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Hyper-Rayleigh scattering in *p*-nitroaniline with excited states obtained by 355 nm optical pump

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Abstract

We report what we believe to be the first experimental demonstration of the dependence of hyper-Rayleigh scattering (HRS) (fundamental wavelength of 1064 nm) and, hence, the first hyperpolarizability in optically pumped *p*-nitroaniline (PNA) molecules on the energy of pump photons. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nonresonant second- and third-order optical nonlinear processes in molecules 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 excitation, 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 frequencies of the 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 electronic excitations can be either the usual fundamental state or optically pumped excited states. Hence nonresonant optical nonlinear processes can be changed using populated electronic excited states [1,2]. This effect is mainly due to the incorporation of new energy levels allowed to the virtual transitions responsible for the nonlinear process.

Experimental studies of excited-state hyperpolarizabilities have been done mainly for second hyperpolarizabilities $\gamma(-\omega_4; \omega_1, \omega_2, \omega_3)$.

In [1,3] the enhancement of the degenerate four wave mixing (DFWM) susceptibility $\gamma(-\omega; \omega, \omega, -\omega)$ in a linear conjugated molecule, diphenylhexatriene, was observed when the first one-photon allowed excited state was populated for

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nanoseconds and then probed nonresonantly through picosecond DFWM. In [4] the third-harmonic component (THG) $\gamma(-3\omega; \omega, \omega, \omega)$ in the conjugated disk-like structure, silicon naphthalocyanine, the THG signal decreased significantly by optical population of the first excited state because of very large and negative $\gamma(-3\omega; \omega, \omega, \omega)$ for the excited state that is orders of magnitudes larger than the value for the ground state. The excited state enhancement of second hyperpolarizability was studied for a square planar complex (2,2'-bipyridine) Pt(1,2-dicyano-1,2-ethylene-dithiolate) [5], a *trans*-stilbene molecule [6], dialkynyl complexes [7], and thiophene-dimethylsilyl co-oligomers [8].

The first hyperpolarizability $\beta(-2\omega; \omega, \omega)$ in the excited states has been more sparsely investigated [9,10]. The hyper-Rayleigh scattering (HRS) measurements in solution of *p*-nitroaniline (PNA) in methanol showed that β increases upon 10 ns pulse excitation at 464 nm and depends on the delay time between a pump and probe pulses. The lifetime of the excited states was estimated from the experimental data to be around 9 ns. By CW excitation (457.9 nm) of the PNA an increase of the HRS signal was also observed.

In this paper we report results of HRS measurements (fundamental wavelength of 1064 nm) in PNA by pulse excitation at 355 nm. We choose this molecule and this excitation energy for the following reasons. The nonlinear properties of the molecule in the ground state are well studied experimentally and theoretically [11–14]. It is important also to have a good knowledge of the photo-physical properties of the molecule studied, in particular to know the way of energy transformation of the molecule after excitation. The excited state properties of the PNA molecule have been investigated by different techniques [15–17]. Also the nonlinear properties of the molecule in excited states can be calculated with reasonable accuracy due to its relative small size and a comparison with experiments can be done in the future. At last, we can compare our results with [9,10]. Unlike [9,10] in our case the energy of pump photons is higher than the transition energy of the first electronic transition in PNA. Therefore our data together with [9,10] give information how the first hyperpolariz-

ability of the molecule with excited states behaves by changing the energy of pump photons.

2. Experimental

2.1. Samples

We used PNA solutions (concentration 10^{20} molecule/cm³) in methanol and in DMSO. The solutions were filtered through a 0.45 μ m teflon membrane filter. All measurements were carried out at room temperature.

The absorption spectra of the studied samples are shown in Fig. 1(a). These spectra have been thoroughly investigated [14,17–19]. 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. A solvatochromism of PNA may be seen in the spectra present: the wavelength of maximal absorption is 385 nm for DMSO solution, and 369 nm for methanol solution. No absorption was observed at either the fundamental frequency (1064 nm) or the second harmonic (532 nm) of the HRS. As Fig. 1 suggests, the experiments [9] were done at the pump energies 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) is higher than the energy of maximal absorption.

2.2. Experimental set up

The set up for hyper-Rayleigh measurements in molecules in excited states is shown in Fig. 2. The unique feature of our experimental configuration comparing with traditional schemes of the HRS (for example [20]) is the introduction of an intense pump beam. The second harmonic signal in our HRS experiments was created inside a glass cell with samples using the 10 ns, up to 30 mJ pulses at 1064 nm generated by a *Q*-switched Nd-YAG laser. After filtering out any residual

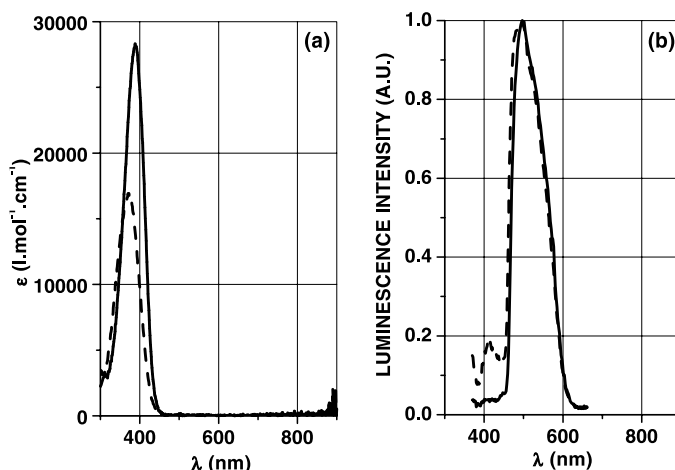


Fig. 1. Absorption (a) and emission (b) spectra of solutions of PNA in DMSO (solid lines) and in methanol (dashed lines). Excitation at 355 nm.

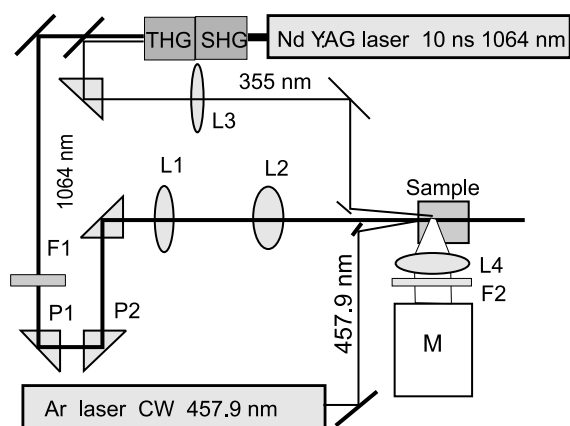


Fig. 2. Experimental set up.

flash lamp light with a high-pass filter F_1 , the fundamental light was collimated by two lenses L_1 and L_2 to form a parallel beam into the glass cell. The use of the collimated beam with a beam radius of 0.5 mm avoided solution dielectric breakdown and ensured an improved signal/noise. The light scattered at right angles to the incident beam was collected by a system of lenses L_4 and was measured by a photomultiplier tube with a low pass filter to suppress the fundamental light. For the high optical power densities used in HRS experiments a fluorescence signal due to multi-photon excitation may also be present (see,

for example [21]) together with the HRS signal at the second harmonic wavelength. To verify the presence of fluorescence we used a monochromator M to record the spectral profile. The broad emission background was then subtracted from the narrow HRS profile. A gated detection electronics permitted data acquisition from the photomultiplier tube at any delay relative to the laser pulse. Each data point is the average of 256 laser shots.

To generate a pump signal the 1064 nm pulse from the laser was first doubled by a nonlinear crystal second-harmonic component (SHG) and then mixed in another nonlinear crystal THG to produce the pump beam at 355 nm. The pump beam was focused by the lens L_3 and was sent to the cell almost parallel with the fundamental pulse. The pump beam diameter was the same as the fundamental beam diameter. The optical delay line formed by the prisms P_1 and P_2 was used to delay the fundamental pulse relative to the pump pulse. With an additional weak 632 nm probe beam we proved that a thermal lens excited by absorption of the pump beam did not produce remarkable defocusing of any beam that propagates parallel to the pump beam.

We also used a CW Ar laser at 457.9 nm as a pump source in order to reproduce the results [10].

3. Results and discussion

First we excited the samples by the CW 457.9 nm pump beam. Measuring the HRS spectra, we observed consistent with [10] a small increase of the HRS intensity for both samples being in the excited state (Figs. 3(a) and (b)). Notice that with our acquisition system the fluorescence at 532 nm by CW excitation at 457.9 nm did not contribute to our measurements. The difference of the signals obtained for different solvents was discussed in [14]. The spectral width of the peak is determined by the resolution of our monochromator.

Then we used the 355 nm pump beam, and without the 1064 nm beam we observed the fluorescence spectra shown in Fig. 1(b). As seen each spectrum consists of two bands of fluorescence: a very weak band with maxima at approximately 409 nm (3.03 eV), and another strong band with maxima near 500 nm (2.48 eV), in agreement with previous observations [15].

One can explain the absorption and fluorescence characteristics of PNA by considering a possible electronic-state diagram [16,17]. The absorption band is due to the transition from the ground state S_0 to an excited singlet state S_1 (the transition energy $E_{S_0,S_1} = 3.25$ 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 lifetime. 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 lifetime determined from the decay of the time-resolved-microwave conductivity measurements was found to be 54 ns for PNA in benzene [17]. 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 [15,16,22]. 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.

When we sent to the sample the 355 nm pump pulse and 1064 nm fundamental pulse (17 mJ) simultaneously (i.e., without the delay line in the fundamental beam path), the fluorescence spectra near 532 nm for different pump power are shown in Fig. 4(a) (solid lines). To subtract the HRS contribution from the total fluorescence intensity for each pump power we measured the fluorescence spectra when the fundamental pulse was blocked (dashed lines). As seen the contribution of

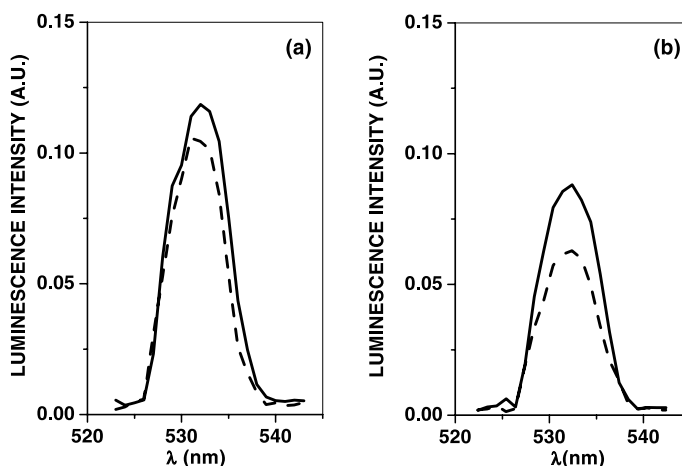


Fig. 3. HRS spectra obtained with CW 457.9 nm excitation (40 mW) (solid lines) and without optical pump (dashed lines) in solutions of PNA in DMSO (a) and methanol (b).

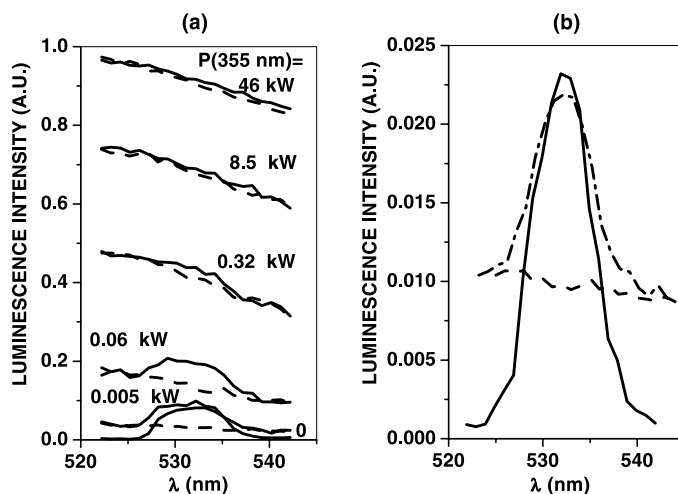


Fig. 4. (a) Fluorescence spectra for different pump power. No delay between the pump and fundamental pulses. (b) Fluorescence spectra obtained with 30 ns delay between the pump and fundamental pulses. Conditions: no pump beam (solid line), no fundamental beam (dashed line), pump and fundamental beams (dot line). Sample: PNA in DMSO.

the HRS signal decreases with pump power, and at the highest pump power no HRS signal was observed. We obtained the similar results for the PNA dissolved in methanol, however the suppression of the HRS signal occurs for lower pump power than for the DMSO solution.

Consider now the results obtained with the fundamental pulse delayed (30 ns) from the pump beam (Fig. 4(b)). (By this delay the HRS pulse was

well separated from the fluorescence pulse generated by the pump beam. See a temporal profile of the signal in Fig. 5(a)). From data in Fig. 4(b) the lifetime of the excited states responsible for the changes of the HRS signal was calculated to be 43 ns for both samples. This time corresponds well to the T_1 lifetime determined by other technique [17]. In Fig. 5(b) we plot the HRS signal (obtained with the gate located at 60 ns, compared with the

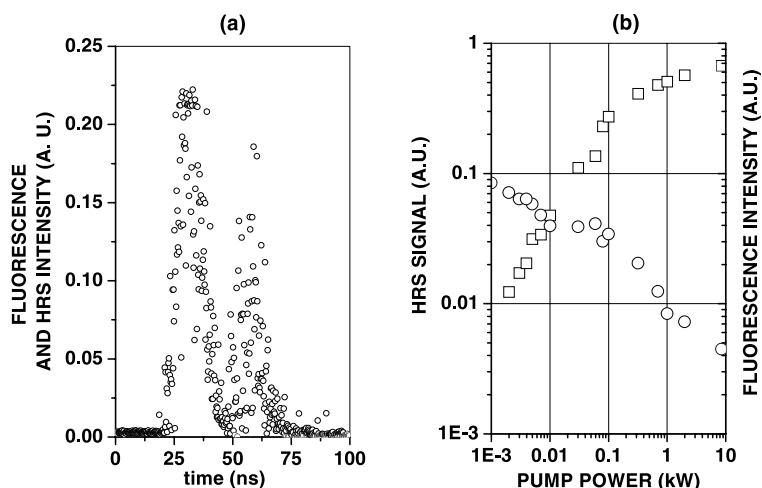


Fig. 5. (a) The temporal response of the fluorescence and HRS signals when the probe fundamental pulse is delayed 30 ns from the pump pulse. (b) The fluorescence (squares) and the HRS (circles) signals versus the pump power.

temporal profile at the Fig. 5(a)) and the fluorescence signal (obtained with the gate at 30 ns) for different pump powers. The fluorescence signal grows almost linearly for small pump powers and then saturates. As the HRS decreases with pump power we can expect that the contribution of the excited states in the first hyperpolarizability $\beta^{S_1T_1}$ has, compared with the ground state, a larger first polarizability but with the opposite sign. Probably, the saturation of population does not allow to observe the further increase of the HRS signal at high pump power. The excited state is not in fact one excited level only but a set of excited states in the range S_1-T_1 and all of them give contributions in the observed changes of the HRS signal and, hence, in the first hyperpolarizability. However, the distribution of population of these excited states depends on the energy of pump photons. If this energy is higher than the highest excited sub-level, as in our case, all excited states can be populated. However, if the pump energy lies in the gap between the highest sub-level and the lowest sub-level, as in [9], a different distribution of population of the sub-levels is achieved resulting an increase in the total first hyperpolarizability.

In conclusion, to the best of our knowledge we observed for the first time that the contribution of optically pumped excited states to the total first hyperpolarizability depends on the energy of pump photons. This pump dispersion calls for further experimental and theoretical study because it offers additional information on molecular electronic excited states.

Acknowledgements

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References

- [1] D.C. Rodenberger, J.R. Heflin, A.F. Garito, *Nature* 359 (1992) 309.
- [2] Q.L. Zhou, J.R. Heflin, K.Y. Wong, O. Zamani-Khamiri, A.F. Garito, *Phys. Rev. A* 43 (1991) 1673.
- [3] D.C. Rodenberger, J.R. Heflin, A.F. Garito, *Phys. Rev. A* 51 (1995) 3234.
- [4] J.R. Heflin, D.C. Rodenberger, R.F. Shi, M. Wu, N.G. Wang, Y.M. Cai, A.F. Garito, *Phys. Rev. A* 45 (1992) R4233.
- [5] J. Si, Q. Yang, Y. Wang, P. Ye, S. Wang, J. Qin, D. Liu, *Opt. Commun.* 132 (1996) 311.
- [6] J. Oberle, G. Jonusauskas, E. Abraham, C. Rullire, *Chem. Phys. Lett.* 241 (1995) 281.
- [7] J. Zhao, Y. Wang, J. Si, P. Ye, S. Li, L. Zhang, Z. Wu, M. Yang, *J. Nonlinear Opt. Phys. Mater.* 6 (1997) 109.
- [8] C. Moreau, F. Serein-Spirau, J.-F. Ltard, R. Lapouyade, G. Jonusauskas, C. Rullire, *J. Phys. Chem. B* 102 (1998) 1487.
- [9] A. Harada, T. Nagamura, *SPIE* 3474 (1998) 127.
- [10] A. Harada, T. Nagamura, *Reports of the Graduate School of Electronic Science and Technology*, vol. 20, Shizuoka University, 1999, p. 15.
- [11] J.L. Oudar, D.S. Chemla, *J. Chem. Phys.* 66 (1977) 2664.
- [12] P. Kaatz, D.P. Shelton, *J. Phys. Chem.* 105 (1996) 3918.
- [13] M. Stahelin, D.M. Burland, J.E. Rice, *Chem. Phys. Lett.* 191 (1992) 245.
- [14] J.N. Woodford, M.A. Pauley, C.H. Wang, *J. Phys. Chem. A* 101 (1997) 1989.
- [15] O.S. Khalil, C.J. Seliskar, S.P. McGlynn, *J. Chem. Phys.* 58 (1973) 1607.
- [16] T.P. Carsey, G.L. Findley, S.P. McGlynn, *J. Am. Chem. Soc.* 101 (1979) 4502.
- [17] W. Schuddeboom, J.M. Warman, H.A.M. Biemans, E.W. Meijer, *J. Phys. Chem.* 100 (1996) 12369.
- [18] V.I. Danilova, Yu.P. Morozova, *Opt. Spectrosc.* 12 (1962) 5.
- [19] I. Corbett, *Spectrochim. Acta* 23A (1967) 2315.
- [20] K. Clays, A. Persoons, *Rev. Sci. Instrum.* 63 (1992) 3265.
- [21] E. Hendrickx, K. Clays, A. Persoons, *Acc. Chem. Res.* 31 (1998) 675.
- [22] G.L. Findley, T.P. Carsey, S.P. McGlynn, *J. Am. Chem. Soc.* 101 (1979) 4511.