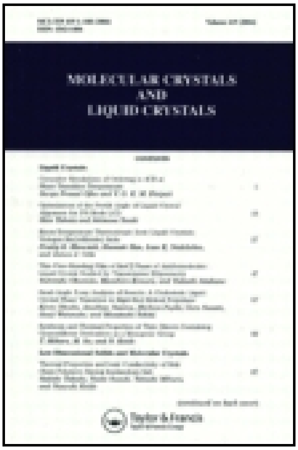

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THEORETICAL STUDIES ON HYPERPOLARIZABILITIES OF NITROXIDE SPECIES II. SECOND HYPERPOLARIZABILITY OF p-NPNN

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Abstract Static second hyperpolarizabilities (γ's) for para-nitrophenyl nitronyl nitroxide (p-NPNN), which is one of thermally stable organic radical systems, are calculated by the finite-field (FF) method in the INDO coupled unrestricted Hartree-Fock (CUHF) approximation. The hyperpolarizability density analysis is performed to elucidate the characteristics of spatial contributions of electrons to the γ's. It is found from these results that the largest component (γ_{xxxx}) of this system is negative and is dominantly determined by the contribution from the γ_{xxxx} densities of nitronyl nitroxide radical group.

INTRODUCTION

Much effort has been made for the elucidation of the mechanism of nonlinear optical phenomena for organic substances. In particular, the theory of second hyperpolarizability (γ), which is the origin of macroscopic third-order nonlinear optical response, has advanced rapidly. However, most organic nonlinear optical systems which have been investigated are neutral closed-shell systems, and only few attempts have so far been made to investigate nonlinear optical effects of open-shell systems. In this study, therefore, we investigate the static γ of para-nitrophenyl nitronyl nitroxide (p-NPNN), which involves a thermally stable nitroxide radical and is also known to constitute an organo-ferromagnetic crystal. The hyperpolarizbility density analysis[1] in the Mulliken approximation is performed in order to elucidate the feature of main spatial contribution of electrons to the γ. On the basis of our classification rule of γ,[2] this molecule is expected to exhibit a large negative γ, which is rarely observed in typical organic nonlinear optical compounds. The sign of γ relates to self-focussing and defocussing effects, and the search of systems with negative γ's is important in quantum optics. In addition, we predicted that the γ's for nitroxide species are very sensitive to subtle chemical and physical perturbations.[3,4] Namely, these systems have a possibility of being promising compounds for the "controllable nonlinear magneto-optical system".

CALCULATION AND ANALYSIS METHODS

Some components of the static γ's for doublet state of p-NPNN (shown in Figure 1) are calculated by the finite-field (FF) method in the INDO coupled unrestricted Hartree-Fock (CUHF) approximation. The geometry of p-NPNN is obtained from the experimental data for β-phase p-NPNN crystal.[5] We use 0.0025 a.u. as the minimum electric field in the FF method. The γ_{iiii} is calculated by the numerical differentiation of total energy E with respect to the field F^i.

The γ_{iiii} can be expressed by[1]

$$\gamma_{iiii} = -\frac{1}{3!}\int \boldsymbol{r}^i \rho^{(3)}_{iii}(\boldsymbol{r}) d\boldsymbol{r}^3, \tag{1}$$

where the $\rho^{(3)}_{iii}(\boldsymbol{r})$ is referred to as γ_{iiii} density defined by

$$\rho^{(3)}_{iii}(\boldsymbol{r}) = \left.\frac{\partial^3 \rho}{\partial F^i \partial F^i \partial F^i}\right|_{\boldsymbol{F}=0}. \tag{2}$$

In this study, we evaluate $\rho^{(3)}_{iii}(\boldsymbol{r})$ in the Mulliken approximation. In order to explain the analysis method employing the plots of γ_{iiii} densities, we consider a pair of localized $\rho^{(3)}_{iii}(\boldsymbol{r})$ shown in Figure 2. The arrow from positive to negative $\rho^{(3)}_{iii}(\boldsymbol{r})$ shows the sign of the contribution determined by the relative spatial configuration between the two $\rho^{(3)}_{iii}(\boldsymbol{r})$'s. Namely, the sign of the contribution becomes positive when the direction of the arrow coincides with the positive direction of the coordinate system. The contribution determined by the $\rho^{(3)}_{iii}(\boldsymbol{r})$'s of the two points is more significant, when their distance is larger.

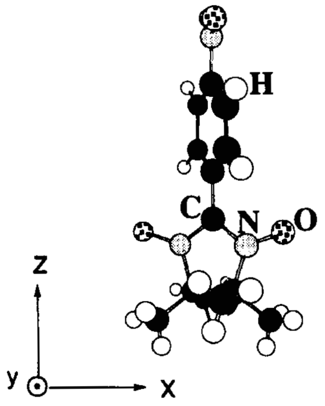

FIGURE 1 Structure of p-NPNN

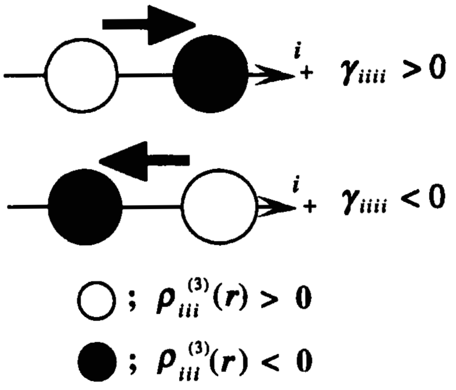

FIGURE 2 γ_{iiii} density plot

RESULTS AND DISCUSSION

The largest and the second largest components of p-NPNN are found to be γ_{xxxx} = -23370 a.u. and γ_{zzzz} = 14750 a.u., respectively. The γ_{xxxx} and γ_{zzzz} density plots for total, alpha (up spin) and beta (down spin) electrons are shown in Figures 3 and 4, respectively. The approximate γ_{iiii}'s (obtained from γ_{iiii} densities in the Mulliken approximation), which qualitatively well reproduce the CUHF γ_{iiii}'s, are also indicated. As shown in Figure 3, the total γ_{zzzz} is primarily contributed from the γ_{zzzz} densities for nitronyl nitroxide (ONCNO) and nitro (NO_2) groups. This implies that a donor (D)-acceptor (A) type charge-transfer (CT) virtual excitation from the nitronyl nitroxide to the nitro group through the phenyl ring is essential for the γ_{zzzz}. On the other hand, Figure 4 shows that the total γ_{xxxx} is almost determined by the contribution of nitronyl nitroxide group. The two nitroxide groups exhibit large negative contributions to the γ_{xxxx}. For both the components, the magnitude of contributions from beta electrons is found to be quite larger than that from alpha electrons. This feature seems to be related to a large ability of fluctuation of beta electrons due to the lack of exchange interactions among an extra alpha electron and beta electrons.

The result obtained here suggests that some crystals constructed from open-shell nitroxide compounds have a possibility of exhibiting large negative components of γ. Actually, for p-NPNN crystal in β-phase, which is known to exhibit ferromagnetic interactions, the nitronyl nitroxide groups are found to be aligned in a one-dimensional

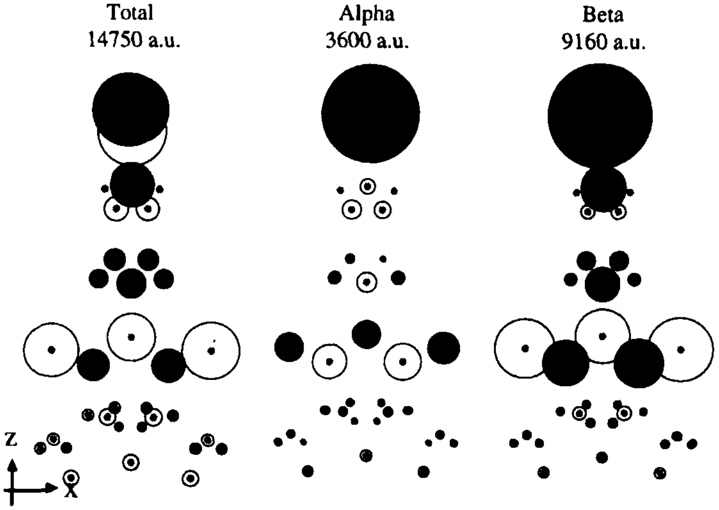

FIGURE 3 γ_{zzzz} density plots and approximate γ_{zzzz}'s (obtained from the γ_{zzzz} densities) for total, alpha (up spin) and beta (down spin) electrons of p-NPNN. The dark, white and black circles denote the positions of atoms, positive and negative γ_{zzzz} densities, respectively.

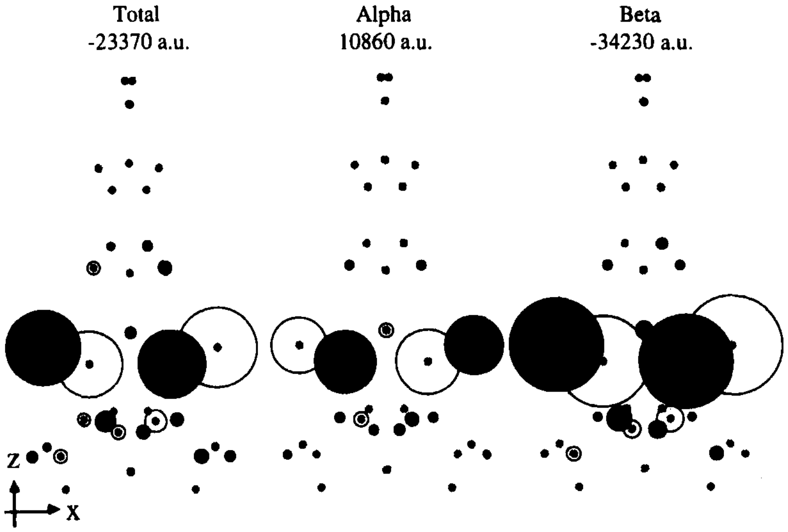

FIGURE 4 γ_{xxxx} density plots and approximate γ_{xxxx}'s for total, alpha and beta electrons of p-NPNN. See Figure 3 for further legends.

direction. Therefore, the macroscopic third-order optical susceptibility in the direction is expected to be large negative. To confirm this prediction, calculations of γ for some cluster models of p-NPNN in the β-phase crystal should be performed.

SUMMARY

From the INDO CUHF calculations, the p-NPNN is expected to possess a large negative component of γ. The γ density analysis elucidates a predominant contribution of nitronyl nitroxide group to this component. This feature seems to be related to large electron fluctuations on the nitronyl nitroxide group.

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