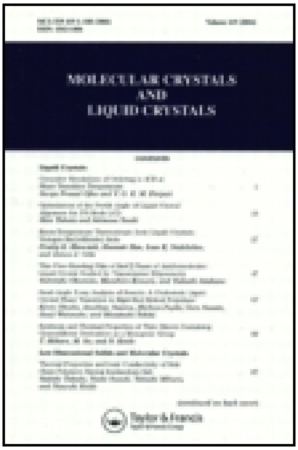

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Ab Initio Calculations of Nonlinear Optical Properties of Silicon Compounds

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AB INITIO CALCULATIONS OF NONLINEAR OPTICAL PROPERTIES OF SILICON COMPOUNDS

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Abstract Third-order hyperpolarizabilities (γ) of silicon compounds are calculated by the *ab initio* coupled-perturbed Hartree-Fock (CPHF) method. The basis set dependencies of the γ-values are first examined. The γ-values calculated for Si compounds by CPHF (6-31G+PD) are compared with those of corresponding carbon compounds.

INTRODUCTION

Previously, the nonlinear optical susceptibilities of several organic substances were studied both experimentally[1] and theoretically.[2,3] The nonlinear optical susceptibilities of macroscopic systems originate in the microscopic polarization (so-called hyperpolarizabilities) of their moleculer components induced by the external electronic field.[4-6] However, until several years ago, *ab initio* calculations of hyperpolarizability of molecules, except for a few small species such as HF[7], H_2O[8], and so forth, had not been carried out or reported. However, recent developments of computer technology, computational algorithms and softwares have enabled us to perform *ab initio* calculations of relatively large molecules such as polyenes[9-10] and organic compounds including benzene rings.[11,12] It was found that the ab initio approach is of practical utility for predicting at least qualitative tendencies for the second (β) and third-order (γ) hyper-polarizabilities of a series of organic compounds under consideration.[9-12]

The nonlinear optical properties, γ-values in particular, of silicon compounds have lately attracted considerable experimental attention[13,14] in relation to future photoelectric applications such as optical devices. However, theoretical calculations are limited for the polarizability[15] of SiH_2 , and therefore computations of the γ-values of silicone compounds would be very interesting in relation to comparisons with corresponding organic molecules. However, the semiempirical calculations[2,16,17] of hyperpolarizabilities of third-row atoms are not so easy since the appropriate selections of the parameter sets are difficult. In the present paper, we examine the γ-values of several silicon compounds by the *ab initio* coupled perturbed Hartree-Fock method (CPHF).[18,19]

BASIS SET DEPENDENCY

It is well known that the magnitudes of the hyperporalizabilities calculated for organic compounds by the ab initio CPHF method depend remarkably on the quality of basis sets employed.[9-12,20] Therefore we first investigate the basis set dependency of the γ-values calculated for SiH_2 molecule. Figure 1 shows the geometry and coordinate axis of SiH_2. The γ-values of SiH_2 calculated by using various basis sets are summarized in Table I. From Table I, it is found that the calculated γ-values vary considerably with the basis sets used. The tendencies recognized for γ-values can be explained by two important factors.

(1) Effects of diffuse basis sets:

The diffuse p, d and f Gaussian type functions are added to the standerd split valence 6-31G basis set. The exponents of the diffuse functions are generated by the even-tempered method. The first augmented diffuse p and d functions, which are referred to as P_1 and D_1, respectively, increase drastically the γ-values of SiH_2. On the other hand, after including both P_1 and D_1 functions, the further augmentations of the diffuse p (P_2), diffuse d (D_2) and diffuse f-functions little affect on the magnitude of γ-values.

(2) Effects of valence basis sets:

The calculated γ-values by the use of the 6-211G, 6-311G and 6-311G* basis sets nearly equal to those of the 6-31G basis set. This fact indicates that the higher quality of the valence part of basis sets little affects on the magnitude of γ-values.

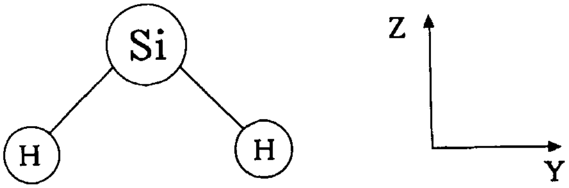

FIGURE 1 Geometry and coordinate axis of SiH_2

TABLE I γ-values of SiH_2 calculated by the *ab initio* CPHF method[a)]

Basis set	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	mean γ
6-31G	2218.0883	-990.6175	1110.1640	196.7432
6-31G+P_1 b)	2820.3118	-1061.0369	1235.4901	328.7005
6-31G+D_1 b)	3504.2660	1188.8181	3915.2457	2072.1028
6-31G+P_1D_1 b)	12576.4531	8380.9487	41614.7548	19502.5792
6-31G+P_1D_1+P_2 b) c)	12760.8094	8705.1757	44677.1736	20623.7866
6-31G+P_1D_1+D_2 b) c)	12033.5109	8204.9189	38969.3534	18469.9420
6-31G+P_1D_1+F b) d)	12331.1739	12340.0398	35952.1659	19552.9983

a) all values are in atomic units : (Bohr**7)/E**2
b) exponents of P_1 and D_1 in Si atom are both 0.025633
c) exponents of P_2 and D_2 in Si atom are both 0.009075
d) exponent of F in Si atom is 0.025633

From these results, we can conclude that, at the SCF level, the reasonable basis function which gives proper γ-values of silicon-including compounds is 6-31G+P_1+D_1, as well as the case of organic compounds.[9-12,20]

COMPARISONS OF THE γ–VALUES OF SILICONE-CONTAINING COMPOUNDS WITH THOSE OF CORRESPONDING HYDROCARBONS

Ab initio CPHF calculations by the use of the 6-31G + PD basis set have been carried out for several Si-compounds which are illustrated in Fig. 2. Table II summarizes the calculated γ–values. From Table II, the γ–values of Si-containing compounds are always larger (4-15 times) than those of corrersponding hydrocarbons. The ratio, $\gamma(Si) / \gamma(C)$, becomes large as the bond orders between the Si(C)-Si(C) atoms increase as follows:

$$\gamma(SiH_4) \approx 4\,\gamma(CH_4)$$
$$\gamma(H_3Si\text{-}SiH_3) \approx 5\,\gamma(H_3C\text{-}CH_3)$$
$$\gamma(H_2Si{=}SiH_2) \approx 10\,\gamma(H_2C{=}CH_2)$$
$$\gamma(HSi{\equiv}SiH) \approx 15\,\gamma(HC{\equiv}CH)$$

The magnitudes of γ–values of a series of the compounds with the same molecular skeletons decrease with the substitution of the Si atom with the C atom. Namely, the following relationship is concluded from Table II.

$$\gamma\,(\text{Si-Si}) > \gamma\,(\text{Si-C}) > \gamma\,(\text{C-C})$$

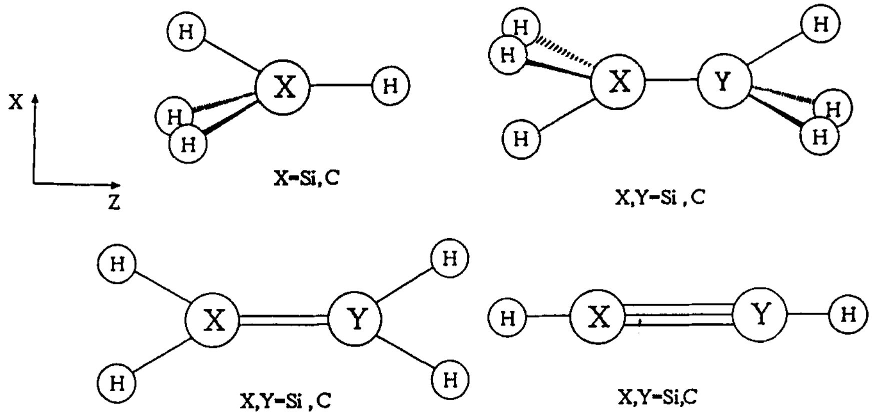

FIGURE 2 Geometries of Si-containing compounds.

TABLE II γ-values calculated by the CPHF (6-31G+PD) method a)

Compounds	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	mean γ
SiH_4 b)	6041.5279	6038.6100	5986.5098	6073.4437
CH_4 c)	1463.5214	1463.4502	1451.2654	1470.8471
$H_3Si\text{-}SiH_3$ b)	10214.8385	10214.8384	30225.1803	15661.4645
$H_3Si\text{-}CH_3$ b) c)	5478.6887	5478.6887	12649.0078	7679.1262
$H_3C\text{-}CH_3$ c)	2147.6962	2147.6962	5280.8451	3105.7479
$H_2Si{=}SiH_2$ b)	18984.5388	119474.2646	7182.9760	58426.2077
$H_2Si{=}CH_2$ b) c)	6768.6785	42990.4477	8418.1531	20719.4496
$H_2C{=}CH_2$ c)	1906.2036	9744.7837	3083.2024	5653.8671
$HSi\equiv SiH$ b)	95645.0310	95645.0310	24879.6483	79175.7213
$HSi\equiv CH$ b) c)	35574.6193	35574.6193	9834.6596	27687.5813
$HC\equiv CH$ c)	6209.0998	6209.0998	3057.5127	5608.9216

a) all values are in atomic units : (Bohr**7)/E**2
b) both exponents of diffuse p and d fuctions in Si atom are 0.025633
c) both exponents of duffuse p and d functions in C atom are 0.052300

This relationship could be applicable to other various silicone and/or carbon compounds with different bond characteristics.

VARIATIONS OF γ-VALUES WITH VARIOUS BOND STRUCTURES

The present ab initio CPHF calculations have revealed several characteristics of γ–values of silicon compounds. These are summarized as follows:

(1) The mean γ–values of the unsaturated hydrocarbons are less than twice of that of the corresponding saturated hydrocarbon

$$\gamma\,(HC{\equiv}CH) \approx \gamma\,(H_2C{=}CH_2) > \gamma\,(H_3C\text{-}CH_3).$$

(2) The γ values of the compounds including the Si-C bonds increase with increasing Si-C bond orders. For example, the following relationships are derived from the computer experiments

$$\gamma\,(H_2Si{=}CH_2) = 2.7\ \gamma\,(H_3Si\text{–}CH_3)$$

$$\gamma\,(HSi{\equiv}CH) = 3.6\ \gamma\,(H_3Si\text{–}CH_3).$$

(3) The more remarkable increase of γ values is achieved with the increase of bond orders between the Si-Si bonds,

$$\gamma\,(H_2Si{=}SiH_2) = 3.7\ \gamma\,(H_3Si\text{–}SiH_3)$$

$$\gamma\,(HSi{\equiv}SiH) = 5.0\ \gamma\,(H_3Si\text{–}SiH_3)$$

From these results, silicon compounds are of particular interest from the view point of design of molecular systems with large γ values, which are esssential for optical devices. Further theoretical calculations are, however, necessary for larger silicon compounds stabilized by organic substituents (organopolysilane)[13,14] in order to obtain useful guides for experimental chemists. They are in progress.

SUMMARY AND CONCLUSION

The present ab initio calculatiosn of silicon compounds have revealed the following characteristics:

(1) The *ab initio* coupled perturbed Hartree-Fock (CPHF) method by the use of the standard 6-31G basis set augmented with 1 diffuse p and d type functions provides reasonable γ-values of silicon compounds.

(2) *Ab initio* CPHF results suggest that the γ values of silicon compounds are remarkably larger than those of the corresponding hydrocarbons. Particularly, the compounds including the double and/or triple Si-Si bonds are predicted to be promising in designing new nonlinear optical materials.

The CPHF calculations do not involve the electron correlation effects. The MP2 corrections are at least desirable for further refinements of γ-values at the SCF level. Probably, such refinements, however, do not change the qualitative tendencies discussed in the present paper.

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