J. Phys. Chem. A **2000,** *104,* 4735−4738

Nonlinear Optical Properties of Threefold Coordinated Paramagnetic Si Centers: An ab Initio Time-Dependent Hartree−Fock Study on SiH_3 Radical[†]

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Received: November 24, 1999; In Final Form: February 9, 2000

Static and dynamic (hyper)polarizabilities of SiH_3 radical have been calculated by ab initio time-dependent unrestricted Hartree−Fock method with the use of a double-ζ plus polarization basis set. In order to examine the effect of a Si dangling bond on the polarizabilities, calculations have also been performed on the diamagnetic SiH_4 molecule using the same method and the basis set. A comparison of the polarizabilities of the two systems reveals that a dangling bond at the Si atom causes only a minor change in the value of polarizability, α. However, a Si-dangling bond in the case of SiH_3 distorts the symmetry in the charge distribution in such a way that the dipole moment, μ, and the first-hyperpolarizability coefficient, β, become nonzero. The calculations also reveal that the contributions of the α-spin electrons and β-spin electrons to (hyper)-polarizabilities of the SiH_3 radical substantially differ from each other. The magnitude of hyperpolarizability coefficient is found to be determined by the contributions from different spins.

Introduction

Since the first observation of second harmonic generation (SHG) of the infrared (IR) light in silica fiber by Österberg and Margulis,[1] there has been a surge in activities related to the nonlinear optical (NLO) effects in amorphous silicon dioxide (a-SiO_2). NLO processes, such as the SHG and electrooptic effects, have been observed in different material compositions and geometries of a-SiO_2 as well as under different experimental conditions.[2−11] While much advance has been made toward enhancing the NLO efficiency of silica-based materials, the origin and the physical mechanism of the SHG in a-SiO_2 remain unexplained. Very early on, after the discovery by Österberg and Margulis,[1] the second-order NLO effect in silica glass was hypothesized to originate from macroscopic effects, such as the creation of local electric field by preferential emission of electrons[12] and generation of dc electric field in the glass by intense laser field.[13] Recent studies on the origin and mechanism of SHG in thermally poled fused silica[14−16] also suggest macroscopic effects that involve generation of dc field, although the exact mechanism of this process remains controversial.

While the macroscopic mechanism involving generation of dc electric field due either to the intense laser field[12,13] or to the transport of ionic species under high-field thermal poling conditions[16] does appear to be consistent with the observed SHG in bulk and fused silica, it fails to explain the observed NLO effects in other samples, such as the electrically and ultraviolet (UV) light-poled silica.[9,18] Since a high-purity a-SiO_2 is a continuous random network of fourfold coordinated Si atoms and twofold coordinated O atoms, its dipole moment and second-order NLO coefficients vanish. Observation of SHG in a silica sample, therefore, must involve short-range order with nonvanising dipole moment in the network. Alignment of these local dipoles in the presence of external electric field would then result in a net nonzero dipole moment of the sample.

The short-range order or a lack of randomness in the silica glass can be intrinsic or may result from the presence of defects, which could themselves be intrinsic or impurity related. The intrinsic defects in a-SiO_2 involve O-vacancies, threefold coordinated Si centers, nonbonded O centers, and trapped charges.[19] A majority of these defects are also quite stable and may be responsible for the observed SHG in silica glass. Indeed, electron spin resonance (ESR) experiments[18,20−21] clearly demonstrate the presence of various intrinsic paramagnetic defects in the silica samples exhibiting SHG. The experiments performed by Fuziwara et al.[20,21] also suggest a good correlation between the SHG intensity and the density of threefold coordinated Si/Ge centers in Ge-doped silica glass. These experiments reinforce the hypothesis that the second-order NLO effects in a-SiO_2 are microscopic in nature and possibly involve defect centers.

As a first-step toward understanding the role of the defect on the microscopic optical nonlinearity of silica glass, we have calculated the (hyper)polarizabilities of a threefold coordinated paramagnetic Si center. While other defects, such as the OH radical, H atom, positively charged H, alkali metal ions, and alkaline earth metal ions, have been detected by various groups in silica glass and have been the subject of experimental[3,17,18] and theoretical[22,23] studies as potential sources of microscopic optical nonlinearity of a-SiO_2, the role of the threefold coordinated Si center has not yet been explored. It is important to note that the threefold coordinated Si centers are the most commonly detected and extensively studied intrinsic defects in a-SiO_2.[19]

We have calculated the (hyper)polarizabilities of SiH_3 radical and SiH_4 molecule using ab initio time-dependent unrestricted Hartree−Fock (TDUHF) theory.[24] The SiH_3 radical is the smallest system representing a threefold coordinated Si center. While SiH_4 and SiH_3 molecules are too small to represent realistic models of Si centers in a-SiO_2, they do provide the essential structural features, i.e., a regular fourfold coordinated Si in tetrahedral (T_d) symmetry (SiH_4) and a threefold coordi-

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[†] Part of the special issue "Electronic and Nonlinear Optical Materials: Theory and Modeling".

10.1021/jp9941817 CCC: $19.00

nated Si with a dangling bond (SiH_3). Therefore, it is hoped that the results obtained in this study would be useful in providing new insights into the (a) microscopic mechanism of second-order NLO effects and (b) the role of threefold coordinated Si centers on the observed SHG in silica glass.

Theory and Calculations

In the time-dependent Hartree−Fock (TDHF) approach[25,26] the elements of the polarizability tensor, $\alpha(-\omega;\omega)$, are calculated as

$$\alpha_{ab}(-\omega;\omega) = -\mathrm{tr}[h_a^{(1)}\,\mathbf{D}_b^{(1)}] \tag{1}$$

where a, $b = x, y, z$ represent the Cartesian components, ω is the angular frequency of the optical electric field, $h_a^{(1)}$ is the dipole moment matrix in direction a, and $\mathbf{D}_b^{(1)}$ is the b-direction component of the first-order perturbed density matrix. In the TDUHF method,[24] as used here, the density matrix $\mathbf{D}^{(1)}$ is written as the sum of contributions from the α-spin electrons, $\mathbf{D}^{\uparrow(1)}$, and β-spin electrons, $\mathbf{D}^{\downarrow(1)}$. This allows one to write the polarizability, $\alpha(-\omega;\omega)$ as

$$\alpha(-\omega;\omega) = \alpha^{\uparrow}(-\omega;\omega) + \alpha^{\downarrow}(-\omega;\omega) \tag{2}$$

where $\alpha^{\uparrow}$ represents the contribution to polarizability from spin quantum number $s = {}^1/_2$ electrons and $\alpha^{\downarrow}$ represents the corresponding contribution from $s = -{}^1/_2$ electrons. Equation 2 provides a convenient and useful means to analyze contributions to the polarizability from electrons of different spins. In the case of closed-shell systems, the contributions from the two spins are the same. However, in the case of paramagnetic systems, as has been noted before,[24] the electric polarization of electrons with different spins may vary from each other in sign, magnitude, or both. This feature of the paramagnetic systems often leads to some interesting effects in the presence of external electric field.[27,28] In the present study, eq 2 is used to analyze the similarity and differences in the contributions from different spins to the total polarizability.

Similar to eq 2, the first-hyperpolarizability tensor, $\beta(-\omega_\sigma;\omega_a,\omega_b)$, is written in the TDUHF approach[24] as

$$\beta(-\omega_\sigma;\omega_a,\omega_b) = \beta^{\uparrow}(-\omega_\sigma;\omega_a,\omega_b) + \beta^{\downarrow}(-\omega_\sigma;\omega_a,\omega_b) \tag{3}$$

In the above equation, $\omega_\sigma = (\omega_a + \omega_b)$, where σ, a, b represent the Cartesian components (x, y, z). The convention for the frequency arguments in eq 3 is such that the first term inside the parentheses represents the angular frequency of the output beam of light and the second and the third terms represent the corresponding frequencies of the input beams. The $\beta^{\uparrow,\downarrow}$ terms are evaluated from a self-consistent solution of the first-order TDUHF equations. The same solution also gives the first-order $\mathbf{D}^{(1)}$ matrix needed to evaluate α from eq 1. The details of the method are given in ref 24.

It is not always possible to measure individual elements of the (hyper)polarizability tensors, α and β, from experiments. The quantities often measured in experiments are the mean polarizability, $\langle\alpha\rangle$, and a vector component, β_μ, of the first-hyperpolarizability tensor projected along the dipole axis. In the quantum mechanical calculations, the mean polarizability is calculated from the elements of α tensor as

$$\langle\alpha\rangle = {}^1/_3\sum_a \alpha_{aa};\quad a = x, y, z \tag{4}$$

and the β_μ vector along the dipole axis is calculated as

$$\beta_{\mu i}(\omega_\sigma;\omega_a,\omega_b) = \frac{\mu_i \cdot \beta_i(\omega_\sigma;\omega_a,\omega_b)}{|\mu|} \tag{5}$$

where

$$\beta_i = {}^1/_5\sum_j (\beta_{ijj} + \beta_{jij} + \beta_{jji};\quad i, j = x, y, z) \tag{6}$$

μ_i and $|\mu|$, respectively, represent the i (=x, y, z) component and the absolute value of the dipole moment. Unfortunately, a number of other definitions are used in the literature[24−26] for the observable part of β. Therefore, it is important to provide the definition used to obtain the reported quantities. Here, $\beta_{\mu i}$ has been calculated according to eq 5.

The calculations on the SiH_4 and SiH_3 molecules were performed at their theoretically optimized equilibrium geometries.[29,30] For the tetrahedral SiH_4 molecule, a value of R(Si−H) = 1.4735 Å was used. For the pyramidal SiH_3 molecule, the geometry used was R(Si−H) = 1.478 Å, ∠H−Si−H = 111°. A double-ζ plus polarization (DZP) basis set[31] was used in the calculations. The TDUHF calculations of (hyper)-polarizabilities were performed with the XNLOP computer code[24] interfaced with PHOTON[32] ab initio electronic structure program.

The α values have been calculated at static electric field ($\lambda = \infty$) and at an optical wavelength, $\lambda = 694.3$ nm corresponding to ruby laser. Generally, the SHG experiments are performed at a fundamental wavelength, $\lambda = 1064$ nm of Nd:YAG laser. However, in the quantum mechanical calculations on small σ-bonded molecular species, such as SiH_4 and SiH_3, this wavelength does not produce discernible changes in polarizabilities with respect to their values at static electric field. Therefore, a relatively low wavelength ($\lambda = 694.3$ nm) was chosen in this calculation.

For the SiH_4 molecule, the dipole moment and the β_μ vector vanish due to the symmetry (T_d) reasons. However, for the SiH_3 (C_{3v}) radical, the dipole moment and the second-order polarizability have nonzero values due to the anisotropy in the charge distribution. For SiH_3, we calculated the β values corresponding to the static first-hyperpolarizability, denoted by $\beta(0;0,0)$, and that corresponding to the electrooptic Pockels effect (EOPE), denoted by $\beta(-\omega;0,\omega)$. β(EOPE) was calculated at a fundamental wavelength, $\lambda = 694.3$ nm.

Results and Discussion

Polarizability, α. The calculated components and the mean value of static polarizability, $\alpha(0)$ and the dynamic polarizability, $\alpha(\omega)$, for the SiH_4 molecule and SiH_3 radical are listed in Table 1. As expected, the polarizability for the SiH_4 molecule is isotropic. In the case of the SiH_3 radical, the component of α along the symmetry (C_{3v}) axis is smaller in magnitude than the nonaxial components (α_{xx}, α_{yy}). These components of α for SiH_3 radical are larger in magnitude by about 10% than the corresponding components of the SiH_4 molecule. However, the axial component of α (α_{zz}) for the SiH_3 radical is much smaller in magnitude by about 25% than the corresponding component in the case of the SiH_4 molecule. As a result, the overall change in polarizability in going from the SiH_4 molecule to the SiH_3 radical is only marginal. This noted trend is both qualitatively and quantitatively the same for the static and the dynamic polarizability. Upon examining the molecular orbitals, we note that that dangling bond on Si that contains a single electron is much less polarizable than the doubly occupied orbitals. As a result, the overall polarizability of the SiH_3 radical consisting

TABLE 1: Calculated Static Polarizability, α(0), and Dynamic Polarizability, α(ω) (in the units of 10^{-24} cm^3), for SiH$_4$ and SiH$_3$[a,b]

polarizability component	α(0)		α(ω)	
	SiH$_4$	SiH$_3$	SiH$_4$	SiH$_3$
$\alpha_{xx} = \alpha_{yy}$	3.285	3.640	3.339	3.734
$\alpha_{zz}(0)$	3.285	2.441	3.339	2.483
$\langle\alpha(0)\rangle$	3.285	3.240	3.339	3.317

[a] Calculated total energy: SiH$_4$: $E = -291.231913$ au; SiH$_3$: $E = -290.611789$ au; dipole moment: SiH$_4$: $\mu_x = \mu_y = \mu_z = 0$; SiH$_3$: $\mu_x = \mu_y = 0$, $\mu_z = 0.1186$ au; $|\mu| = 0.301$ debye. [b]Dynamic polarizability, α(ω), calculated at $\lambda = 694.3$ nm.

TABLE 2: Calculated Components of Static First Hyperpolarizability, β(0;0,0), and EOPE, $\beta(-\omega;0,\omega)$ (in 10^{-32} esu) for SiH$_3$ Radical[a]

component	β(0; 0, 0)	$\beta(-\omega; 0, \omega)$	component	β(0; 0, 0)	$\beta(-\omega; 0, \omega)$
β_{xxx}	−1.85	−0.20	β_{zzz}	−6.97	−7.29
β_{xxz}	−20.63	−22.35	β_z	−28.94	−30.82
β_{xyy}	1.85	0.20	β_μ	−28.94	−30.82
β_{yyz}	−20.63	−22.35			

[a] $\beta(-\omega;0,\omega)$ calculated at an optical wavelength, $\lambda = 694.3$ nm.

TABLE 3: Spin Contributions to the Static and Dynamic Polarizabilities, α (10^{-24} cm^3), of SiH$_3$ Radical[a]

component	α-spin	β-spin	component	α-spin	β-spin
$\alpha_{xx}(0)$	2.337	1.303	$\alpha_{xx}(\omega)$	2.419	1.315
$\alpha_{yy}(0)$	2.337	1.303	$\alpha_{yy}(\omega)$	2.419	1.315
$\alpha_{zz}(0)$	1.431	1.010	$\alpha_{zz}(\omega)$	1.455	1.028

[a] Dynamic polarizability, α(ω), calculated at $\lambda = 694.3$ nm.

TABLE 4: Spin Contributions to the Components of Static First Hyperpolarizability, β(0;0,0), and EOPE, $\beta(-\omega;0,\omega)$, for SiH$_3$ Radical[a]

NLO coefficient	β(0; 0, 0)		$\beta(-\omega; 0, \omega)$	
component	α-spin	β-spin	α-spin	β-spin
β_{xxx}	5.86	−7.71	7.62	−7.82
β_{xxz}	−14.80	−5.83	−16.20	6.15
β_{xyy}	−5.86	7.70	−7.62	7.82
β_{yyz}	−14.80	−5.83	−14.20	−6.15
β_{zzz}	13.10	−20.07	13.55	−20.84

[a] The unit for the components of β is 10^{-32} esu.

of a threefold coordinated Si center is slightly smaller than that of the fourfold coordinated SiH$_4$ molecule.

The polarizability in both molecules exhibits dispersion due to the frequency of the optical field. The magnitude of dispersion, however, is larger in the case of the SiH$_3$ radical than that in the case of SiH$_4$ molecule. Again, the axial component of the polarizability, α_{zz}, in the case of SiH$_3$ radical exhibits smaller dispersion than the other two components, α_{xx} and α_{yy}.

First Hyperpolarizability, β. The components of static first-hyperpolarizability tensor, β(0;0,0), and those corresponding to EOPE, $\beta(-\omega;0,\omega)$, along with the vector components β_z and β_μ are listed in Table 2. For both second-order effects, the tensor components β_{xxz} and β_{yyz} have the largest magnitude. Also, due to the positive sign of μ_z, the β_μ vector is identical to the β_z vector. Between β(0;0,0) and $\beta(-\omega;0,\omega)$, the magnitude of β_{xxz} and β_{yyz} components increases by about 10% due to the optical field. Components with smaller magnitude do not exhibit a definite trend. The β_μ vector also increases, albeit by small amount, in going from static case to EOPE.

Spin Contributions to α and β for SiH$_3$. Calculated spin contributions to α and β values for SiH$_3$ radical are listed in Table 3 and Table 4, respectively. From Table 3 it is noted that all components of α have the same (positive) sign. Therefore, the polarizability contributions of the two spins simply add to each other. For both static and dynamic cases, the contributions of the α-spin electrons to various polarizability components are considerably larger than the corresponding contributions of the β-spin electrons.

The spin contributions to the components of the first-hyperpolarizability tensor, β, exhibit somewhat different but interesting features. One notes from Table 4 that the sign of the α-spin contribution to β_{xxx}, β_{xyy}, and β_{zzz} is opposite to that of the corresponding β-spin contributions. As a result, the net values of these components are quite small. The spin contributions to the other two components, β_{xxz} and β_{yyz}, with significant value have the same (negative) sign. These components contribute significantly to the observable vector β_μ.

It is clear from the calculated results for the SiH$_3$ radical that for a threefold coordinated paramagnetic Si center, not only the overall symmetry but also the spin contributions play important roles in determining (hyper)polarizabilities. The spin contributions to the polarizability have the same sign, although their magnitudes vary. However, for the first-hyperpolarizability, β, the spin contributions to different components do not always have the same sign. Spin contributions with opposite sign cancel each other, yielding a substantially reduced value for the observable, β_μ. Thus, while a noncentrosymmetric charge distribution is an essential requirement for a nonzero β_μ value, its magnitude in the case of a paramagnetic system is determined by the relative contributions of the spin components.

Summary

As a first step toward understanding the role of threefold coordinated Si centers on the microscopic NLO properties of *a*-SiO$_2$, we have calculated the polarizabilities of SiH$_4$ molecule and SiH$_3$ radical with the use of ab initio TDUHF method and a DZP basis set. A comparison of the calculated static and dynamic polarizabilities of SiH$_4$ and SiH$_3$ reveals that individual components of α(ω) in the case of the two molecules differ substantially from each other. However, little change occurs in the value of the mean polarizability, $\langle\alpha(\omega)\rangle$, between the two molecular species. The contribution to polarizability due to the singly filled (dangling) bond at the Si center in SiH$_3$ is somewhat underestimated while those of the doubly filled bonds are overestimated with respect to the contributions from corresponding bonds in SiH$_4$. The presence of a dangling bond at Si, in the case of SiH$_3$ radical, however, creates a nonspherical charge distribution that yields a nonvanishing value for the dipole moment, μ, as well as the second-order NLO coefficient, β.

The elements of α and β exhibit small but noticeable dispersion due to the frequency of the optical field. In the case of the paramagnetic SiH$_3$ radical, the spin contributions to the elements of the polarizability tensor, α(ω), and the first-hyperpolarizability tensor, $\beta(\omega_\sigma;\omega_a,\omega_b)$ differ substantially from each other. The sign of the spin contributions to the elements of α(ω) is the same. Therefore, the spin contributions to α(ω) are additive. In contrast, the spin contributions to the elements of $\beta(\omega_\sigma;\omega_a,\omega_b)$ do not always have the same sign. The elements of β having spin contributions of opposite sign either completely cancel out or end up in small magnitude.

The results presented here suggest that threefold coordinated Si centers may be responsible for the observed SHG in *a*-SiO$_2$, since their presence results in nonvanishing values for the second-order NLO coefficients. Furthermore, these results

provide new insights into the properties of second-order NLO coefficient, β. We note that in the case of paramagnetic species, the β tensor depends not only on the symmetry of the charge distribution but also on the spin contributions to various nonvanishing elements. Further investigation of this effect as well as the role of threefold coordinated Si centers on the microscopic optical nonlinearity of silica glass is underway and will be the subject of a forthcoming communication.

Acknowledgment. The author thanks Professor Henry Kurtz, Dr. Prakashan Korambath, and Dr. Gerry Lushington for helpful discussions. The author is also indebted to the referees for valuable suggestions.

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