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Theoretical and experimental investigation of the second hyperpolarizabilities of methyl orange

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(Received 7 October 2004; accepted 27 December 2004; published online 11 March 2005)

We describe experimental and theoretical studies of the third-order nonlinear optical coefficients of methyl orange solutions under different *p*H conditions. A combination of semiempirical and *ab initio* methods was adopted to investigate the most stable geometrical structures possible for this molecule. The experimental data obtained using the *Z*-scan technique for the third-order nonlinear optical properties of this compound has allowed the determination of the nonlinear refractive index and nonlinear absorption coefficient under picosecond excitation in the visible (532 nm) spectral region. From those experimental results, the second hyperpolarizability of methyl orange was inferred both for acidic and alkaline solutions. Comparison of these values to the results predicted by semiempirical methods suggests that even at low *p*H, when the probability of *cis-trans* isomerization is increased, the *trans* conformation of the methyl orange molecule should dominate the nonlinear spectra of this compound. The theoretical results were used as an auxiliary tool to identify possible trends on the nonlinear properties changes as a function of the distinct molecular conformations adopted by the methyl orange molecule under different *p*H conditions. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1860372]

I. INTRODUCTION

The nonlinear optical properties of organic materials have been subject to extensive studies aimed not only to the understanding of their intrinsic origin but also to the possible use of these systems in photonic applications. In this regard, different authors have considered the possibility of exploiting the characteristic large optical nonlinearities of organic materials in optoelectronic and photonic devices.[1–4] Of special interest is the fact that a measurable variation of the nonlinear optical response of a given system may result from structural or conformational changes of conjugated molecules that could be externally induced by appropriate modification of the ambient conditions. For instance, derivatives of the retinal molecule have their nonlinear refraction index decreased as a result of a photoinduced *trans* to *cis* isomerization of the chain[4] and the protein Bacteriorhodopsin (found in the purple membrane of the *Halobacterium salinarium*), which is conjugated to a retinoid molecule, has its structural and nonlinear properties changed upon absorption of visible light.[5,6] In fact, it has been demonstrated that Bacteriorhodopsin conformational changes can be exploited for the development of an all-optical switch.[7] Several other conjugated systems have been shown to exhibit a similar behavior and therefore the theoretical and experimental studies of the effect of structural changes upon the nonlinear optical properties of organic compounds have flourished in recent years.[3] In this work, we determine the third-order nonlinear coefficients of methyl orange ($C_{14}H_{14}N_3O_6S^-$) solutions under different *p*H conditions and compare the measured values to theoretical estimates of the corresponding molecular hyperpolarizabilities. Due to its sudden color change in response to a relatively narrow window of variation of the protonic concentration under acidic conditions, methyl orange (MO) is a well-known indicator of the titration of weak bases with strong acids.

In common with other *p*H indicators, there is the less discussed fact that changes in the *p*H of the medium not only modify its linear optical properties but also lead to measurable variations of the corresponding nonlinear coefficients, a process that has been exploited to determine the p_{Ka}, value of weak molecular acids.[8] As an azobenzenoid molecule, MO can suffer photoisomerization between the *cis* and *trans* forms, a phenomenon that has been investigated through the measurement of its nonlinear susceptibilities when dispersed in a polymeric film.[9,10] Light-induced orientation effects that are important for rigid samples[11] play a lesser role in solution studies, where the maximum of the absorption spectra shift to longer wavelengths with the increase of the protonation level and of the solvent polarity.[12]

The external control of the onset of the nonlinear optical (NLO) properties of organic compounds would represent significant progress in the field, especially if that could be done in a reversible manner and following a well-defined change of macroscopic parameters. Previously, this has been accomplished either by electrochemical switching of the oxidation

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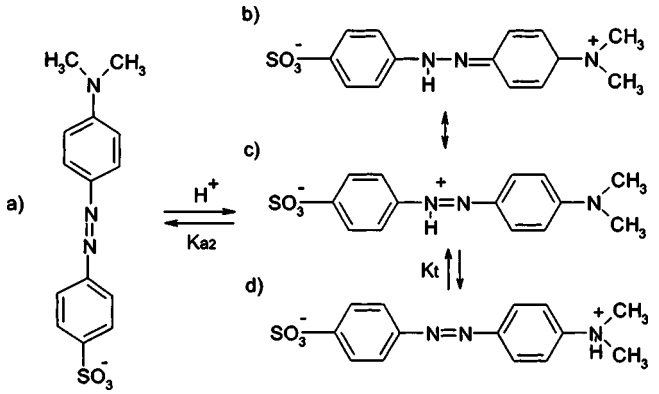

FIG. 1. Alkaline form of MO (a) and its monoprotonated zwitterionic structures under acidic conditions: quinine diimine (b), the resonant form azonium (c), and the ammonium tautomer (d).

state of organometallic complexes[13] or by varying the protonation level of azafulleroids, when it was shown that a small variation in the concentration of the protonated form resulted in a larger change in the hyper-Rayleigh scattering results.[14] In that regard, it has been shown to be possible the reversible optical control of the third-order molecular hyperpolarizability of the chromophores in azo polyimide spin-casted films.[15]

In our case, for the experimental investigation of the third-order nonlinear coefficients of MO solutions under different *p*H conditions we have used the *Z*-scan technique,[16] which allows the determination of both the sign and the absolute value of the nonlinear refractive index, $n_2 \propto \mathrm{Re}[\chi^{(3)}]$, and the determination of the nonlinear absorption coefficient, $\alpha_2 \propto \mathrm{Im}[\chi^{(3)}]$, where $\chi^{(3)}$ is the second-order nonlinear susceptibility of the samples. From the theoretical point of view, the large size of the MO molecule has so far restrained a more wide use of *ab initio* computational methods in conformational studies.[17] Here, *ab initio* methods were adopted to confirm that the optimized semiempirical conformation of each possible MO structures correspond to an actually stable geometrical form. In addition, semiempirical methods were adopted for the prediction of the nonlinear polarizabilities. With the appropriate combination of these methods we were able to complete the desired investigation of the *p*H-induced changes upon the hyperpolarizability of the MO molecules.[4,18]

Before presenting the experimental and theoretical methodologies used in this work, we will briefly discuss some of the relevant characteristics of MO that make this molecule a very interesting compound for chemical and NLO applications.

II. METHYL ORANGE UNDER ALKALINE AND ACIDIC CONDITIONS

In Fig. 1 we present some of the possible structures of MO in solutions of different protonic concentrations. In its alkaline form [Fig. 1(a)], MO exists as an anion of orange-yellow color, and the double bond in the azo (i.e.,–N═N–) group connecting the two aromatic rings represents a well-defined barrier for the *cis-trans* isomerization. Under progressive protonation, the color of the solution changes to red due to the formation of the monoprotonated form of the MO molecule, which is believed to exist as a resonance hybrid between its quinine diimine [Fig. 1(b)] and azonium [Fig. 1(c)] structures.[17,19] In this manner, the double bond character of the NN bond in the azo group is lessened and the barrier to the *cis-trans* isomerization becomes smaller.[17] In fact, this isomerization is known to occur 10^8 times faster in protonated forms of azobenzenes than in the corresponding full conjugated species.[20] A tautomeric structure (i.e., one that results from a simple change in the protonation site) of the MO molecule containing the ammonium group is also possible[21] [Fig. 1(d)]. It should be noted that the zwitterionic structures—i.e., those presenting charge separation in the ground state—represented in Figs. 1(b)–1(d) are the most stable forms possible because the weak bases character of the alkaline anion precludes the direct proton attack to the charged sulfonate terminal group [Fig. 1(a)]. Moreover, as will be discussed later, diprotonated structures of the MO molecule are also possible under extreme acidic conditions.

The characteristic bright colors of MO solutions make it an important dye for the textile and photographic industry.[22] The change from an orange-yellow to red color of the molecule following the decrease of *p*H is associated to the modification of the π system delocalization pattern, since the acidic structures absorb light mainly in the green-red region of the spectrum. The equilibrium between the monoprotonated and unprotonated forms is attained at a *p*H of 3.37 [the value of the pK_a of MO (Ref. 19)] and the very noticeable transition between the two colored forms is sufficiently rapid (i.e., the color change is completed while the *p*H of the medium changes from 4.4 to 3.1) to make this compound a convenient indicator for the titration of strong acids by weak bases. The interested reader can find an extensive discussion of the microscopic equilibriums between the different MO structures in Ref. 19.

III. EXPERIMENTAL METHODOLOGY

The analysis of the linear optical absorption is one of the methods most commonly used to study structural changes of dye molecules in solutions.[22] The linear absorption spectra of MO solutions with different *p*H values were obtained in experiments using a water solution of the sodium salt of methyl orange at a concentration of 0.9 mM. Experimental UV-visible absorption spectra of the MO solutions were obtained over the 200–800 nm range using a model DV-Z500 spectrophotometer (Beckman, USA). Small quantities of an aqueous HCl solution were added to control the *p*H value, which was monitored through the use of a commercial *p*H meter. The same set of measurements was repeated using acetone, a solvent that although presenting a higher dipole moment than water (2.88 D vs 1.85 D) is aprotic and therefore does not dissolve MO very well, as well as ethanol (that has a dipole moment of 1.65 D).

To determine the nonlinear coefficient $\chi^{(3)}$ of the samples, the *Z*-scan technique[16] was employed. This method exploits the light-matter interaction so that an incident beam propagating inside the nonlinear medium induces a self-change in the phase that gives rise to a wave front distortion of the beam. By measuring the variation of the transmitted

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beam intensity through a circular aperture placed in front of a detector in the far-field region, one can determine the sign and magnitude of n_2. Moreover, when the entire light beam passing through the sample is detected, it becomes possible to determine α_2. The *Z*-scan measurements were performed using the second harmonic of a Q-switched and mode-locked Nd:YAG (YAG—yttrium aluminum garnet) laser delivering pulses of 70 ps (FWHM—full width at half maximum) at 532 nm as the light source. A single pulse at a repetition rate of 10 Hz was selected using a pulse picker. A 10 cm focal distance lens focused the laser beam, so that the measured beam waist was $\approx 40\ \mu$m. All experiments were made with the sample contained in a 1 mm long quartz cuvette at room temperature. The nonlinear experiment was performed only for the aqueous MO solution. The sample was mounted in a support placed in a computer-controlled translation stage that could be moved along the focus region in order to allow direct measurements of the nonlinear properties. A photodetector with an adjustable aperture in front of it was placed in the far-field region. The aperture size r_a is related to S, the linear aperture transmittance, by $S=1-\exp(-2r_a^2/w_a^2)$, with w_a denoting the beam radius at the aperture for very low incident power.[16] A small aperture *Z*-scan experiment corresponds to $S<1$, which is employed for n_2 measurements, and a wide or absent aperture means $S=1$, necessary for the determination of α_2. The z ordinate is measured along the beam propagation direction, and $z<0$ corresponds to locations of the sample between the focusing lens and its focal plane. A boxcar integrator was used in connection with a computer to record the signal. It is worth to mention that the measurements were always performed using fresh samples to guarantee that the *p*H value remained constant throughout the data acquisition process (that lasted only few minutes).

IV. THEORETICAL METHODOLOGY

The geometries of the MO molecules were fully optimized using the semiempirical parametric method 3 (PM3) (Ref. 23) and *ab initio* calculations were performed to confirm the stability of the corresponding structures. For all structures shown in Fig. 1, a planar configuration was assumed as the starting point of the geometry optimization calculations. Since our final goal is to compare the estimated theoretical hyperpolarizabilities of MO to the experimentally inferred values, in this first analysis of the minimal energy structures we have not considered the explicit contribution of solvent effects. In fact, only recently have special methods been used to incorporate solvent effects in the determination of ground state geometries of MO under different *p*H conditions.[17]

For the semiempirical calculations we have adopted the standard MOPAC parameters,[24–26] except for the convergence criterion, where a maximum step size of 0.05 was used. The standard 3-21G* basis set was used for all *ab initio* calculations, performed using the GAUSSIAN 94 program.[27]

V. RESULTS AND DISCUSSION

In Fig. 2 we show how the 250–700 nm absorption spectrum, of two different solutions of the MO molecule, changes when the *p*H of the medium is increased. In general terms, the absorption bands are consistent with the existence of π-π^* electronic transitions.[12] One can see in Fig. 2(a) that for an aqueous solution, the absorption spectrum at *p*H $\sim 6.6(>\mathrm{pK}_a)$ is characterized by two absorption bands centered at ≈ 460 nm and at ≈ 280 nm. For an acidic solution (*p*H ~ 2.9), however, the more intense absorption band is shifted to a longer wavelength and the solution acquires a red color. The isobestic point around 475 nm points out to the existence of acid-base equilibrium,[19] and the 500–540 nm band is attributed to the azonium ions.[20] The evolution of these observed features at two different *p*H values is also dependent on the type of solvent used, as one can see in Fig. 2(b), where we show the results for an acetone solution. At *p*H values greater than the pK_a, the more intense band is centered at 416 nm,[28] with a small peak at 312 nm also present. For this solvent, we also find that at low *p*H the most intense band is redshifted to 536 nm.

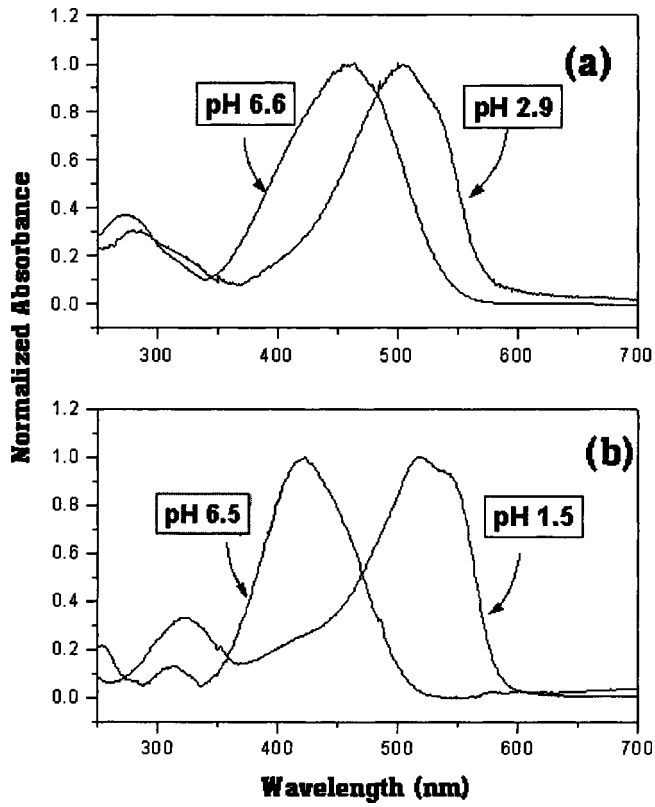

FIG. 2. Experimental UV-visible spectra of (a) aqueous and (b) acetone solutions of methyl orange in alkaline and acidic conditions.

Analysis of the effect of the solvent upon the linear absorption spectrum allows the identification of some important distinctions. First, in alkaline medium a blueshift of the spectrum is observed in going from water to acetone. This is what it should be expected, since it is standard chemistry knowledge that polar aprotic solvents do not solvate anions well.[29] As pointed out in Ref. 12, both the dielectric constant ε and the refractive index n of the solvent used affect the absorption spectrum of azo indicators, and the decrease of the solute-solvent interactions when the alkaline form of MO is dissolved in acetone ($\varepsilon=21.7$; $n=1.36$) instead of water ($\varepsilon=80$; $n=1.33$) should contribute to make the optical gap

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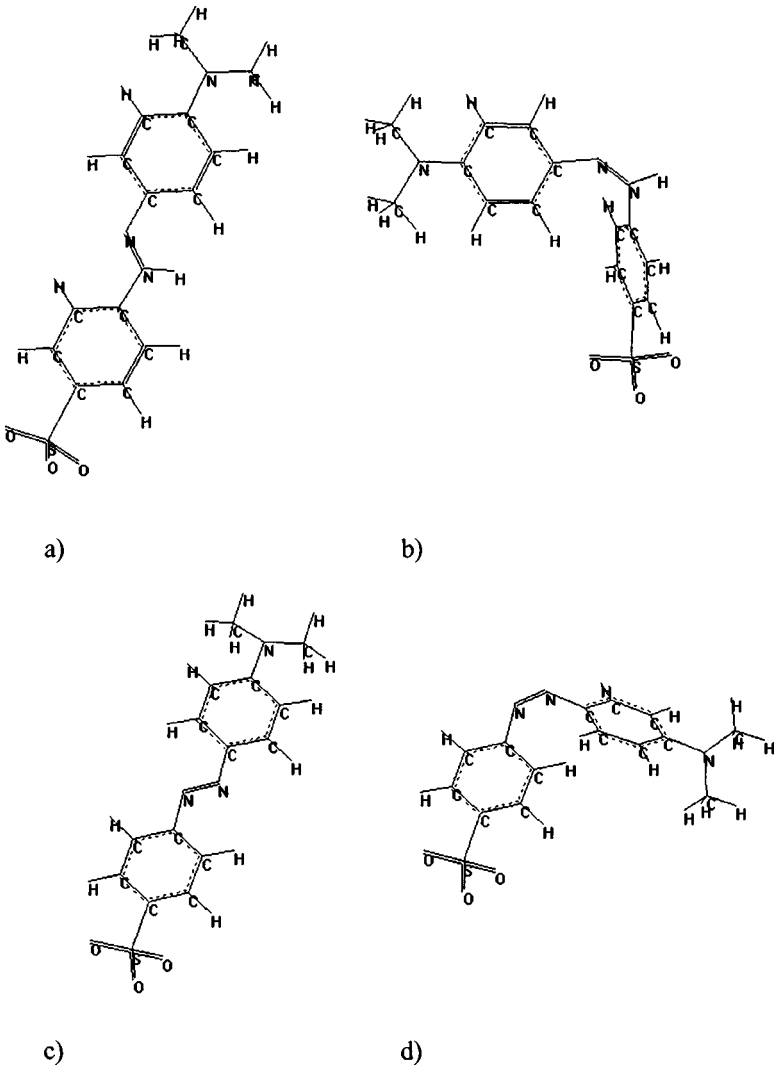

FIG. 3. The minimum energy conformations of the *cis* and *trans* isomers of the azonium (a and b) and alkaline (c and d) forms of the MO molecule as calculated at the PM3 level. The dihedral angle between the rings is zero for the *trans* forms, and corresponds to 90° and 60° for the *cis* conformations in b and d, respectively.

larger. On the other hand, under acidic *p*H a small displacement of the maximum absorption intensity to larger wavelengths can be noticed, while the absorption band in the UV region (and centered in 325 nm) becomes significantly more intense. This band is usually attributed to the ammonium zwitterionic form [Fig. 1(d)], with the isobestic point ~360 nm indicating the tautomeric equilibrium.[19] At the same time, the low energy shoulder seen under acidic conditions evolves to an independent peak when acetone is used as solvent, a fact that can be rationalized by assuming that in this polar aprotic medium the interaction among the MO molecules themselves becomes favored.[30]

The optimized geometries of MO molecules under different *p*H conditions were determined. As an illustrative example, the minimum energy conformations of the *cis* and *trans* isomers of the azonium and alkaline forms of MO are depicted in Fig. 3. Due to electron delocalization, even for the acidic structures the double bond character of the bridge in the azo group is large enough to establish a potential barrier [estimated in 6.6 kcal/mol (Ref. 17)] between the *trans* [Fig. 3(a)] and *cis* [Fig. 3(b)] configurations. Figures 3(c) and 3(d) depict the *trans* and *cis* conformations of the MO molecule in alkaline solutions, respectively. In each case, the *trans* structures were found to be the most stable and essentially planar, with a twisted conformation predicted for the *cis* isomers. The structure calculated for the *cis* ammonium form is in good agreement to that found in Ref. 17, in which solvent effects are explicitly considered. We have observed that the interaction between the N^+ and SO_3^- groups contributes to the fact that the *cis* ammonium form has a more closed conformation than that estimated for the *cis* azonium. The more planar structures predicted for the *trans* isomers are consistent with the fact that, for each *p*H condition, the corresponding PM3 calculated dipole moments were found to be smaller for the *cis* than for the *trans* forms (Table I).

TABLE I. Estimated PM3 dipole moments for the ground state of different forms of the methyl orange molecule.

MO molecule		Dipole moment (d)
Acidic form	*trans*-azonium	29.8
	cis-azonium	24.5
	trans-ammonium	28.5
	cis-ammonium	18.3
Basic form	*trans*	33.3
	cis	25.7

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TABLE II. Theoretical (PM3) and experimentally inferred (from *Z*-scan measurements) γ values for different forms of the methyl orange and the corresponding nonlinear refraction index n_2.

MO molecule		$\gamma_{\text{theor}}(\times 10^{-34}$ esu)	$\gamma_{\text{expt.}}(\times 10^{-36}$ esu)	$\lvert n_2\rvert(\times 10^{-14}$ cm^2/W)
Acidic form	*trans*-azonium	1.76	1.07	2.1
	cis-azonium	0.29		
	trans-ammonium	2.39		
	cis-ammonium	0.07		
Alkaline form	*trans*	0.44	<0.30	<0.6
	cis	0.40		

For the latter, the dipole moment is essentially oriented along the main molecular axis, a fact that has implications for the photoisomerization poling of azobenzene films.[31] On the other hand, the relatively low value of the dipole moment of the *cis* ammonium molecule is consistent with its predicted almost closed loop conformation.

The experimental investigation of the third-order nonlinear properties of the MO solutions was based on the Q-scan technique. We have observed that for $S<1$ (a experimental setup that leads to the determination of the n_2 value) the normalized transmittance ΔT is larger for the basic solutions (i.e., those with $p\text{H}>p_{\text{K}a}$) than for the acidic ones. On the other hand, for $S=1$ (from which α_2 is inferred), a higher value of ΔT was obtained for solutions with pH values lower than the $p_{\text{K}a}$. In the present case, the nonlinear coefficient has a negative signal for both small and large apertures ($S<1$ and $S=1$), as a result of the self-defocusing characteristic of n_2 and of the saturable absorption effect that originates α_2. From the transmittance curves, the values of n_2 and α_2, obtained using the procedure of Ref. 16, vary from $\lvert n_2\rvert = 2.1\pm 0.2\times 10^{-14}$ cm^2/W and $\lvert\alpha_2\rvert<0.2$ cm/GW for pH $=6.3$, to $\lvert n_2\rvert<0.6\times 10^{-14}$cm^2/W and $\lvert\alpha_2\rvert=1.45\pm 0.08$ cm/GW for $p\text{H}=3.2$. The n_2 and α_2 are related to the third-order susceptibility of the molecule.[16] On the other hand, the values of the corresponding second hyperpolarizabilities γ can be found from the determined experimental susceptibilities through the relation $\chi^{(3)}=Nf^4\gamma d$, where N is the number of molecules per cm^3 and f is a local field correction factor. The corresponding results and the experimentally determined values of γ and n_2 are shown in Table II.

The theoretical values of the second hyperpolarizabilities γ of the MO molecules under acidic and alkaline conditions were calculated using the PM3 Hamiltonian. A maximum integration step size of the 0.01 was adopted and third Harmonic generation forms were utilized. In Table II we also compare the estimated value of γ to the corresponding experimental results. As found before in the investigation of the nonlinear properties of the retinal derivatives,[4] more important than the agreement between the absolute values of the theoretically estimated and experimentally inferred hyperpolarizabilities is the correct description of the general trends of the change of γ as a function of the molecular conformation. In spite of the increased probability of *cis-trans* isomerization of the MO molecule under acidic conditions, from the data presented in Table II for the dependence of the nonlinear properties on the pH of the medium we can see that the response of the *trans* isomers continues to be dominant for the aqueous solution of MO at low pH values. On the other hand, note that opposite to what is predicted for the acidic forms, the estimated theoretical values of γ for the *trans* and *cis* alkaline forms are almost identical. In fact, while the *trans* conformations are planar (Fig. 3), the value of the dihedral angle between the aromatic rings in the *cis* isomers is predicted to be smaller for the alkaline than for the acidic case (60°compared to 90°). Also, the polarizability of the alkaline form is likely to be smaller because of the absence of a definite charge separation in this structure.

VI. SUMMARY

We have performed an experimental and theoretical study of the electronic structure of methyl orange, a well-known pH indicator. It has been shown that the comparison between the predicted geometries and nonlinear polarizabilities and the results of an experimental investigation on the linear and nonlinear optical properties of this molecule can provide useful insights into how the different structural forms of this indicator can affect its electronic properties. After one takes into account the different structural forms of the methyl orange molecule at low and high pH values, the analysis of the experimental linear absorption spectra reveals evidence of the presence of the ammonium zwitterionic structure of MO in acidic ($p\text{H}=2.9$) solutions, as previously suggested in the literature.[30] Also, formation of molecular aggregates seems to be favored under acidic conditions.[32] In fact, it has been established[33] that dimerization of MO should occur for acidic aqueous solutions for concentrations above 0.2 mM. Dimerization should also account for the shift of the maximum of absorption to ~450 nm.[22]

At the same time, the third-order nonlinear coefficient of methyl orange has been experimentally determined for picosecond pulses in the visible spectral region. From the experimental results, the second hyperpolarizability of methyl orange in acidic and basic media were inferred and calculated.

Although *cis*-azonium ions are proposed to easily isomerize via rotation around the –N═N– bond due to a decrease in the double bond character,[20] the analysis of the observed trends in the nonlinear response of the different possible molecular structures under distinct pH conditions suggest that the *trans* form of the ammonium variant of the MO molecule should dominate the observed nonlinear response of the compound under acidic conditions. This can be understood by considering that in the ammonium form the rotation around the –N═N– bond is less favored and that, as

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a consequence, more closed conformations are not favored. Since no definite charge separation occurs in the alkaline structure, the differences in the theoretical values of γ for the corresponding *trans* and *cis* forms are not as large as those predicted for the acidic structures.

ACKNOWLEDGMENTS

This work had the financial support of the Brazilian agencies CNPq, CAPES and FACEPE. J.D.N. was the recipient of a postdoctoral fellowship from CNPq.

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