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Negative Second Hyperpolarizability of the Nitronyl Nitroxide Radical

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The static second hyperpolarizability (γ) for a symmetric open-shell system including nitroxide radical groups, nitronyl nitroxide radical, has been studied using ab initio molecular-orbital methods, including various electron-correlation effects. This system is predicted to exhibit a negative γ by our classification rule of γ based on symmetric resonance structures with inversible polarization (SRIP). A remarkable electron correlation dependence has been observed in the magnitude and sign of γ, which has been found to be negative by using high-order electron correlation methods. This tendency has also been investigated in terms of the second hyperpolarizability density, which is defined as the third-derivative of the charge density with respect to the applied electric field.

The nonlinear optical properties for many organic compounds have been actively studied both experimentally and theoretically[1—3] because of their large nonlinearity and fast responses. In particular, the second hyperpolarizability (γ), which is the origin of a macroscopic third-order nonlinear optical response, has been investigated using quantum-mechanical calculations.[2] We recently presented a new class of third-order nonlinear optical compounds, open-shell systems with nitroxide radicals (aminyloxyl radicals), which are thermally stable and also exhibit attracting magnetic interactions.[4] From ab initio calculations of γ for a small-size open-shell system, i.e., H_2NO, a large γ and its remarkable electron correlation dependence have been observed.[5] The sign of γ is also known to be important in quantum optics: The positive value causes a self-focussing effect of an incident beam, while the negative one causes the self-defocussing effects.[6] It is well-known that most organic nonlinear optical systems exhibit a positive γ. In previous papers,[7—13] we have proposed a criteria for exhibiting a negative γ, and presented several systems with negative γ, e.g., ion-radical condensed-ring conjugated systems and charged soliton-like oligomers. On the basis of our three-type analysis[7,8] using virtual excitation processes involved in a perturbative formula of γ, symmetric systems with large ground-state polarizabilities have a possibility of exhibiting a large negative γ. It has also been found that these systems exhibit intense electron correlation dependences and high sensitivities to subtle changes in the electronic structures.[9—13] In other words, the sign and magnitudes of the γ for these systems are expected to be easily controlled by subtle chemical and physical perturbations.

As a model of these systems, we investigated the γ for *para*-nitrophenyl nitronyl nitroxide (2-(4-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl-3-oxide), which is referred to as *p*-NPNN, in the INDO coupled Hartree–Fock (CHF) approximation.[14] The calculated results suggest that the largest component of γ for this system is negative, and is primarily determined by a contribution from the nitronyl nitroxide radical unit. As mentioned above, however, the γ for such an open-shell nitroxide system is suggested to have a tendency of showing a remarkable electron-correlation dependence. In this study, therefore, the basis set and electron-correlation dependences of the γ were investigated using ab initio molecular-orbital (MO) methods, i.e., Hartree–Fock (HF), MØller-Plesset (MP) perturbation, quadratic configuration interaction (QCI), and coupled-cluster (CC) methods. However, a correct evaluation of electron-correlation effects cannot be performed by merely comparing the γ for various correlation methods. Accidental agreements of γ among various correlation methods frequently occur. In previous papers,[12,15,16] we introduced a new concept of "hyperpolarizability density" and proposed an analysis method in terms of a spatial contour plot of the hyperpolarizability density. This analysis method can clearly elucidate qualitative differences in the spatial contributions of electrons to hyperpolarizabilities, even in the case of such accidental agreements. Therefore, a hyperpolarizability density analysis was employed in this study. The obtained features of the γ are also discussed from the viewpoint of a simple structure–property correlation based on the resonance structures with inversible polarizations.[13]

Calculation Methods and Molecular Geometry

Figure 1 shows the molecular geometry and a coordinate system of nitronyl nitroxide radical (N^2-oxidoformamidin-N^1-yloxyl radical) optimized by the MP second-order perturbation (MP2) method using the 6-311C** basis set. The experimental geometry data are not available for this molecule. The purpose of our study was to obtain a qualitative electron correlation and basis-set dependence and the sign of γ for a nitronyl nitroxide radical model, which satisfies our structure–property correlation rule.[13] Although the geometry optimized by the MP2 method may not be in good agreement with the unobserved experimental geometry, the obtained geometry satisfies the structure–property correlation rule and is considered to be sufficient for our purpose. The calculations were performed using

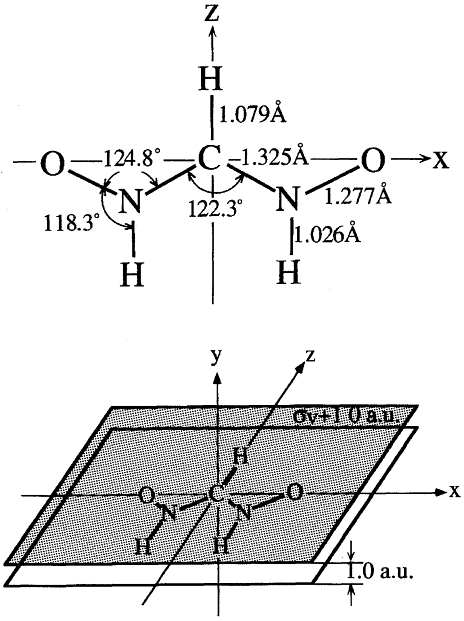

Fig. 1. Molecular geometry and the coordinate system of nitronyl nitroxide radical optimized by UMP2 method using 6-311G** basis set. The plane (σ_v+1 a.u.) is located at 1.0 a.u. above the reflection plane σ_v

the GAUSSIAN 94 program package.[17)]

Since it is suggested that the basis set and electron-correlation dependences of the γ for nitroxide radical species are large compared with those of neutral closed-shell systems,[5)] we first investigated the basis-set dependence of the γ using the standard (minimal (STO-3G), split-valence (6-31G)) and extended basis sets augmented by diffuse and polarization functions (p and d), which are known to be essential for reproducing semi-quantitative γ for organic π-conjugated systems. It is noted that diffuse s-type functions are involved, since we used diffuse six-membered d type functions. The extended basis sets are give in Table 1. These exponents were all determined from the outermost two exponents of 6-31G by an even-tempered method. Secondly, the effects of electron correlations on the γ were examined by the MP2, MP3, MP4DQ, MP4SDQ, MP4SDTQ, CCD(=QCID), QCISD, CCSD, and CCSD(T) methods. Here, the symbols S, D, T, and Q denote the inclusion of correlation effects caused by the single, double, triple and quadruple excitations, respectively. The CC method can include these correlation effects to infinite-order.

We consider the γ_{xxxx} of nitronyl nitroxide radical calculated by numerical differentiation of the total energy (E) with respect to the applied field by

$$\gamma_{xxxx} = \{E(3F_x) - 12E(2F_x) + 39E(F_x) - 56E(0) \\ +39E(-F_x) - 12E(-2F_x) + E(-3F_x)\}/36(F_x)^4. \quad (1)$$

Table 1. Exponential Gaussian Orbital Parameters for Polarization and Diffuse Functions

Basis set	C		N		O	
	p	d	p	d	p	d
6-31G+p	0.0523		0.0582		0.0719	
6-31G+d		0.0523		0.0582		0.0719
6-31G+pd	0.0523	0.0523	0.0582	0.0582	0.0719	0.0719

Here, $E(F_x)$ indicates the total energy in the presence of a field F_x applied in the x-direction. From the γ_{xxxx} values calculated using several minimum field strengths (F_x) from 0.0005 to 0.005 a.u., the numerically stable γ_{xxxx} is adopted. Numerically stable γ_{xxxx} values were found to be obtained by using fields of around 0.0015 a.u.

Hyperpolarizability Density Analysis

In this section we explain the concept of the hyperpolarizability density, and briefly show how to analyze the spatial contributions to the hyperpolarizability. This quantity is a derivative of the charge density with respect to the applied fields. This method is shown to be useful for obtaining a pictorial and intuitive understanding of the spatial characteristics of the static hyperpolarizability.

From an expansion of the charge-density function in powers of the field $\boldsymbol{F}$, the static γ can be expressed by

$$\gamma_{ijkl} = -\frac{1}{3!}\int r_i \rho^{(3)}_{jkl}(\boldsymbol{r})\mathrm{d}^3\boldsymbol{r}, \quad (2)$$

where

$$\rho^{(3)}_{jkl}(\boldsymbol{r}) = -\left.\frac{\partial^3 \rho}{\partial F^j \partial F^k \partial F^l}\right|_{F=0} \quad (3)$$

This third-order derivative of the electron density with respect to the applied electric fields is referred to as the γ density. In this study, we confined our attention to the γ densities ($\rho^{(3)}_{xxx}(\boldsymbol{r})$) corresponding to γ_{xxxx}, which were calculated at each spatial point in discretized space using the following third-order numerical differentiation formula:

$$\rho^{(3)}_{xxx}(\boldsymbol{r})=\{\rho(\boldsymbol{r},2F_x) - \rho(\boldsymbol{r},-2F_x) - 2(\rho(\boldsymbol{r},F_x) - \rho(\boldsymbol{r},-F_x))\}/2(F_x)^3, \quad (4)$$

where $\rho(\boldsymbol{r},F_x)$ represents the charge density at spatial point $\boldsymbol{r}$ in the presence of the field F_x. The charge densities over a three-dimensional grid of points were evaluated by the density matrix using the routines involved in the GAUSSIAN 94 program package.

Next, we explain a method used for the analysis by employing plots of the hyperpolarizability densities. Let us consider a pair of localized γ densities ($\rho^{(3)}_{xxx}(x_1,y,z)$ and $\rho^{(3)}_{xxx}(x_2,y,z)$, $x_2>x_1$), shown in Fig. 2. The arrow from a positive to a negative γ density shows the sign of the contribution determined by the relative spatial configuration between the two γ densities. As shown in Fig. 2(a) ($\rho^{(3)}_{xxx}(x_1,y,z)>0$, $\rho^{(3)}_{xxx}(x_2,y,z)<0$) and Fig. 2(b) ($\rho^{(3)}_{xxx}(x_1,y,z)<0$, $\rho^{(3)}_{xxx}(x_2,y,z)>0$), the sign of the contribution becomes positive when the direction of the arrow coincides with the positive direction of the coordinate system, while the sign of the contribution becomes negative when the direction of the arrow is opposite to the positive direction of the coordinate system. The contribution determined by the γ densities of the two points is more significant when their distance is larger.

Results and Discussion

Basis Set Dependence of γ_{xxxx}. Figure 3 shows variations in γ_{xxxx} of the nitronyl nitroxide radical for different basis sets and electron-correlation methods. This figure indicates that the minimal (STO-3G) and standard split-valence (6-31G) basis sets cannot provide a sufficient magnitude of

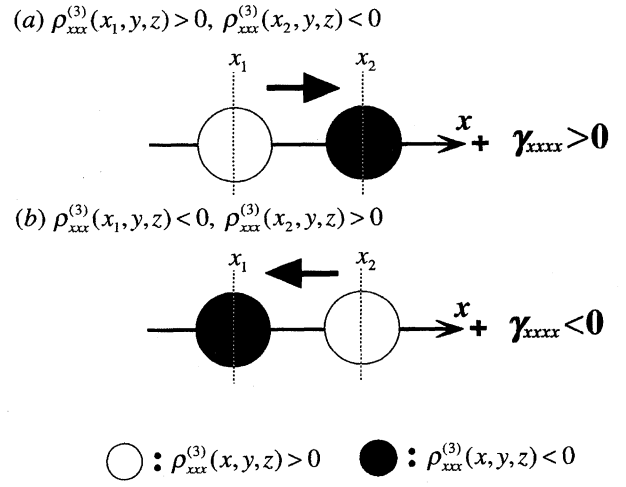

Fig. 2. Schematic diagram of the second hyperpolarizability (γ_{xxxx}) densities ($\rho^{(3)}_{xxx}(x_1,y,z)$ and $\rho^{(3)}_{xxx}(x_2,y,z)$). The size of circle represents the magnitude of γ_{xxxx} density and the arrow shows the sign of γ_{xxxx} determined by the relative spatial configuration between these two γ_{xxxx} densities. In the case of (a) $\rho^{(3)}_{xxx}(x_1,y,z)>0$, $\rho^{(3)}_{xxx}(x_2,y,z)<0$, γ_{xxxx} becomes positive, while in the case of (b) $\rho^{(3)}_{xxx}(x_1,y,z)<0$, $\rho^{(3)}_{xxx}(x_2,y,z)>0$, γ_{xxxx} becomes negative.

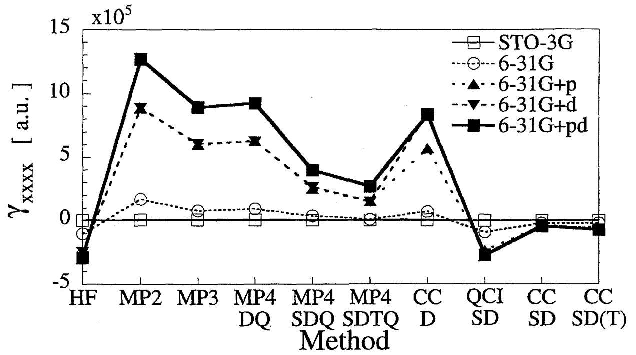

Fig. 3. Variations in the γ_{xxxx} of nitronyl nitroxide radical for various basis sets and electron correlation methods.

γ_{xxxx}. In contrast, extended basis sets (6-31G+*p* and 6-31G+*d*) are shown to significantly increase the magnitudes of γ_{xxxx}. The 6-31G+*pd* basis set is found to provide similar electron correlation dependences to those at the 6-31G+*p* and 6-31G+*d* basis sets, though the magnitudes of γ_{xxxx} at the 6-31G+*pd* are slightly enhanced. Therefore, we consider that the 6-31G+*pd* basis can provide a qualitative description of the dependence of γ_{xxxx} on the various electron correlation effects. This feature is similar to those of other closed-shell conjugated organic systems. This basis-set dependence was investigated using the hyperpolarizability densities for the results by using 6-31G and 6-31G+*pd* at the HF level. In the following discussion concerning the electron-correlation dependence of γ_{xxxx}, the γ_{xxxx} calculated using the most extended basis set, 6-31G+*pd*, are used.

Electron-Correlation Dependence of γ_{xxxx}. As shown in Fig. 3, a remarkable electron correlation dependence of the γ_{xxxx} is observed. The HF method provides a large negative γ_{xxxx}, while the D effects by the MP2 method change the sign and enhance the magnitude of γ_{xxxx} by the HF method. The D effects by the MP3 method decrease γ_{xxxx} by the MP2 method. The D and Q effects involved in the MP4 method are found to provide only a slight positive contribution to the γ_{xxxx}. A comparison between the CCD and MP4DQ γ_{xxxx} indicates that the correlation effects originating from the higher-order D beyond the fourth-order are not important. The S and T effects involved in the MP4 method decrease γ_{xxxx}. Particularly, the S effects involved in the CCSD method remarkably decrease CCD γ_{xxxx} and then reverse its sign. This feature implies that the contribution from the higher-order S effects beyond the fourth-order are indispensable for a reliable description of the γ for this system. The QCISD method cannot satisfactorily reproduce γ_{xxxx} by the CCSD method, though its approximation level is generally considered to be similar to that of the latter method. However, the sign of γ_{xxxx} by the QCISD method coincides with that by the CCSD method, and is thus considered to be a good approximation of that by the CCSD method. The γ_{xxxx} by the CCSD(T) method is shown to be nearly equal to that by the CCSD method. Therefore, γ_{xxxx} by the CCSD method seems to be sufficiently converged.

Analysis of Spatial Contributions to γ_{xxxx} by the Hyperpolarizability Density. In order to elucidate the relationships among the spatial contributions of electrons, the basis set and electron-correlation dependences of γ_{xxxx}, the γ_{xxxx} density ($\rho^{(3)}_{xxx}(\boldsymbol{r})$) plots were investigated. Figure 4 gives contour plots of $\rho^{(3)}_{xxx}(\boldsymbol{r})$ on the σ_v+1 a.u. plane of the nitronyl nitroxide radical shown in Fig. 1.

From the plots of $\rho^{(3)}_{xxx}(\boldsymbol{r})$ by the HF method (Figs. 4(a) and 4(b)), diffuse *p* and *d* functions are not shown to change the qualitative spatial contributions of electrons to the γ_{xxxx}, except for their size differences. As can be seen from all of the $\rho^{(3)}_{xxx}(\boldsymbol{r})$ plots, the $\rho^{(3)}_{xxx}(\boldsymbol{r})$ mainly contributing to the γ_{xxxx} are distributed along the bond region of the O–N–C–N–O unit. This implies that a charge fluctuation in the bond region of the O–N–C–N–O unit predominantly determines the features of γ_{xxxx}. This is in contrast to the usual case for a neutral closed-shell π-conjugated system, where the contributions to γ from expanded regions remote from the bond regions are dominant.

The tendency of the distribution of the $\rho^{(3)}_{xxx}(\boldsymbol{r})$'s at the HF and QCISD levels is found to be dramatically different from that at other levels, and therefore the distribution of $\rho^{(3)}_{xxx}(\boldsymbol{r})$ can be classified into two types. The first type (type A) includes the $\rho^{(3)}_{xxx}(\boldsymbol{r})$ by the HF and QCISD methods, and the second type (type B) includes the $\rho^{(3)}_{xxx}(\boldsymbol{r})$ by the MP2, MP3, MP4DQ, MP4SDQ, and CCD methods. As shown in Fig. 4, γ_{xxxx} of type A are negative, while those of type B are positive. A common feature of both types is that contributions from the vicinity of the (α-)carbon atom (in the ONCNO skeleton) are appreciably small, or can be negligible, so that the γ_{xxxx} are contributed primarily from the vicinity of the NO groups on the left- and right-hand sides. For type A, it is surprising that there is no difference between the feature of distribution of $\rho^{(3)}_{xxx}(\boldsymbol{r})$ at the HF level and that at the QCISD level. The contributions from the $\rho^{(3)}_{xxx}(\boldsymbol{r})$ in the vicinity of the N atoms

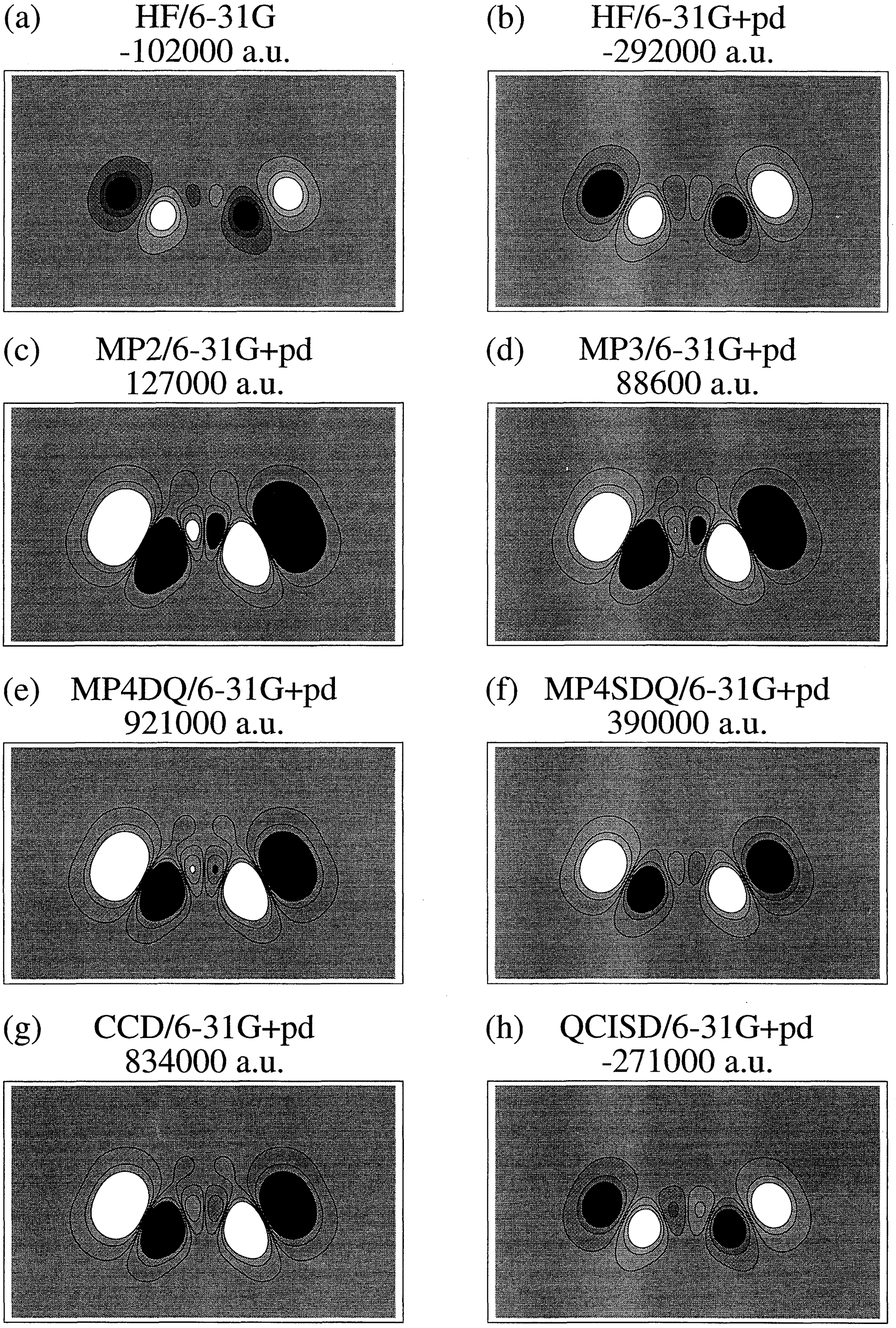

Fig. 4. Contour plots of γ_{xxxx} densities on the σ_v+1 a.u. plane of nitronyl nitroxide radical (Fig. 1) and γ_{xxxx} for various calculation methods. Contours are drawn from -10 to 10 a.u. Lighter areas represent the spatial regions with larger $\rho^{(3)}_{xxx}(\boldsymbol{r})$ values. The white regions correspond to those with $\rho^{(3)}_{xxx}(\boldsymbol{r})$ larger than 10 a.u., while the black regions correspond to those with $\rho^{(3)}_{xxx}(\boldsymbol{r})$ smaller than -10 a.u.

in both NO groups are shown to be positive, while those of the O atoms in both NO groups are shown to be negative. As can be seen from Eq. 2, the contribution from a pair of $\rho^{(3)}_{xxx}(\boldsymbol{r})$ is more significant when the distance of the pair of $\rho^{(3)}_{xxx}(\boldsymbol{r})$ is larger. In the present case, since the O–O distance is larger than the N–N distance, the total γ_{xxxx} is mainly determined by the contribution from both O atoms, and becomes negative. In contrast, for type B, which mainly include the D or Q effects, the contributions from $\rho^{(3)}_{xxx}(\boldsymbol{r})$ distributed over the vicinity of the N atoms in both NO groups are shown to be negative, while those of O atoms in both NO groups are shown to be positive, so that the total γ_{xxxx} becomes positive.

As can be seen from the MP4DQ and MP4SDQ results, the S effects tend to decrease $|\rho_{xxx}^{(3)}(\boldsymbol{r})|$ in the O atom regions in both NO groups, so that γ_{xxxx} at the MP4SDQ level becomes smaller than that at the MP4DQ level. The distribution of $\rho_{xxx}^{(3)}(\boldsymbol{r})$ at the CCD level is shown to provide a positive γ_{xxxx} similarly to that at the MP4DQ level. In contrast, the S effects involved in the higher-order (beyond the fourth-order) perturbation methods are found to reverse the sign of $\rho_{xxx}^{(3)}(\boldsymbol{r})$ at the CCD level. As a result, an inclusion of the D and Q effects up to infinite-order cannot reproduce the qualitative features of the distributions of $\rho_{xxx}^{(3)}(\boldsymbol{r})$ at the QCISD level. It is also noteworthy for this system that the features of $\rho_{xxx}^{(3)}(\boldsymbol{r})$ at the HF level (Fig. 4(b)) is very similar to that at the QCISD level (Fig. 4(h)). This suggests that a cancellation among the S and DQ effects is qualitatively achieved at infinite-order. For this system, an incomplete or unbalanced consideration of electron correlations will lead to incorrect features of the sign and magnitude of the γ_{xxxx}.

Resonance Structures for Nitronyl Nitroxide Radical. In a previous paper[13] we proposed a structure–property correlation rule concerning the feature of a system with a negative γ on the basis of a symmetric resonance structure with inversible polarization (SRIP). Namely, a system whose ground state has a large contribution from the SRIP tends to exhibit a negative γ and exceptionally large dependences on the electron correlations and subtle changes of the electronic structure. Several systems with a large negative γ, such as charged soliton-like oligomers[12] and ion radical condensed-ring conjugated systems,[9,13] are shown to exhibit remarkable electron correlation dependences, and are found to possess a negative γ at high-order electron correlation levels. As shown in the previous paper, these systems are found to possess ground states with significant contributions from the SRIP. Figure 5 shows the corresponding resonance structures for the nitronyl nitroxide radical. Apparently, the radical and charge on the NO groups are liable to move from one side to the other-side of the NO group. This represents an important contribution of the SRIP to the ground state of the nitronyl nitroxide radical. Therefore, we can say that the electron fluctuation along the O–N–C–N–O unit causes a negative γ in the direction and its sensitivity to the electron correlations and the change in the electronic structure.

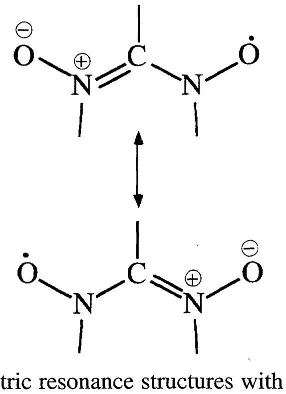

Fig. 5. Symmetric resonance structures with inversible polarization (SRIP) for nitronyl nitroxide radical.

Concluding Remarks

It is found that there are some unique features of γ_{xxxx} for the nitronyl nitroxide radical. First, it is found from plots of $\rho_{xxx}^{(3)}(\boldsymbol{r})$ that γ_{xxxx} is primarily determined by the electron fluctuations in the bond region of the O–N–C–N–O unit. This feature is different from the usual case, where the extended spatial region remote from the bond region provides a dominant contribution to γ.[5] The second unique feature is the qualitatively good coincidence between $\rho_{xxx}^{(3)}(\boldsymbol{r})$ by the HF and QCISD methods. However, this does not immediately imply a good convergence of $\rho_{xxx}^{(3)}(\boldsymbol{r})$ by including low-order MP electron correlations. Actually, the MP2, MP3, and MP4 methods cannot sufficiently reproduce converged γ_{xxxx}, even in the sign. From a comparison among the MP4DQ, MP4SDQ, CCD, and QCISD $\rho_{xxx}^{(3)}(\boldsymbol{r})$, a balanced inclusion of electron correlations with S and DQ effects beyond the fourth-order is essential for obtaining at least the correct sign of γ_{xxxx}. Judging from the qualitative coincidence of the spatial distributions of $\rho_{xxx}^{(3)}(\boldsymbol{r})$'s at the HF and QCISD methods, a cancellation among the S and DQ effects seems to be qualitatively achieved at the infinite-order; thus the previous INDO CHF results[14] for large nitroxide systems, e.g., *p*-NPNN, are considered to provide at least a qualitatively correct description of the dominant contribution from its nitronyl nitroxide radical unit.

By using the hyperpolarizability density analysis, a dominant contribution to γ_{xxxx} is found to be determined by the electron fluctuation in the O–N–C–N–O unit, where the SRIP largely contributes to the stability of the nitronyl nitroxide radical. As shown in the plot of the $\rho_{xxx}^{(3)}(\boldsymbol{r})$ at the QCISD level, the contributions from the vicinity of the N and O atoms on the left- and right-hand sides are different in sign. Since the magnitude of the positive contribution from the N atom regions both in NO groups is smaller than that of the negative contribution from the O atom regions both in NO groups, the total γ_{zzzz} is found to become negative from the Eq. 2.

Considering the sensitive electron fluctuation of the O–N–C–N–O radical unit, the high-order nonlinear optical responses would be dramatically changed by adding subtle chemical and physical perturbations. It is further expected from its attracting magnetic property that these systems with nitronyl nitroxide radicals would be one of the feasible candidates of high-order magnetic and optical systems in the future.

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