J. Phys. Chem. A **2007,** *111,* 11867−11872

Role of Charge Transfer Interaction and Conjugation Length on Electrical Polarizability of Doped *trans*-Polyacetylene Oligomers

Sabyasachi Sen and Swapan Chakrabarti*

Department of Chemistry, University of Calcutta, 92, A.P.C. Ray Road, Kolkata 700 009, India

Received: April 23, 2007; In Final Form: September 5, 2007

The effects of charge transfer and molecular chain length on the electrical polarizability of doped *trans*-polyacetylene oligomers have been investigated using a series of quantum chemical methods ranging from Hartree−Fock to current density functional theory. Polarizability tensors of pristine and metal-doped *trans*-polyacetylene oligomers have been estimated. The nature of variations of polarizability tensor components are quite different for pristine and doped oligomers. For doped samples, distinct minima in the average static polarizabilities per acetylene unit have been observed. The results suggest that the competitive role of charge-transfer interaction and oligomer chain length are responsible for the observed minima. To simulate the ab initio results on polarizability variation, we propose a mathematical model that describes the minima quite satisfactorily.

Introduction

Electric polarizability and hyperpolarizabilities of molecular systems are significant because they are associated with the fundamental characteristics of electronic structure such as hardness/softness, acidity/basicity, ionization potential, and so forth.[1−8] In recent years, the center of attention of exploring optical properties of materials has been shifted gradually from conventional inorganic solids to organic conjugated molecules. In organic conjugated systems, π electrons play a significant role in determining the optical activity of these materials.[9,10] Apart from the conjugation length,[11−13] the optoelectrical properties of long-chain conjugated systems are affected tremendously by many factors, namely, the effect of donor and acceptor substitutions,[14,15] the presence of dopants[16] or defects,[17−19] and so forth. Exploring the optoelectrical properties of such systems is thus significant both from a theoretical as well as an experimental standpoint.

Of the many conjugated long-chain systems identified so far, polyacetylene takes a special position in this family owing to its structural simplicity, and this in turn makes the system a role model for many quantum chemical calculations. Besides the important electrical properties of polyacetylene and other conjugated polymers, the optoelectrical properties of these materials are also very fascinating. With the advent of modern sophisticated quantum computational techniques, investigation at the theoretical level to elucidate the mechanism behind the high degree of linear and nonlinear optical coefficients for such long-chain molecular systems becomes easier. Earlier, static polarizabilities and hyperpolarizabilities of closed-shell π-conjugated systems have been estimated using Hartree−Fock (HF) and semiempirical calculations.[16,20−22] Perturbative density matrix treatment has also been applied to investigate the static first- and second-order hyperpolarizabilities of long-chain conjugated system, C_nH_{n+2}.[23] In the closed-shell π-conjugated system, the electron correlation is much stronger because the motion of the electron is confined only in the chain direction. This role of electron correlation on polarizability and hyperpolarizability of long-chain closed-shell π-conjugated system has been studied extensively by the Møller−Plesset (MP_2) perturbation technique.[24−26]

Because doped conjugated polymers have different physicochemical properties in comparison to their undoped analog, various models with soliton-, polaron-, and bipolaron-type charged lattices have been proposed for doped materials. An et al.[21] studied the response properties of charged soliton in a polyenic chain using the HF technique. Champagne et al.[16] investigated the effect of charging on the longitudinal second hyperpolarizabilities of the *trans*-polyacetylene chain. In their work, optoelectrical properties were computed for pristine as well as alkali metal atom (Li, Na ,and K) doped samples. The major disadvantage of both works was the absence of electronic correlation in their theoretical model. In a more recent work, Hu et al.[27] reported theoretical results on longitudinal polarizability and second-order hyeperpolarizabilities for *trans*-polyacetylene systems. They employed the Pariser−Paar−Pople model for the estimation of polarizability and hyperpolarizability, and in their work electron correlation has been introduced through the density matrix renormalization group method. The main drawback of this work was the absence of actual dopants in the *trans*-polyacetylene backbone.

The objective of the present investigation is to explicate the role of charge transfer from real dopants (Li, Na, and K) and conjugation length on the static polarizability of *trans*-polyacetylene oligomers. Polarizability tensors of undoped as well as doped *trans*-polyacetylene have been estimated through a series of calculations using time-dependent current density functional theory (TDCDFT),[28] time-dependent density functional theory (TDDFT) with ALDA,[29,30] the finite field DFT/B3LYP[31−33] method, and the HF level of theory.

Computational Details

The geometry optimization of both doped and undoped unit cells of *trans*-polyacetylene has been implemented in the Amsterdam density functional package (ADF 2006.01).[34] The

---

* Corresponding author. E-mail: swapanchem@yahoo.co.in. Fax: 91-33-23519755.

10.1021/jp0731147 CCC: $37.00

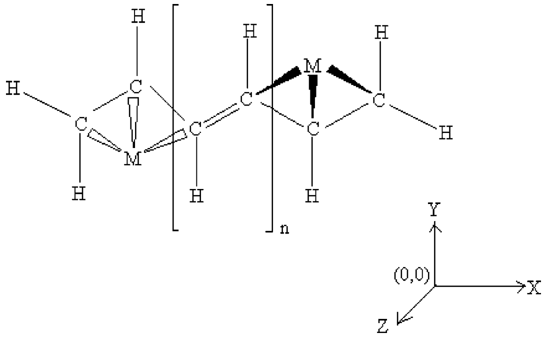

Figure 1. Unit cell of a metal-doped *trans*-polyacetylene oligomer. The directions of the axes are given aside. M: Li/Na/K.

geometry of the unit cells at different doping levels have been optimized through unconstrained relaxation search. The relaxation has been carried out using the BLYP-type[33,35] exchange-correlation functional and the TZ2P basis set, which consists of a triple-ζ basis augmented with two polarization functions. The relevant unit cell is depicted in Figure 1. In the optimized structure of the undoped *trans*-polyacetylene unit cell, the C−C single and double bond lengths are 1.420 and 1.340 Å, respectively. For the doped samples, the C−C double bond lengths are 1.380 Å for Li and Na doping and 1.391 Å for K doping. Likewise, C−C single bond lengths are 1.410, 1.400, and 1.401 Å for Li, Na, and K doping, respectively. In doped samples, the dimerization amplitude varies between 0.02 and 0.03 Å and C−Li, C−Na, and C−K bond distances are 2.00, 2.52, and 2.71 Å, respectively.

Response calculations have been implemented in the Amsterdam density functional (ADF 2006.01)[34] package and the GAUSSIAN 03 suite of programs.[36] Within ADF, the Vignale−Kohn functional[37−39] and adiabatic local density approximation (ALDA)[29,30] have been used under the spin-restricted TDCDFT and TDDFT scheme. Alternatively, the GAUSSIAN 03[36] program has been used for the calculation of static polarizabilities at the DFT/B3LYP and HF levels of theory.

Results and Discussion

The variation of axial static polarizability (α_{XX}) per acetylene unit against N (N is the number of acetylene units up to which the present investigation has been carried out) for undoped oligomers is depicted in Figure 2. The relevant variations are nonlinear in all of the approaches. Earlier, van Fassen et al.[28] applied TDCDFT with the Vignale−Kohn functional (VK) for conjugated systems like *trans*-polyacetylene, polydiacetylene, polyyne, and polythiophene, and their results were quite comparable with other correlated methods like the MP2 technique.[40] In this work, the axial static polarizabilities (α_{XX}) per acetylene unit of undoped oligomers show a similar trend and the absolute values are very close to those of van Fassen et al.[28] The transverse components (α_{YY} and α_{ZZ}) of static polarizability are relatively small in comparison to those of the axial component.

For doped oligomers, the addition of dopant atoms to the *trans*-polyacetylene backbone initiates a charge-transfer interaction. Therefore, both charge-transfer interaction and oligomer chain length will affect the net static polarizability. Hence, the average polarizability is physically more meaningful than axial or transverse components alone. The average static polarizability tensor is defined[41] in terms of Cartesian components as

$$\langle\alpha\rangle = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

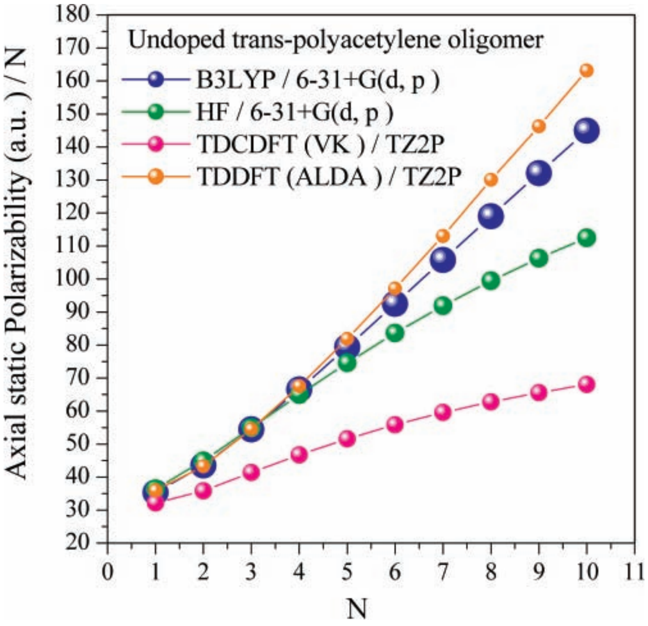

Figure 2. Variation of axial static polarizability per acetylene unit against the number of acetylene units, N, for an undoped *trans*-polyacetylene oligomer at different quantum chemical levels.

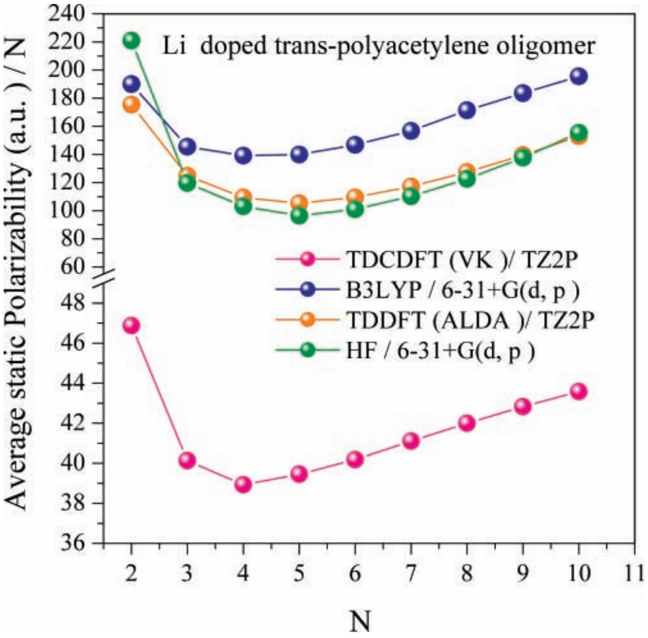

Figure 3. Variation of average static polarizability per acetylene unit against the number of acetylene units, N, for a Li-doped *trans*-polyacetylene oligomer at different quantum chemical levels.

where, α_{xx}, α_{yy}, and α_{zz} are the diagonal elements of the polarizability tensor matrix. Figure 3 illustrates the variation of average static polarizability per acetylene unit against N for Li-doped *trans*-polyacetylene oligomers at different levels of theory. Interestingly, it has been observed that the average static polarizability per acetylene unit passes through a minimum in all of the quantum chemical approaches. The minimum appears at $N = 4$ in the case of the TDCDFT (VK) and DFT/B3LYP approaches. With the TDDFT (ALDA) and HF techniques, the minimum occurs at $N = 5$. Appearance of the minima in average static polarizability per acetylene unit in all of the quantum chemical methods is quite consistent and completely different from that of the undoped analog.

Similar results are obtained in case of Na doping. Relevant variations are plotted in Figure 4. The minimum in average static

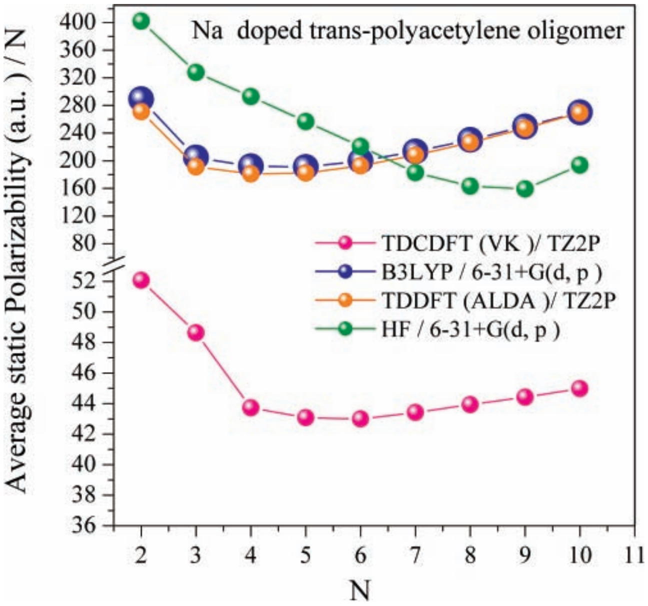

Figure 4. Variation of average static polarizability per acetylene unit against the number of acetylene units, *N*, for a Na-doped *trans*-polyacetylene oligomer at different quantum chemical levels.

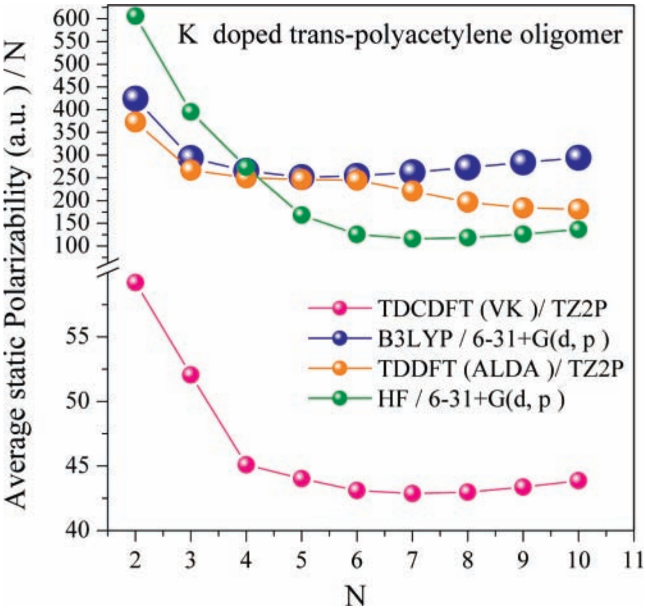

Figure 5. Variation of average static polarizability per acetylene unit against the number of acetylene units, *N*, for a K-doped *trans*-polyacetylene oligomer at different quantum chemical levels.

polarizability per acetylene unit has been obtained at $N = 6$, 5, 9, and 4 for TDCDFT (VK), DFT/B3LYP, HF, and TDDFT (ALDA) techniques, respectively. The variation of average static polarizability per acetylene unit in the case of K doping is shown in Figure 5. The results obtained are comparable except for that of TDDFT (ALDA). Although the minimum in average static polarizability occurs at $N = 5$ for DFT/B3LYP, the same is observed at $N = 7$ for the TDCDFT (VK) and HF approaches.

The observed discrepancies between various quantum chemical techniques can be explained if we look at the methods and nature of the chosen functionals. For undoped samples, TDCDFT (VK) gives better results in comparison to other methods. In TDCDFT (VK), the exchange correlation potential is nonlocal in time but local in space with current as the basic variable. Because the current density in the bulk of the system measures the charge buildup at the boundaries, it can be used as the local

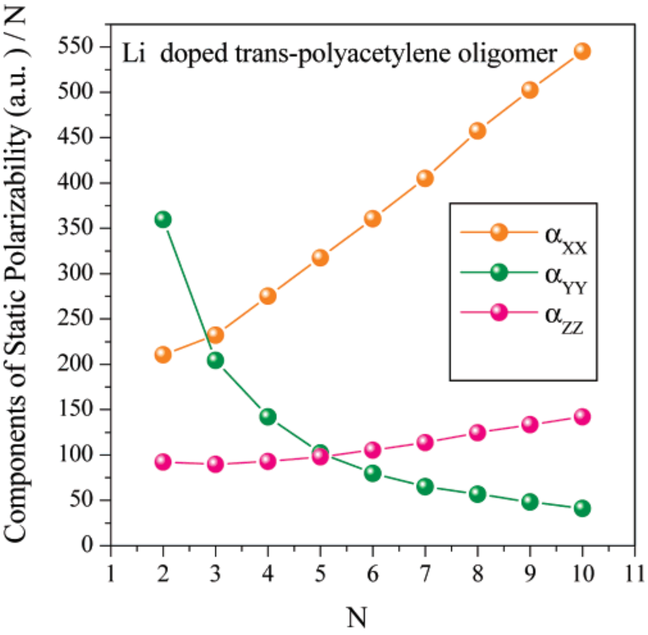

Figure 6. Variation of different components (α_{XX}, α_{YY}, α_{ZZ}) of static polarizability per acetylene unit against *N* for a Li-doped *trans*-polyacetylene oligomer estimated at the DFT/B3LYP level of theory.

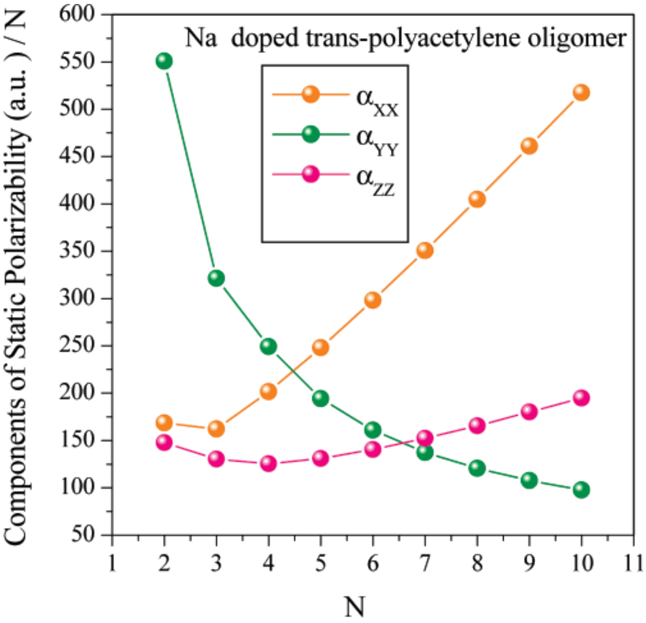

Figure 7. Variation of different components (α_{XX}, α_{YY}, α_{ZZ}) of static polarizability per acetylene unit against *N* for a Na-doped *trans*-polyacetylene oligomer estimated at the DFT/B3LYP level of theory.

indicator of the global changes in the system. The overestimation of polarizability in TDDFT (ALDA) may be due to the poor representation of electron–hole correlations within the TDDFT method. Although TDCDFT/VK gives better results for undoped oligomers, it fails to produce consistent results for doped samples. If we compare Figures 3–5, it is quite evident that the observed minima in average static polarizability per acetylene unit are most consistent with the DFT (B3LYP) approach for all types of dopants and this may possibly be due to the fact that B3LYP accounts better charge-transfer interactions over other functionals used in the present investigation.

At this stage, it is inevitable to answer the question of why these minima occur in the polarizability variation with chain length for all dopants. To address this question, we examine the variation of individual components (α_{XX}, α_{YY}, and α_{ZZ}) of

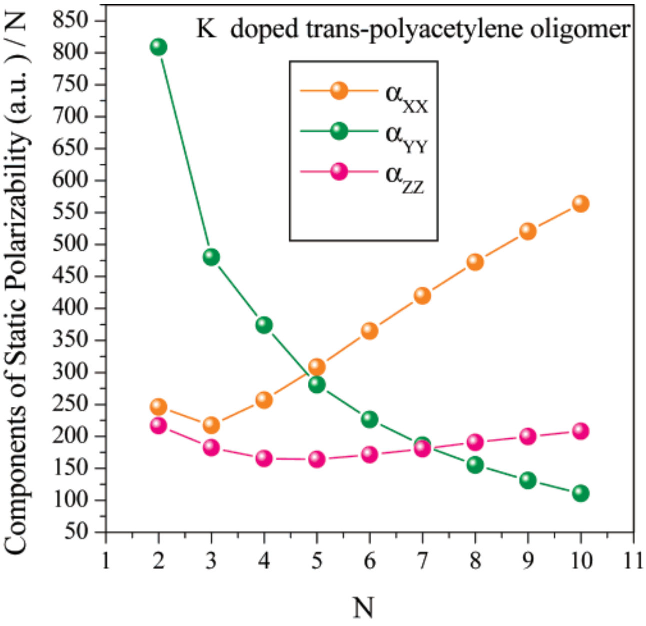

Figure 8. Variation of different components (α_{XX}, α_{YY} , α_{ZZ}) of static polarizability per acetylene unit against N for a K-doped *trans*-polyacetylene oligomer estimated at the DFT/B3LYP level of theory.

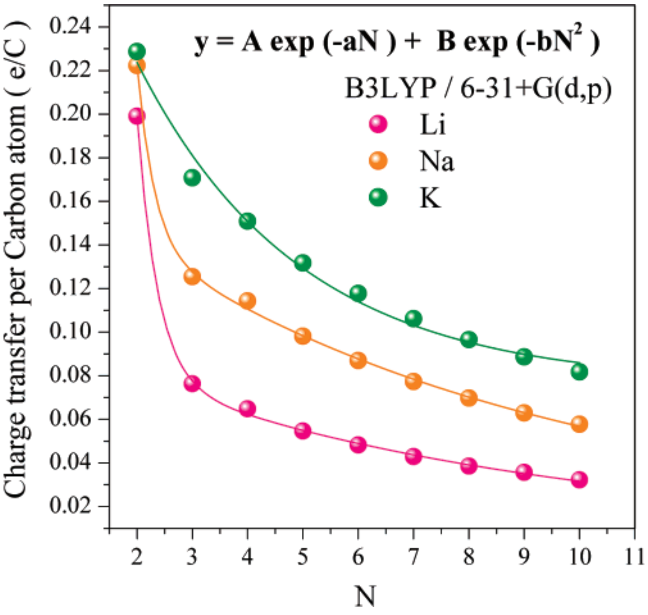

Figure 9. Variation of charge transfer per carbon atom (e/C) from metal atoms to the *trans*-polyacetylene backbone (B3LYP/6-31+G(d, p) results).

polarizability tensors for all types of dopants at the B3LYP level of theory. The relevant variations are presented in Figures 6−8. It is quite clear from these figures that in the net polarizability value the α_{YY} component plays a role opposite of that of the other two components. It is also noticeable from Figure 1 that charger transfer from the metal atom to the *trans*-polyacetylene backbone takes place in the Y direction. The variation of charge transfer per carbon atom (Figure 9) illustrates a second-order exponential decrease with N. Remarkably, α_{YY} also follows a similar trend (Figures 6−8). The nature of variation of charge transfer per carbon atom and α_{YY} being similar indicates that apart from oligomer chain length, charge-transfer interactions play a significant role in determining the average polarizability values of doped oligomers.

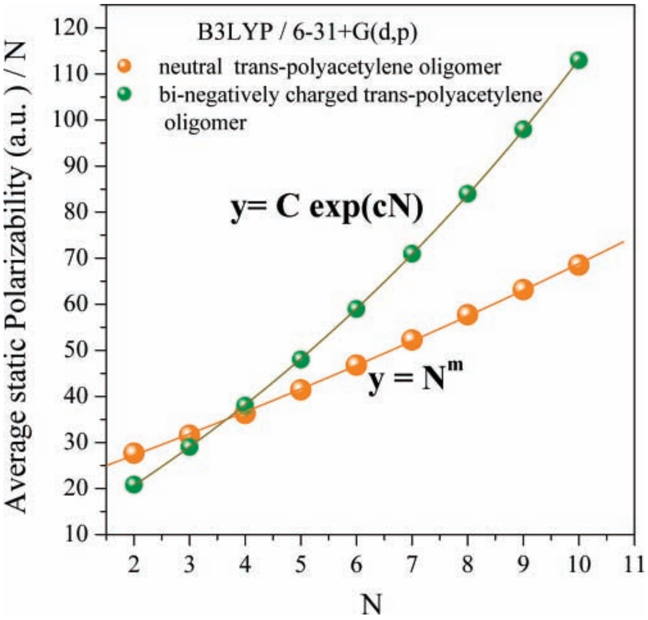

Figure 10. Variation of average static polarizability per acetylene unit against N for bi-negatively charged and neutral *trans*-polyacetylene oligomers estimated at the DFT/B3LYP level of theory.

Earlier, Lee et al.[42] estimated the intermolecular charge-transfer-driven polarizability of donor/acceptor substituted polyene and polyyne. In their study, the polyene and polyyne systems behave like insulating spacer units between donor and acceptor moiety, for example, NH_2/NO_2. They employed the HF scheme to evaluate the size dependence of optical polarizability for such donor−spacer−acceptor systems. Remarkably, they found a maximum in the polarizability variation curve with chain length of the spacer and proposed a mathematical model to clarify the observed variation in polarizability. According to their model, the change in polarizability depends on two factors, namely, length of the spacer and screened effective charge of the lattice. The length dependence enters into the picture following a power law, N^m, where N is the number of spacer unit and m is the power law exponent. Alternatively, the screened effective charge on the lattice follows a first-order exponential decay. On the basis of this model, Lee et al.[42] rationalized the observed maximum in the polarizability variation curve of the donor−spacer−acceptor system. Instead of a maximum, we found minima in the variation of average static polarizability for our model systems and this is in clear contradiction with the prediction of Lee et al.[42] Unlike their work,[42] the dopant metal atom acts as a donor and the *trans*-polyacetylene oligomer backbone itself acts as an acceptor as well a spacer in our model system. Because our model system is significantly different from that of Lee et al.,[42] reinvestigation of the role of these two factors on polarizability is very essential.

To provide a mathematical model for the observed polarizability variation, we consider only the B3LYP results because they are the most consistent. Figure 9 demonstrates the B3LYP results of charge transfer per carbon atom from donor atoms to the acceptor/spacer unit. The best fit (see the Supporting Information) for the relevant variation follows a second-order exponential decay of the form $[A\ \exp(-aN) + B\ \exp(-bN^2)]$ instead its first-order counterpart. In a pristine *trans*-polyacetylene oligomer, the average static polarizabiltiy per acetylene unit exhibits a power law increament (N^m; $m = 1.45$ for B3LYP results). In the present scenario, to examine the role of chain length independently, we considered binegatively charged *trans*-polyacetylene oligomers for polarizability calculations because

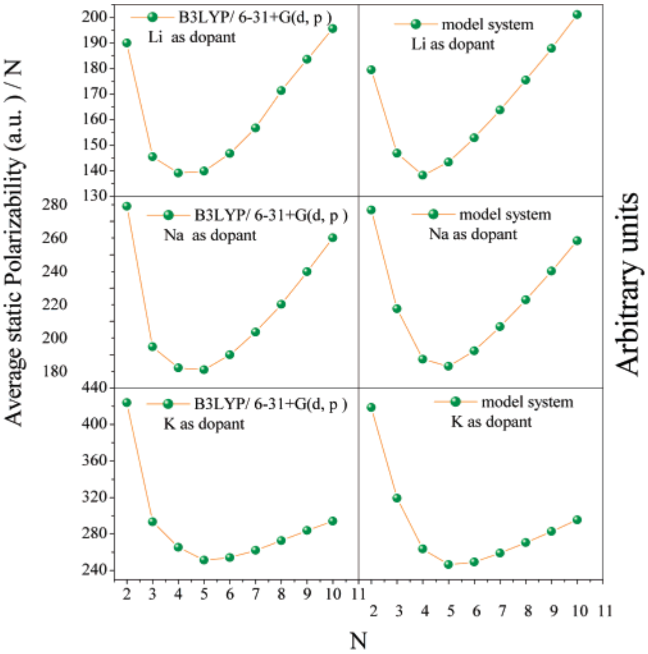

Figure 11. Variation of average static polarizability per acetylene unit against N calculated from the proposed mathematical model and the DFT/B3LYP-level calculations.

they mimic our acceptor moiety (charge is transferred from the donor to the acceptor/spacer moiety). Interestingly, variation of the static polarizability per acetylene unit shows an exponential growth instead of a power law increment (Figure 10). Therefore, the role of chain length and screened effective charge on polarizability for our model system is significantly different from that of Lee et al.[42] We propose a new mathematical form $[A_1 \exp(-aN) + B_1 \exp(-bN^2) + C_1 \exp(cN)]$ to simulate the observed variation in average static polarizability per acetylene unit. In this expression, the first two terms resemble charge-transfer variation per carbon atom from donor (metal atoms) to acceptor/spacer (*trans*-polyacetylene oligomer backbone) and the last term represents chain length dependence when the acceptor becomes the spacer. The values of fitted exponents and coefficients are given in the Supporting Information. A comparison of the B3LYP results and those obtained from our model calculations are presented in Figure 11, which clearly indicates that the model calculation agrees well with the B3LYP results. Finally, it is important to note that the present mathematical model is not valid when N is very large because of the divergence problem of $C_1 \exp(cN)$.

Conclusions

We calculated the static polarizability tensors per acetylene unit for pristine and doped (Li, Na, and K as dopant) *trans*-polyacetylene oligomers using a wide range of quantum chemical techniques. The investigations suggest that the nature of variation of static polarizability per acetylene unit for doped and undoped samples are quite different. Instead of a nonlinear rise, distinct minima have been observed in the polarizability variation curves of the doped samples. We conclude that the competitive role of charge-transfer interactions and molecular chain length is responsible for the observed minima. We also propose a mathematical model that can successfully explain the observed variation in average static polarizability per acetylene unit in doped samples. It is worth mentioning that the results obtained could be improved if vibrational, rotational, and other frequency dependent effects are included.

Acknowledgment. The financial support from DST, Govt. of India (Under FIST Program) to purchase the GAUSSIAN 03 program is gratefully acknowledged. We also acknowledge the financial support from UGC, Govt. of India (Xth plan) to purchase the ADF program. S.S. acknowledges Prof. A. Guha, Director, JIS College of Engineering.

Supporting Information Available: Various power law exponents, chosen coefficients along with χ^2 for the best fit of B3LYP results for all types of dopants, and components of the polarizability tensors for doped and undoped samples. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Vela, A.; Gázquez, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 1490.
(2) Nagle, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 4741.
(3) Lee, M.; Katz, E. H.; Erben, C.; Gill, D. M.; Gopalan, P.; Heber, J. D.; McGee, D. J. *Science* **2002**, *298*, 1401.
(4) Shi, Y.; Zhang, C.; Zhang, H.; Bechtel, J. H.; Dalton, L. R.; Robinson, B. H.; Steier, W. H. *Science* **2000**, *288*, 119.
(5) Luo, J.; Haller, M.; Li, H.; Tang, H.-Z.; Jen, A. K.-Y.; Jakka, K.; Chou, C.-H.; Shu, C.-F. *Macromolecules* **2004**, *37*, 248.
(6) Zhang, C.; Dalton, L. R.; Oh, M. C.; Zhang, H.; Steier, W. H. *Chem. Mater.* **2001**, *13*, 3043.
(7) Sen, S.; Chakrabarti, S. *Phys. Rev. B* **2006**, *74*, 205435.
(8) Karamanis, P.; Maroulis, G.; Pouchan, C. *J. Chem. Phys.* **2006**, *124*, 071101.
(9) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31.
(10) Kanis, D.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195.
(11) Heflin, J. R.; Wong, K. Y.; Zammani-Khamiri, O.; Garito, A. F. *Phys. Rev. B* **1988**, *38*, 1573.
(12) Hurst, G. J. B.; Dupuis, M.; Clementi, E. *J. Chem. Phys.* **1988**, *89*, 385.
(13) Mukamel, S.; Takahashi, A.; Wang, H. X.; Chen, G. *Science* **1994**, *266*, 250.
(14) Garito, A. F.; Heflin, J. R.; Wong, K. Y.; Zamani-Khamiri, O. *Proc. SPIE* **1988**, *971*, 2.
(15) Marder, S. R.; Torruellas, W. E.; Blanchard-Desce, M.; Ricci, V.; Stegeman, G. I.; Gilmour, S.; Bredas, J. L.; Li, J.; Bublitz, G. U.; Boxer, S. G. *Science* **1997**, *276*, 1233.
(16) Champagne, B.; Spassova, M.; Jadin, J.; Kirtman, B. *J. Chem. Phys.* **2002**, *116*, 3935.
(17) de Melo, C. P.; Silbey, R. *Chem. Phys. Lett.* **1987**, *140*, 537.
(18) de Melo, C. P.; Fonseca, T. L. *Chem. Phys. Lett.* **1996**, *261*, 28.
(19) An, Z.; Wong, K. Y. *J. Chem. Phys.* **2001**, *114*, 1010.
(20) Champagne, B.; Luis, J. M.; Duran, M.; Andre's, J. L.; Kirtman, B. *J. Chem. Phys.* **2000**, *112*, 1011.
(21) An, Z.; Wong, K. Y. *J. Chem. Phys.* **2003**, *119*, 1204.
(22) Gu, F. L.; Bishop, D. M.; Kirtman, B. *J. Chem. Phys.* **2001**, *115*, 10548.
(23) de Melo, C. P.; Silbey, R. *J. Chem. Phys.* **1988**, *88*, 2567.
(24) T-Sucarrat, M.; Solà, M.; Duran, M.; Luis, J. M.; Kirtman, B. *J. Chem. Phys.* **2003**, *118*, 711.
(25) Fonseca, T. L.; Castro, M. A.; Cunha, C.; Amaral, O. A. V. *Synth. Met.* **2001**, *123*, 11.
(26) Oliveira, L. N.; Amaral, O. A. V.; Castro, M. A.; Fonseca, T. L. *Chem. Phys.* **2003**, *289*, 221.
(27) Hu, W.; Ma, H.; Liu, C.; Jiang, Y. *J. Chem. Phys.* **2007**, *126*, 044903.
(28) van Faassen, M.; de Boeij, P. L.; van Leeuwen, R.; Berger, J. A.; Snijders, J. G. *Phys.Rev. Lett.* **2002**, *88*, 186401.
(29) Runge, E.; Gross, E. K. U. *Phys. Rev. Lett.* **1984**, *52*, 997.
(30) Gross, E. K. U.; Kohn, W. *Adv. Quantum Chem.* **1990**, *21*, 255.
(31) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.
(32) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
(33) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(34) http://www.scm.com.
(35) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(36) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.;

Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(37) Vignale, G.; Kohn, W. *Phys. Rev. Lett.* **1996**, *77*, 2037.

(38) Vignale, G.; Kohn, W. *Electronic Density Functional Theory: Recent Progress and New Directions*; Dobson, J. F., Vignale, G., Das, M. P., Eds.; Plenum Press: New York, 1998.

(39) Vignale, G. *Int. J. Mod. Phys. B* **2001**, *15*, 1714.

(40) Toto, T. T.; Toto, J. L.; de Melo, C. P.; Hasan, M.; Kirtman, B. *Chem. Phys. Lett.* **1995**, *244*, 59.

(41) Buckingham, A. D. *Adv. Chem. Phys.* **1967**, *12*, 107.

(42) Lee, J. Y.; Mhin. B. J.; Mukamel, S.; Kim, K. S. *J. Chem. Phys.* **2003**, *119*, 7519.