rate constant k_{ij} will then be electric field dependent.

According to Marcus,¹⁰ the dependence of the rate constant for electron transfer on the free energy difference between initial and final states is given by

$$k_{ij} = \frac{(2\pi)^2}{h} \frac{J^2}{\sqrt{4\pi k_B T \lambda_s}} \exp\left(-\frac{(\Delta G_{ij} + \lambda_s)^2}{4k_B T \lambda_s}\right) \quad (13)$$

where h is Planck's constant. J is the transfer integral which is determined by the overlap between the initial and the final-state electronic wave functions and λ_s is the reorganization energy. As before, we will consider only the first, linear, term

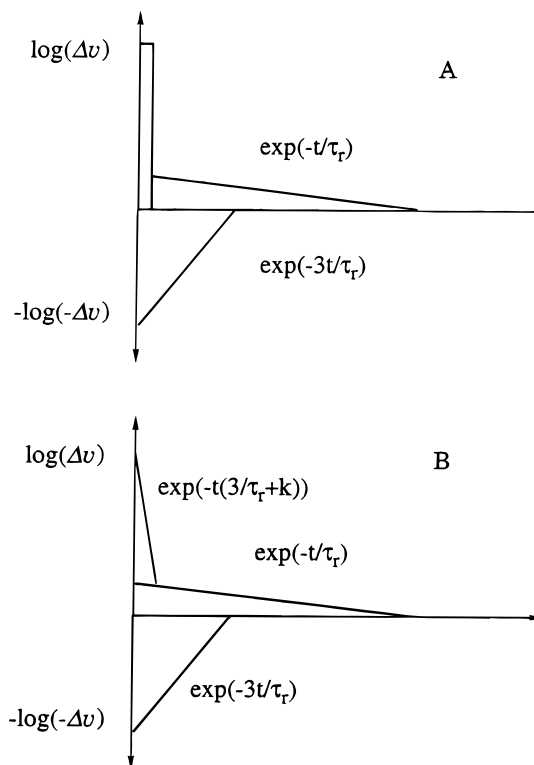


Figure 2. Sketch of depolarization signals in (A) two state model with nonzero ground state dipole moment and (B) three state model with zero ground state dipole moment but electric field dependent electron transfer rate constant.

with respect to the field E in the series expansion of k_{ij}

$$k_{ij} = k_{ij}^0 \left(1 + \frac{b_{ij} f_c E}{k_B T} \xi(\mu_i - \beta_{ij} \mu_j) \right) \quad (14)$$

where

$$b_{ij} = -1/2(\Delta G_{ij}^0/\lambda_s + 1) \quad (15)$$

reflects the slope of the dependence of k_{ij} on ΔG . Appendix B shows the evaluation of the photoresponse for this case in detail. Here we discuss only features of the depolarization signal, $\Delta\nu$, in comparison with that for no electric field dependence of k_{ij} .

$$\Delta\nu = \frac{3B\mu_s^2}{5\tau_r} \left(\frac{10}{3} \frac{1 - \frac{5}{3}bk\tau_r}{k\tau_r + 2} ((k\tau_r + 3)e^{-t(k+3/\tau_r)} - e^{-t/\tau_r}) + e^{-t/\tau_r} - 3e^{-3t/\tau_r} \right) \quad (16)$$

Equation 16 represents the depolarization signal for the case where a dipolar state with a dipole moment μ_2 is formed from an intermediate nondipolar excited state with electric field dependent rate constant $k(I - b\mu E/kT \cos\Theta)$. The ground state dipole moment is also assumed to be zero. Figure 2B gives a sketch of the depolarization signal. As one can see, the second term in eq 16 is exactly the same as that in eq 12.

Experimental Section

For excitation at different wavelengths, the third harmonic of a Nd:YAG laser (355 nm) was transformed by a set of interchangeable Raman shifters filled with different gases under high pressure. We used H_2 for 416 nm pulses, CH_4 for 396 nm, and Brillouin scattering on N_2 gas for 355 nm. In all cases the backward travelling beam (more compressed in time) was

used. It was separated from the original beam by a dichroic plate and provided up to 400 μJ at each wavelength with FWHM of 1.6, 2.2, and 2.6 ns for 416, 396, and 355 nm, respectively. Typically during the experiment, the incident energy was kept below 100 μJ . A small N_2 laser (VSL-337, Laser Science Inc.) was used for excitation at 337 nm (FWHM = 3.2 ns). The incident energy delivered to the cell did not exceed 30 μJ . Light polarization was altered by a half wave double Fresnel rhomb retarder.

A steady state high voltage of up to 1400 V was applied across the electrode gap (0.6, 0.36, and 0.16 mm were used) of a specially designed conductivity cell.⁴ In early experiments some photochemical instability was noticed. Because of that, the cell was modified to allow solution to flow through the electrode gap. The dipole photoresponse signal and the laser energy were measured simultaneously using two Tektronix oscilloscopes, a TDS 540 and a 2467 (see ref 4 for details). The latter was equipped with a Tektronix C1001 digitizing camera system interfaced to an IBM personal computer.

As previously discussed,⁵ the transient dc photoconductivity technique can be used either in a displacement current or a displacement charge mode. In the displacement current mode, one minimizes the RC time of the circuit by matching the impedances of the cell and connecting cables.⁴ In this way, the signal at the 50 Ω scope input is proportional to the current variation within the cell. If a large load resistor is used instead, then for times small compared to the circuit RC, the signal is proportional to the time dependence of the charge displacement inside the cell. The latter approach is useful because the signal is proportional to the concentration of dipolar species rather than to their time derivative, as in the displacement current mode. The charge displacement mode is less sensitive to variations in the laser time profile. A Tektronix P6201 (with Tektronix 1101A power supply) 100 k Ω active probe was used as a load. Unfortunately, because of stray capacitance of the connections from the cell to high voltage and the probe, the charge displacement signal has to be calibrated, but as a measure of relative signal intensities at different wavelengths, it is accurate and useful.

Preparation of MA-ANI-NI (see Figure 1) is described elsewhere.¹ Solutions in toluene (Baxter, B&J Brand, high purity) were either freeze-pump-thaw degassed prior to measurements or (in the case of the flow cell) bubbled with nitrogen gas. The typical optical density (limited by low solubility) was about 0.1 in a 1 cm cell at 416 nm. Low optical density reduces the accuracy of the absorbed energy measurements and, thus, limits the accuracy of the absolute values of dipole moments.

A program for the fitting of experimental data was based on numerical solution of eqs 5 and 9 or, in the case of field dependent rate constants, eq B.5. Optimization of fitting (by minimization of χ^2) uses Marquardt's method with an optional choice of variable parameters.

Results and Discussion

Figure 3 shows experimentally measured photoresponse signals in a toluene solution of MA-ANI-NI at room temperature for parallel and perpendicular polarizations of light with respect to the applied field. The depolarization signal, *i.e.*, the difference between the signals of Figure 3, is shown in Figure 4.

According to transient absorption measurements,¹ this molecule undergoes multistep electron transfer. Excitation at 416 nm primarily of the naphthalimide moiety leads in 8 ps to a hole jump to the methoxyphenyl group with >99% yield. In

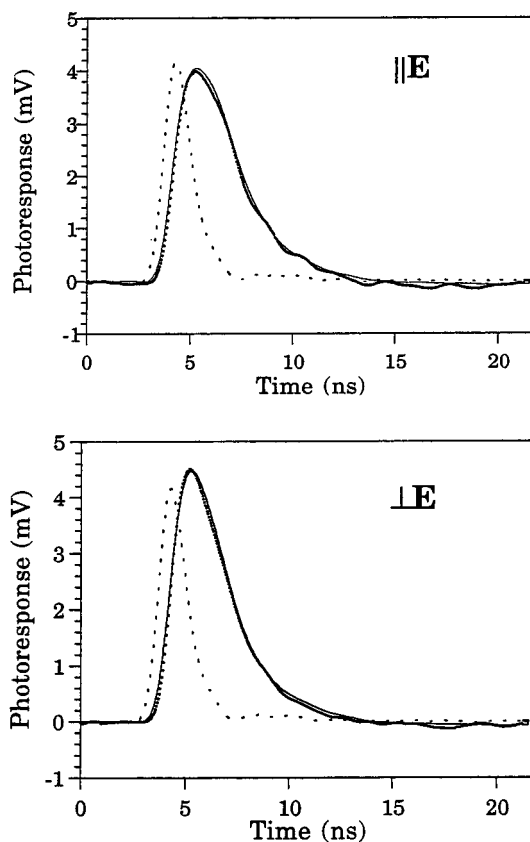


Figure 3. Photoresponse signals of MA-ANI-NI in toluene after absorption of 7.4 μJ at 416 nm in the cell with electric field of 1000 V across a 0.6 mm gap between electrodes; top—light polarization is parallel to the external electric field, bottom—corresponds to perpendicular polarization. Points show experimental signals, dashed lines describe laser pulse time profile, and solid lines are theoretical fits with the following parameters: ground state dipole moment $\mu_g = 16 \pm 5$ D, dipole moment of the intermediate state $\mu_1 = 35 \pm 10$ D, and dipole moment of the last state $\mu_2 = 87 \pm 6$ D with its lifetime $\tau = 290 \pm 10$ ns; isotropic rotational time $\tau_r = 1.6 \pm 0.15$ ns for all three states. The lifetimes $\tau_1 = 5.3$ ns and $\tau_2 = 0.43$ ns were taken from transient absorption¹.

the next step an electron transfer to the naphthalene-diimide group competes with relaxation to the ground state (5.3 ns) and takes 0.43 ns in toluene at room temperature. The resultant long range charge separated state lasts for about 300 ns (see Figure 1).

Since our time resolution does not allow us to distinguish processes on a picosecond time scale, we simplified this scheme and assumed that the first charge separation occurs instantaneously. Rate constants for the second step electron transfer and the lifetime of the intermediate state were taken from transient absorption measurements.¹ Among variable parameters were the lifetime of the state with complete charge transfer, τ_3 , rotational time, τ_r , and the dipole moments of three states—ground (μ_g), intermediate (μ_1), and complete charge transfer (μ_2).

First of all, it is important to point out that in the simplest possible scheme with only two dipolar states (ground and first excited), the photoresponses for parallel and perpendicular polarizations (Figure 3) could not be fit with the same parameters of rotational time and ground state dipole moment. Even more, treated independently in the two state model, each of the traces from Figure 3 had χ^2 on the order of 10^{-2} and a substantially different set of parameters. It requires all three states to get reasonably good fits for both curves. Second, even for the three state model, the best fit for each of the parallel and perpendicular traces in Figure 3 has a slightly different set

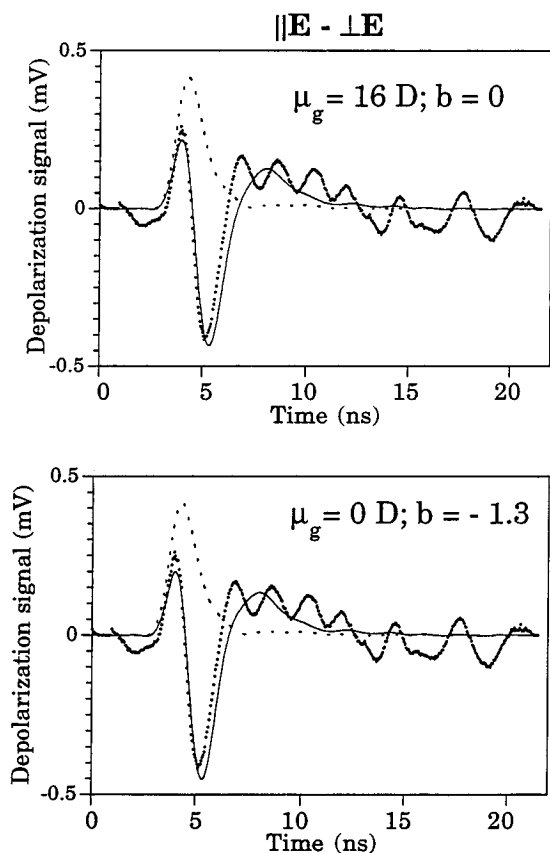


Figure 4. Difference between photoresponse signals of Figure 3 (depolarization signal) shown by points together with laser pulses (dashed lines) and best theoretical fits (solid lines) with top: the same parameters as in Figure 3 and bottom: the same parameters as in Figure 3 except that μ_g was assumed to be zero and $\tau_2 = 0.43$ ns $(1 - b\mu_1 E/kT \cos \theta)^{-1}$ where best fit was obtained for $b = -1.3$.

of optimum parameters, but the final values, which we present, are obtained for simultaneous optimization of fits to both traces. The depolarization signal in Figure 4 has no additional information because it is the result of numerical subtraction of the two curves of Figure 3, but it emphasizes differences in the two signals. The optimum fit for both curves gives $\mu_g = 16 \pm 5$ D, $\mu_1 = 35 \pm 10$ D, $\mu_2 = 87 \pm 6$ D, and $\tau_r = 1.6 \pm 0.15$ ns. The anisotropy factor A (see eq A6) was assumed to be zero (very prolate molecule) for the final state and 1/3 for ground and first excited states (spherical cavities). The latter approximation is questionable and gives some uncertainty for μ_g and μ_1 values. Most of the uncertainty in the moment μ_2 comes from the absorbed energy measurement, but, for the other three quantities, the accuracy of the fit is dominant. As an illustration, let us consider the signal for parallel polarization in Figure 3. The χ^2 value at the optimum ($\mu_2 = 87$ D, $\chi^2 = 2.3 \times 10^{-3}$) increases by an order of magnitude when μ_2 is increased or decreased by 6 D. Variation of the ground state dipole moment, μ_g , by 5 D increases the χ^2 value by a factor of 3 to 4. The best fit rotational time for the parallel signal was 1.52 ns with $\chi^2 = 1.1 \times 10^{-3}$. If instead we take the rotational time optimum of the perpendicular signal (1.7 ns), the χ^2 increases to 3.5×10^{-3} . Analogous variations were observed for the perpendicular signal. The relatively large uncertainty in μ_1 arises from the short lifetime of that state; the indicated uncertainty corresponds to a ten-fold increase in χ^2 .

As was discussed in the theoretical section, varying the electric field dependence of the electron transfer rate constant has almost the same effect on the calculated signal as does varying the ground state dipole moment. To estimate the b_{ij}

TABLE 1: Redox Potentials of the Three Moieties in Butyronitrile (vs SCE)

moiety	function	E_{ox}/E_{red} (V)
MA	donor	0.60/...
ANI	chromophore	1.02/-1.54
NI	acceptor	.../-0.70

TABLE 2: $-\Delta G$ (with Respect to the Ground State) in Toluene

state	R (Å)	$-\Delta G$ (eV)
MA^+-ANI^--NI	7.7 ^a	2.92, ^b 2.48 ^c
$MA-ANI^+-NI^-$	15.2 ^a	2.89, ^b 2.46 ^c
$NA^+-ANI^--NI^-$	19.1	1.55, ^b 2.11 ^c
$MA-ANI^*-NI$		2.80 ^c
$MA-ANI-NI^*$		3.25 ^c

^a Note that positive charge and negative charge in ANI have different locations, see ref 1 for details. ^b Estimated from Weller's equation with cavity radii $a = b = 3.5$ Å, see eq 17. ^c Estimated from the absorption/fluorescence spectra, see ref 1 for details.

parameters in eq 15, we need to find the free energy change $-\Delta G$ and reorganization energy λ for each step of the reaction. Using Weller's¹¹ equation

$$-\Delta G = E'_{ox} - E'_{red} - \frac{e^2}{\epsilon R} + e^2 \left(\frac{1}{2a} + \frac{1}{2b} \right) \left(\frac{1}{\epsilon} - \frac{1}{\epsilon'} \right) \quad (17)$$

and redox potentials for the three moieties in butyronitrile (see Table 1), we estimate $-\Delta G$ (with respect to the ground state) for each state: 2.92 eV for MA^+-ANI^--NI and 2.55 eV for $MA^+-ANI-NI^-$ (see also Table 2). All moieties were assumed to have equal radii: $a = b = 3.5$ Å. Distances between the donor and the chromophore of $R_{DC} = 7.7$ Å and between the donor and the acceptor $R_{DA} = 19.1$ Å have been estimated by molecular mechanics energy minimization.¹ Dielectric constants are for toluene $\epsilon = 2.38$ and for butyronitrile $\epsilon' = 24.8$.

Equation 17 gives a rather crude estimate for $-\Delta G$. It relies on the Born equation for solvation energies and approximates the electron donor and acceptor by spheres. Both assumptions are stressed in our system, where it is difficult to determine appropriate radii of the moieties involved. On the other hand, the semicontinuum model itself for nonpolar solvents like toluene is questionable because much of the solvation energy comes not only from electronic polarization but from an ion-quadrupole interaction as well.¹² All that accounts for the evident discrepancy with spectroscopic data¹ also shown in Table 2. One faces the same problems in estimating the reorganization energy λ_s . The outer term of the reorganization energy, λ_{out} , according to the Born approximation for solvation equals¹³

$$\lambda_{out} = e^2 \left(\frac{1}{2a} + \frac{1}{2b} - \frac{1}{R} \right) \left(\frac{1}{\epsilon_{opt}} - \frac{1}{\epsilon} \right) \quad (18)$$

For a nonpolar solvent, where the dielectric constant ϵ coincides with the optical dielectric constant ϵ_{opt} , λ_{out} should be close to zero. But, as mentioned above, because of electron-quadrupole interaction, λ_{out} , for solvents like toluene, can actually be nonzero. Taking into account also that the internal reorganization energy, λ_{in} , is typically in the range 0.1–0.3 eV,¹⁴ we can estimate the reorganization energy, $\lambda_s = \lambda_{out} + \lambda_{in}$, for the last electron transfer step as exceeding 0.3 eV but less than 1 eV. Hence, the coefficient b for electric field dependence in eq 15 $0 > b > -0.35$. Figure 4 illustrates that in order to get a reasonable fit for the depolarization signal Δv , one has to assume that b is approximately -1.3 . Thus, in the studied system most of the anisotropy in photoresponse comes from a nonzero ground state dipole moment and cannot be explained by electric field

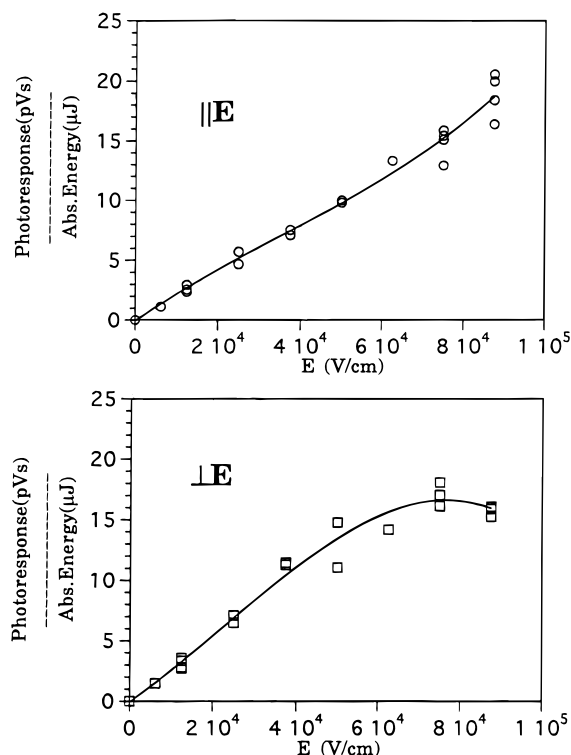


Figure 5. Electric field dependence of photoresponse signal measured in 0.16 mm gap cell for two light polarizations. Here the photoresponse is a measure of the integral of the positive part of the signal (in pVs) normalized by the absorbed energy (in μJ). Solid lines correspond to best polynomial fits $a_0 + a_1E + a_2E^2 + a_3E^3$ with the following parameters for the two polarizations (E is in V/cm): $\perp E$: $a_1 = 2.46 \times 10^{-4}$; $a_2 = 2.12 \times 10^{-9}$; $a_3 = -3.25 \times 10^{-14}$; $\parallel E$: $a_1 = 2.41 \times 10^{-4}$; $a_2 = -1.64 \times 10^{-9}$; $a_3 = 1.54 \times 10^{-14}$.

dependent electron transfer rates. Even use of the extreme value of $b = -0.35$ changes the value of the ground state dipole moment only slightly to $\mu_g = 12 \pm 5$ D.

The dipole moment for the giant dipole state, $\mu_2 = 87 \pm 6$ D (or 18.1 ± 1.3 Å), reasonably agrees with the 19.1 Å charge separation estimated by molecular mechanics.¹ It is worth mentioning that if the molecular cavity was assumed to be a sphere rather than a prolate ellipsoid, then the dipole moment would be 11% less, *i.e.*, the charge separation would be 16.3 ± 1.1 Å, substantially different from geometrical estimates. The large dipole moment is noticeable in nonlinearities of the dependence of the signal on the electric field. Figure 5 shows that in the cell with the small gap between electrodes, where high electric fields are accessible, the signal has an apparent nonlinear electric field dependence. Such peculiarities will be discussed elsewhere, but at this point we can see that a cubic polynomial fit to the field dependences for both polarizations gives the same linear term. That slope was actually used in normalization of both curves in Figure 3 to the same absorbed energy.

Figure 6 shows how the absorption spectrum of the MA-ANI-NI triad can be deconvoluted into the spectra of MA-ANI and NI moieties. The relative intensity of ANI chromophore absorption decreases with photon energy. Thus, one can expect that, because of different pathways of energy utilization, shown in Scheme 1, there might be wavelength dependence of the charge separation yield.

Since signal intensity in the displacement current mode (50 Ω load resistor) is sensitive to a laser time profile, we decided to use the charge displacement mode (100 k Ω load resistor) for measurement of the wavelength dependence of the charge separation yield. Figure 7 shows the transient conductivity

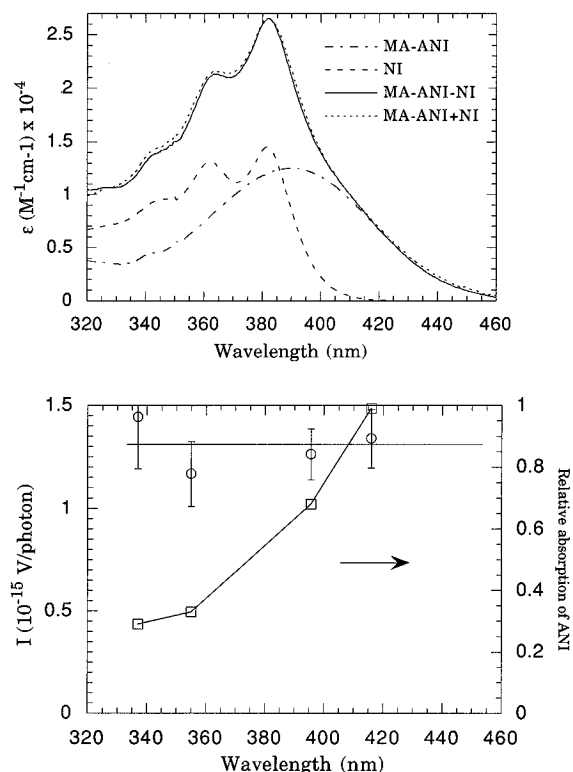
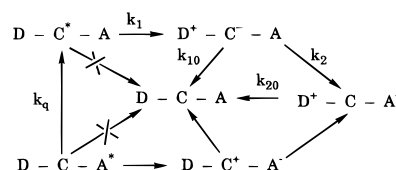


Figure 6. Top: Absorption spectra of MA-ANI-NI, MA-ANI, and NI in toluene. The sum of the last two spectra fits the absorption spectrum of MA-ANI-NI. The spectrum of ANI (not shown) differs from that for MA-ANI by a 9 nm red shift. Bottom: Wavelength dependence of the charge displacement signal for MA-ANI-NI in toluene normalized by the number of absorbed photons (circles). Relative intensity of the chromophore (MA-ANI) absorption as a function of wavelength is shown by squares.

SCHEME 1



photoresponse signals after excitation at 416 nm measured in both the displacement current and the charge displacement modes. Analogous measurements were done at three other wavelengths, and results are summarized in Figure 6. Within our accuracy, the quantum yield of dipolar states does not depend on the excitation wavelength despite a substantial decrease of the relative absorption by the ANI chromophore with excitation energy. Since the chromophore has the lowest excited state energy in the triad, intramolecular energy transfer (with rate constant k_q) is, apparently, fast enough to compete with relaxation to the ground state (see Scheme 1). Even after excitation in the acceptor band, the giant dipole state can be formed with close to unit probability via an initial energy transfer step. An alternative sequence of electron transfer events, in which, after acceptor excitation, an electron is transferred from the donor to the acceptor via the chromophore, has entirely different energetics than that for energy transfer (see Table 2). However, the time resolution of our technique does not allow the study of subnanosecond kinetics needed to distinguish between the two pathways.

A charge displacement signal on an extended time scale is shown in the insert of Figure 7. The apparent decay of the signal in the charge displacement mode, k_{20}' , is slightly faster

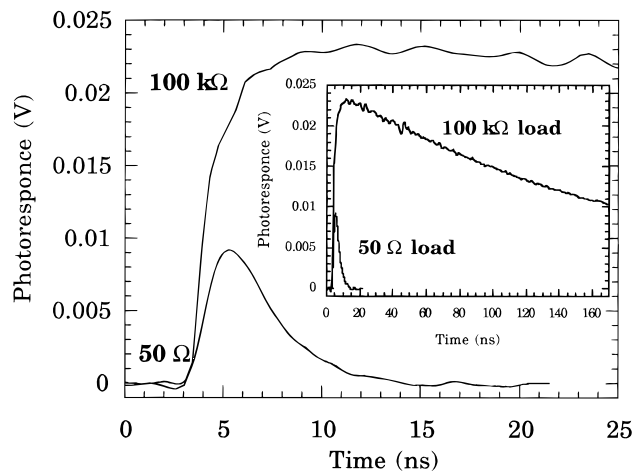


Figure 7. Photoresponse signal for MA-ANI-NI in toluene measured: (A) in the charge displacement mode, *i.e.*, with 100 kΩ load (B) in the displacement current mode, *i.e.*, with 50 Ω load. Both signals were measured for the same 7.4 μJ of absorbed energy at 416 nm in the same cell with 800 V applied across a 0.36 mm electrode gap.

than the decay of the dipolar states because of the limited RC time of the circuit (about 0.5 μs in Figure 7). The renormalized lifetime $(k_{20})^{-1}$ (see eq 46 in ref 5) is, actually, 290 ± 10 ns, close to the transient absorption value of 300 ns¹.

Conclusions

The theory of light polarization effects in the transient dc photoconductivity of dipolar species has been extended. It is shown that anisotropic photoresponses exist even for molecules with a zero ground state dipole moment. Additional anisotropy can be caused by either a ground state dipole moment or (and) electric field dependence of electron transfer rate constants.

These mechanisms have been considered for the triad molecule MA-ANI-NI (methoxyaniline-aminonaphthalimide-dimethylphenyl-naphthalenediimide-octyl) in toluene with excitation at 416 nm. It is found that the best fit to signals at both polarizations corresponds to ground (μ_g), first (μ_1), and second (μ_2) excited state dipole moments as follows: $\mu_g = 12 \pm 5$ D, $\mu_1 = 35 \pm 10$ D, and $\mu_2 = 87 \pm 6$ D. The lifetime of the giant dipole state is $\tau = 290 \pm 10$ ns, and the molecule's rotational time is $\tau_r = 1.6 \pm 0.15$ ns. Electric field dependence of the electron transfer rate constant is estimated to have very little effect.

It has been also shown that charge separation for MA-ANI-NI in toluene solution is independent of excitation wavelength (in the range 337–416 nm).

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Appendix A. Derivation of Eq 9. Both Excited and Ground State Dipoles Are Nonzero

Let us now analyze the solution of eq 9 for a two state model. For simplicity we also assume that the lifetime of the excited state is very long. Equations 9 are then simplified:

$$\begin{aligned} \tau_r \frac{dy_s}{dt} &= -y_s + \gamma_s E \left(n_s - \frac{2}{5} z_s e^{-3t/\tau_r} \right) \\ \tau_r \frac{dy_g}{dt} &= -y_g + \gamma_g E \left(n_g - \frac{2}{5} z_g e^{-3t/\tau_r} \right) \end{aligned} \quad (\text{A.1})$$

In order to calculate boundary conditions at time zero, we multiply the distribution function for the ground state $f_g = 1/2(1 + \gamma_g E \xi_g)$ by the angle-dependent probability of excitation which is proportional to ξ_s^2 for parallel and $1 - \xi_s^2$ for perpendicular light polarizations. Then creation of excited state dipoles μ_s with concentration n^0 corresponds to the boundary conditions at time zero

$$y_s^0 = \left(1 + \frac{2}{5} \chi \right) \beta \gamma_g E n^0 \quad z_s^0 = \chi n^0 \frac{3\beta^2 - 1}{2}$$

$$y_g^0 = \gamma_g E \left(n - \left(1 + \frac{2}{5} \chi \right) \beta n^0 \right) \quad z_g^0 = -\chi n^0 \frac{3\beta^2 - 1}{2} \quad (\text{A.2})$$

where n is the concentration of dipoles μ_g before excitation and β is the cosine of the angle between the directions of μ_s and μ_g in the molecular frame. The transition dipole moment for excitation is assumed to be parallel to μ_s . The parameter χ depends on light polarization and equals $\chi_{||} = 2$ for parallel and $\chi_{\perp} = -1$ for perpendicular polarizations, respectively. For any other polarization

$$\chi = \chi_{||} \cos^2 \psi + \chi_{\perp} \sin^2 \psi \quad (\text{A.3})$$

where ψ is the angle between the direction of light polarization and the applied electric field.

Solution of eqs A.1 with these boundary conditions gives the time dependence of the polarization $P = 1/3 (\mu_g y_g + \mu_s y_s)$:

$$P = \frac{f_c n^0 E}{3k_B T} \left((\mu_s^2 - \mu_g^2) \left(1 - e^{-t/\tau_r} + \frac{\chi 3\beta^2 - 1}{5} (e^{-3t/\tau_r} - e^{-t/\tau_r}) \right) + \left(1 + \frac{2\chi}{5} \right) \beta \mu_g (\mu_s - \mu_g) e^{-t/\tau_r} \right) \quad (\text{A.4})$$

In the limit of small RC time τ , the signal v , which we measure, is proportional to the time derivative of P (see eq 1). Thus, after substitution of eq A.4 into eq 1 we find that v is given by

$$v = B \left(\frac{(\mu_s^2 - \mu_g^2)}{\tau_r} \left(e^{-t/\tau_r} + \frac{\chi 3\beta^2 - 1}{5} (e^{-t/\tau_r} - 3e^{-3t/\tau_r}) \right) + \left(1 + \frac{2\chi}{5} \right) \beta \mu_g (\mu_s - \mu_g) \left(\delta(0) - \frac{e^{-t/\tau_r}}{\tau_r} \right) \right) \quad (\text{A.5})$$

where $\delta(0)$ is a delta function centered at time zero and describes an instantaneous response; B includes all the scaling coefficients (see elsewhere³ for details):

$$B = \frac{\epsilon}{\epsilon + (1 - \epsilon)A(2\epsilon + 1)(2\epsilon^2 + \epsilon_{\infty}^2)} \frac{3\epsilon (2\epsilon + \epsilon_{\infty})^2 4\pi\tau_0 V_0 n^0}{3k_B T} \quad (\text{A.6})$$

Here, as discussed in detail elsewhere,³ a change in the polarization caused by surrounding solvent leads to an additional coefficient Φ

$$\Phi = \frac{3\epsilon (2\epsilon + \epsilon_{\infty})^2}{(2\epsilon + 1)(2\epsilon^2 + \epsilon_{\infty}^2)} \quad (\text{A.7})$$

where ϵ_∞ is the refractive index squared $\epsilon_\infty = n^2$. The anisotropy factor A characterizes molecular nonsphericity¹ and changes from zero for a very long prolate molecule to 1.3 for a sphere.

Appendix B. Derivation of Signal with Electric Field Dependent Electron Transfer Rate Constant

The Marcus theory of charge transfer¹⁰ describes a connection between the rate constant, k_{ij} , and the free energy between initial and final states, ΔG_{ij} , via eq B.1

$$k_{ij} = \frac{(2\pi)^2 J^2}{h \sqrt{4\pi k_B T \lambda_s}} \exp\left(-\frac{(\Delta G_{ij} + \lambda_s)^2}{4k_B T \lambda_s}\right) \quad (\text{B.1})$$

where h is Planck's constant. J is the transfer integral and λ_s is the reorganization energy. The external electric field E changes the free energy of each dipolar state and thus, changes ΔG_{ij} by

$$\delta G_{ij} = f_c E (\mu_i \cos \Theta_i - \mu_j \cos \Theta_j) \quad (\text{B.2})$$

Retaining only the first term in a Taylor series for eq B.1 with respect to δG_{ij} , we have a linear dependence of the rate constant on E

$$k_{ij} = k_{ij}^0 \left(1 - \frac{\Delta G_{ij}^0 + \lambda_s}{2k_B T \lambda_s} \delta G_{ij}\right) = k_{ij}^0 \left(1 + \frac{b_{ij} f_c E}{k_B T} (\mu_i \xi_i - \mu_j \xi_j)\right) \quad (\text{B.3})$$

where

$$b_{ij} = -1/2(1 + \Delta G_{ij}^0/\lambda_s) \quad (\text{B.4})$$

shows that the higher the reaction rate is ($\Delta G_{ij} + \lambda_s \approx 0$), the less dependent on electric field it should be. It also specifies a sign for the b_{ij} : negative for the normal Marcus region (*i.e.*, rate increases with field if dipole moment increases) and positive for the inverted region (rate decreases with field).

The use of eq B.3 for the rate constant transforms eqs 5 and 9 into the following:

$$\frac{dn_i}{dt} = \sum_{j \neq i} (k_{ji}^0 n_j - k_{ij}^0 n_i) \quad (\text{B.5})$$

and

$$\begin{aligned} \frac{dy_i}{dt} = & \frac{1}{\tau_r} \left(-y_i + \gamma_i E \left(n_i - \frac{2z_i}{5}\right)\right) + \sum_{j \neq i} \left\{ k_{ji}^0 \left(y_j + b_{ji} E (\beta_{ij} \gamma_j - \gamma_i) \right. \right. \\ & \left. \left. \left(n_j + \frac{2z_j}{3}\right) - k_{ij}^0 \left(y_i + b_{ij} E (\gamma_i - \beta_{ij} \gamma_j) \left(n_i + \frac{2z_i}{3}\right)\right) \right\} \\ \frac{dz_i}{dt} = & -\frac{3z_i}{\tau_r} + \sum_{j \neq i} \left\{ k_{ji}^0 \frac{3\beta_{ij}^2 - 1}{2} z_j - k_{ij}^0 z_i \right\} \quad (\text{B.6}) \end{aligned}$$

Let us solve these equations for the case where the ground and first excited state dipole moments are zero. The second excited state which has a nonzero ground state dipole moment is formed from the first excited state via a field dependent rate constant (see eq B.3). In what follows, we again assume that the second state is long lived, *i.e.*, both the back reaction to the first state and relaxation to the ground state are neglected. The transition dipole moment is also assumed to be parallel to μ_2 . Since both μ_g and μ_1 are zero, then y_g and y_1 are zero as well. Thus, eqs

B.5 and B.6 are simplified to

$$\begin{aligned} \frac{dy_2}{dt} = & \frac{1}{\tau_r} \left(-y_2 + \gamma_2 E \left(n_2 - \frac{2z_2}{5}\right)\right) - k \left(b E \gamma_2 \left(n_1 + \frac{2z_1}{3}\right)\right) \\ \frac{dz_2}{dt} = & -\frac{3z_2}{\tau_r} + k z_1; \quad \frac{dz_1}{dt} = -\frac{3z_1}{\tau_r} - k z_1 \quad (\text{B.7}) \\ \frac{dn_2}{dt} = & -\frac{3n_2}{\tau_r} + k n_1; \quad \frac{dn_1}{dt} = -\frac{3n_1}{\tau_r} - k n_1 \end{aligned}$$

where subscripts on b_{12} and k_{ij} have been dropped for simplicity. The only boundary condition is $z_1^0 = \lambda n^0$, where n^0 have the same meaning as in eq A.2. Solution of eqs B.7 gives the time dependence of the polarization P

$$\begin{aligned} P = & \frac{f_c n^0 \mu_2^2 E}{3k_B T} \left(1 - e^{-t/\tau_r} + \frac{\lambda}{5} (e^{-3t/\tau_r} - e^{-t/\tau_r}) + \frac{1 - b k \tau_r}{k \tau_r - 1} \times \right. \\ & \left. (e^{-t/\tau_r} - e^{-kt}) + \frac{2\lambda}{9} \frac{3 - 5b k \tau_r}{k \tau_r + 2} (e^{-t/\tau_r} - e^{-t(k+3/\tau_r)})\right) \quad (\text{B.8}) \end{aligned}$$

the time derivative of which gives the signal v

$$\begin{aligned} v = & \frac{B \mu_2^2}{\tau_r} \left(e^{-t/\tau_r} + \frac{\lambda}{5} (e^{-t/\tau_r} - 3e^{-3t/\tau_r}) + \frac{1 - b k \tau_r}{k \tau_r - 1} (k \tau_r e^{-kt} - \right. \\ & \left. e^{-t/\tau_r}) + \frac{2\lambda}{9} \frac{3 - 5b k \tau_r}{k \tau_r + 2} ((k \tau_r + 3)e^{-t(k+3/\tau_r)} - e^{-t/\tau_r})\right) \quad (\text{B.9}) \end{aligned}$$

From eq B.9 a depolarization signal Δv (difference between the signals for parallel and perpendicular polarization of the light with respect to the applied field) is calculated using $\Delta \lambda = 3$

$$\begin{aligned} \Delta v = & \frac{3B \mu_2^2}{5\tau_r} \left(e^{-t/\tau_r} - 3e^{-3t/\tau_r} + \frac{10}{3} \frac{1 - 5b k \tau_r}{k \tau_r + 2} \times \right. \\ & \left. ((k \tau_r + 3)e^{-t(k+3/\tau_r)} - e^{-t/\tau_r})\right) \quad (\text{B.10}) \end{aligned}$$

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