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Onsager Reaction Field Description of Optical Properties of Octupolar Molecules in Solution

Yi Luo*

Fysikum, University of Stockholm
Box 6730, S-113 85 Stockholm, Sweden

Patrick Norman and Hans Ågren

Department of Physics and
Measurement Technology
Linköping University
S-581 83 Linköping, Sweden

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Two groups of organic compounds are commonly considered as useful for second harmonic generation; one is given by one-dimensional charge-transfer organic molecules, such as disubstituted benzenes and push−pull polyenes, and the other is given by so-called octupolar molecules. Significant solvent effects on the one-dimensional charge-transfer organic molecules have been verified both experimentally[1,2] and theoretically.[3−7] It has been shown for this group of molecules, having large permanent dipole moments, that the solvent effects can be well explained by the Onsager reaction field model.[3−7]

Since the proposal by Zyss,[8] many octupolar molecules have been studied.[9−14] Due to the lack of a permanent dipole moment, one has commonly assumed that these molecules are only a little solvent dependent and that the Onsager reaction field model does not apply. Contrasting this common notion, we show in this paper that a solvent indeed can have significant effects on the nonlinear optical properties of octupolar molecules and that, while the dipolar contributions certainly vanish for the total energy, they can be significant for the *molecular properties*. This means that the *Onsager model is adequate for describing the solvent effects on optical properties of octupolar molecules*. This observation can be explained by means of a simple semiclassical model.

1,3,5-Triamino-2,4,6-trinitrobenzene, TATB, is chosen as a prototype octupolar molecule in the present study. The geometry of TATB was optimized at the Hartree−Fock level with a double ζ valence (DZV) basis set[15] and found to be planar with D_{3h} symmetry. The solvent is simulated by a dielectric continuum in a multipolar expansion self-consistent reaction field (SCRF) model. The cavity radius is chosen to be 9.82 au in accordance with previous work on *p*-nitroaniline.[3] The polarizabilities α and β in solutions are calculated using quadratic response theory at the random phase approximation level.[16] All calculations were performed with the DALTON program package.[17]

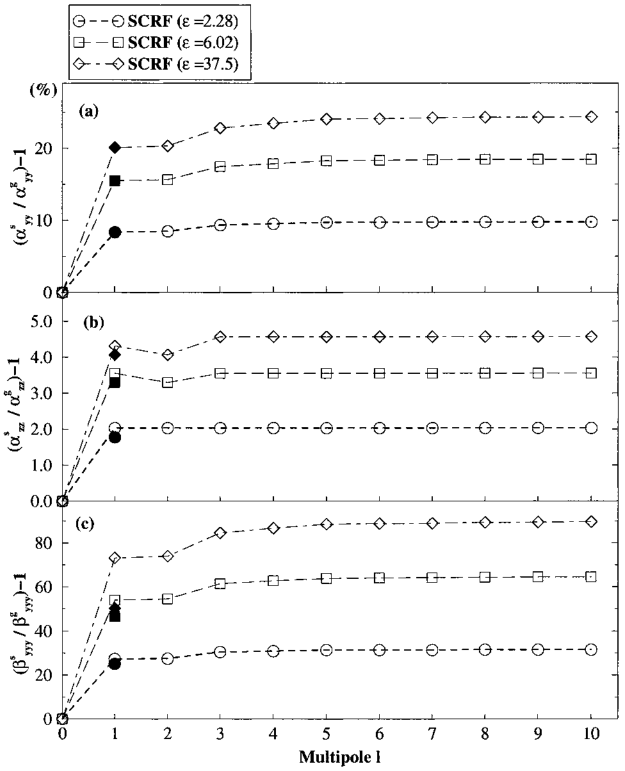

Figure 1. The dependence on multipole expansion (L) for $\Delta P = P^s/P^g - 1$ for TATB in three different dielectric media; $\epsilon = 2.28$ (circle, empty for SCRF, filled for SC), $\epsilon = 6.02$ (square, empty for SCRF, filled for SC), $\epsilon = 37.5$ (diamond, empty for SCRF, filled for SC). P is (a) α_{yy}, (b) α_{zz}, (c) β_{yyy}.

Figure 1 shows the nonzero components of the polarizability, α_{yy} ($= \alpha_{xx}$) and α_{zz}, and of the first hyperpolarizability β_{yyy} ($= -\beta_{yxx} = -\beta_{xyx} = -\beta_{xxy}$) of TATB in three different solutions characterized by the static dielectric constants $\epsilon = 2.28$, 6.02, and 37.5, respectively. All properties are given as cumulative functions of the multipolar expansion of the solute charge field and are found to be well-converged already at the multipole $l = 8$. It is predicted that the solvents have profound effects on the optical properties of TATB. For instance, at $\epsilon = 37.5$, corresponding to acetonitrile, the first hyperpolarizability β has increased by 90% with respect to the free, gas-phase value. A most striking fact is that the solvent effects are dominated by the dipolar term ($l = 1$).

Usually, the dipolar reaction field is viewed as a classical electric field, proportional to the permanent dipole moment of the molecule. This view can easily lead to the erroneous idea that without a permanent dipole moment, the reaction field is zero within the Onsager model and consequently that the solvent effects cannot be predicted. We will clarify this misconception by proposing a so-called semiclassical (SC) approximation. A detailed description of this approximation will be published elsewhere;[18] here we confine the presentation to the main elements.

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(1) Stähelin, M.; Burland, D. M.; Rice, J. E. *Chem. Phys. Lett.* **1992**, *191*, 245.

(2) Marder, S. R.; Gorman, C. B.; Meyers, F.; Perry, J. W.; Bourhill, G.; Brédas, J. L.; Pierce, B. M. *Science* **1994**, *265*, 632.

(3) Mikkelsen, K. V.; Luo, Y.; Ågren, H.; Jørgensen, P. *J. Chem. Phys.* **1994**, *100*, 8240.

(4) Yu, J.; Zerner, M. C. *J. Chem. Phys.* **1994**, *100*, 7487.

(5) Di Bella, S.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1994**, *116*, 4440.

(6) Dehu, C.; Meyers, F.; Hendricks, E.; Clays, K.; Persoons, A.; Marder, S. R.; Brédas, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 10127.

(7) Albert, I. D. L.; Marks, T. J.; Ratner, M. A. *J. Phys. Chem.* **1994**, *100*, 9714.

(8) Zyss, J. *Nonlinear Opt.* **1991**, *1*, 3.

(9) Joffre, M.; Yaron, D.; Silbey, R. J.; Zyss, J. *J. Chem. Phys.* **1992**, *97*, 5607.

(10) Zyss, J. *J. Chem. Phys.* **1993**, *98*, 6583.

(11) Brasseletc, S.; Zyss, J. *J. Opt. Soc. Am. B* **1998**, *15*, 257.

(12) Zyss, J.; Ledoux, I. *Chem. Rev.* **1994**, *94*, 77.

(13) Verbiest, T.; Clays, K.; Samyn, C.; Wolff, J.; Reinhoudt, D.; Persoons, A. *J. Am. Chem. Soc.* **1994**, *116*, 9320.

(14) Dhenaut, C.; Ledoux, I.; Samuel, I. D. W.; Zyss, J.; Bourgault, M.; LeBozec, H. *Nature* **1995**, *374*, 339.

(15) Dunning, T. H.; Hay, P. J. *Modern Theoretical Chemistry*; Plenum: New York, 1977.

(16) Sylvester-Hvid, K. O.; Jonsson, D.; Norman, P.; Ågren, H.; Mikkelsen, K. V. *J. Chem. Phys.* **1998**, *108*, xx.

(17) Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.; Ruud, K.; Ågren, H.; Andersen, T.; Bak, K.-L.; Bakken, V.; Christiansen, O.; Dahle, P.; Dalskov, E. K.; Enevoldsen, T.; Heiberg, H.; Hettema, H.; Jonsson, D.; Kirpekar, S.; Kobayashi, R.; Koch, H.; Mikkelsen, K. V.; Norman, P.; Packer, M. J.; Saue, T.; Taylor, P. R.; Vahtras, O. *Dalton, an ab initio electronic structure program, Release 1.0 (1997).* See [http://www.kjemi.vio.no/software/dalton/dalton.html.

(18) Luo, Y.; Norman, P.; Ågren, H. *J. Chem. Phys.* **1998**, *109*, 3589.

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Within the Onsager model, the total energy of the solvated molecule E_{sol} is given by

$$E_{\mathrm{sol}} = E_0 + W_{\mathrm{sol}} \tag{1}$$

$$W_{\mathrm{sol}} = -{}^{1}/_{2} f^{\mathrm{R}} \sum_i \mu_i \mu_i \tag{2}$$

where E_0 is the energy of the isolated molecule and W_{sol} is the solvation energy. μ_i is the dipolar operator, f^{R} the reaction field factor

$$f^{\mathrm{R}} = \frac{1\ 2(\epsilon - 1)}{a^3\ (2\epsilon + 1)} \tag{3}$$

a the radius of the spherical cavity, and ϵ the dielectric constant of the surrounding medium. The molecular properties can be defined as derivatives of the total energy with respect to the external perturbing field

$$\mu_j^{\mathrm{sol}} = -\left(\frac{\partial E_{\mathrm{sol}}}{\partial F_j}\right)_{F=0} \tag{4}$$

$$\alpha_{jk}^{\mathrm{sol}} = \left(\frac{\partial \mu_j^{\mathrm{sol}}}{\partial F_k}\right)_{F=0} \tag{5}$$

$$\beta_{jkl}^{\mathrm{sol}} = \left(\frac{\partial \alpha_{jk}^{\mathrm{sol}}}{\partial F_l}\right)_{F=0} \tag{6}$$

It follows that

$$\mu_j^{\mathrm{sol}} = \mu_j + f^{\mathrm{R}} \sum_i \mu_i \alpha ij \tag{7}$$

$$\alpha_{jk}^{\mathrm{sol}} = \alpha_{jk} + f^{\mathrm{R}} \sum_i (\alpha_{ji}\alpha_{ik} + \mu_i \beta_{ijk}) \tag{8}$$

$$\beta_{jkl}^{\mathrm{sol}} = \beta_{jkl} + f^{\mathrm{R}} \sum_i (\beta_{jli}\alpha_{ik} + \alpha_{ji}\beta_{ikl} + \alpha_{li}\beta_{ijk} + \mu_i \gamma_{ijkl}) \tag{9}$$

For a system without permanent dipole moment one has

$$\alpha_{jk}^{\mathrm{sol}} = \alpha_{jk} + f^{\mathrm{R}} \sum_i (\alpha_{ji}\alpha_{ik}) \tag{10}$$

$$\beta_{jkl}^{\mathrm{sol}} = \beta_{jkl} + f^{\mathrm{R}} \sum_i (\beta_{jli}\alpha_{ik} + \alpha_{ji}\beta_{ikl} + \alpha_{li}\beta_{ijk}) \tag{11}$$

i.e., the Onsager reaction field model predicts the changes of optical properties for molecules without permanent dipole moment upon solvation. The semiclassical approximation provides the connection between properties in gas phase and in solution and can be used to pinpoint the origin of the solvent effects on the optical properties of nonpolar molecules. The SC formula presented here can be only used for the static case; the extension to the dynamic case, which is possible, will not be discussed. We have calculated the solvent-induced changes on the polarizability and hyperpolarizability of TATB from the gas phase results. One can see from Figure 1 that the results for the polarizability obtained from the semiclassical approximation are in excellent agreement with the ones obtained from self-consistent reaction field calculations for solvents corresponding to all three dielectric constants chosen. For the hyperpolarizability, a deviation is observed for the large dielectric constant, whereas agreement remains good for the smaller dielectric constants, indicating that the model is useful for the hyperpolarizability of molecules in organic, nonpolar solvents. This can be understood by considering the fact that in the SC model the relaxation of the solute charge distribution, or to say, the feedback of the induced moment on the reaction field, is not included. Such a relaxation effect increases for larger dielectric constants.

We have shown that solvent effects on the linear and nonlinear optical properties for octupolar molecules are significant and that most of the contributions are derived from the dipolar interactions. This phenomenon was explained and also quantified by a proposed semiclassical approximation, in which the molecular dipole is treated quantum mechanically. The semiclassical approximation is an efficient method for simulating molecular properties in solution, since it relies only on gas phase calculations.

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