

## Ab Initio Calculations of Silicon-Halogen-Silicon Double Bridges

Arndt Jenichen\*

Central Institute of Isotope and Radiation Research, D-O-7050 Leipzig, Federal Republic of Germany

**Summary.** Structure and stability of molecular clusters modelling halogen (F, Cl) double bridges between silicon atoms,  $\text{H}_3\text{SiF}_2\text{SiH}_3$  (1),  $\text{H}_3\text{SiF}_2\text{SiF}_3$  (2),  $\text{H}_3\text{SiCl}_2\text{SiH}_3$  (3), and  $\text{H}_3\text{SiCl}_2\text{SiCl}_3$  (4), have been investigated by an ab initio pseudopotential method. Asymmetrical bridges Si-X...Si with one strong Si-X bond and one weak Si...X bonding interaction ( $X = \text{F, Cl}$ ) result from the geometry optimization using the LP-31 G basis set. Dissociation energy calculations using the MP2/LP-31G\*//LP-31G procedure and considering the basis set superposition error provide a decrease of stability of the structures in the order  $2 > 4 > 3 > 1$ . The results are discussed with respect to formation and decomposition of halogenated reaction overlayers formed during the etching of silicon by halogen atoms.

**Keywords.** Silicon; Fluorine; Chlorine; Etching; Cluster model; Ab initio method.

### Ab-Initio-Berechnungen von Silizium-Halogen-Silizium-Doppelbrücken

**Zusammenfassung.** Struktur und Stabilität von molekularen Clustern, die Halogen(F, Cl)-Doppelbrücken zwischen Siliziumatomen modellieren,  $\text{H}_3\text{SiF}_2\text{SiH}_3$  (1),  $\text{H}_3\text{SiF}_2\text{SiF}_3$  (2),  $\text{H}_3\text{SiCl}_2\text{SiH}_3$  (3) und  $\text{H}_3\text{SiCl}_2\text{SiCl}_3$  (4), werden mittels eines Ab-Initio-Pseudopotentialverfahrens untersucht. Bei der Geometrieoptimierung unter Verwendung des LP-31 G-Basissatzes ergeben sich asymmetrische Brücken Si-X...Si mit einer starken Si-X-Bindung und einer schwachen bindenden Si...X-Wechselwirkung ( $X = \text{F, Cl}$ ). Dissoziationsenergieberechnungen durch das MP2/LP-31 G\*//LP-31 G-Verfahren unter Berücksichtigung des Basissatzüberlagerungsfehlers liefert eine abnehmende Stabilität der Cluster in der Reihenfolge  $2 > 4 > 3 > 1$ . Die Resultate werden im Zusammenhang mit der Bildung und dem Zerfall von halogenierten Reaktionsschichten, welche während des reaktiven Ätzens von Silizium mit Halogenatomen gebildet werden, diskutiert.

### Introduction

Reactive etching is the removal of surface atoms by interaction with reactive species. The mechanisms of elementary etching reactions are of particular interest due to the fundamental role in the processing of microelectronic devices. Considerable effort has centered on reactions of halogen atoms as well as halogen-containing molecules with silicon surfaces [1–12].

Fluorine atoms or some fluorine containing molecules (e.g.  $\text{XeF}_2$ ,  $\text{BrF}_3$ ,  $\text{ClF}_3$ ) etch silicon spontaneously [5]. In a first step of a fluorine etch process a thick (about 6 monolayers) reaction layer is formed before the desorption of  $\text{SiF}_4$  (but

also  $\text{SiF}_n$ ,  $n < 4$ ) species starts. The reaction layer consists of highly fluorinated silicon, is non-polymeric and exhibits poor connectivity [4–8]. In comparison to fluorine, chlorine atoms or chlorine-containing molecules ( $\text{Cl}_2$ ) etch silicon more slowly at room temperature. The desorption of silicon chlorides already sets in at submonolayer coverages, whilst for fluorine a rather thick corrosion phase is formed at first [9–12].

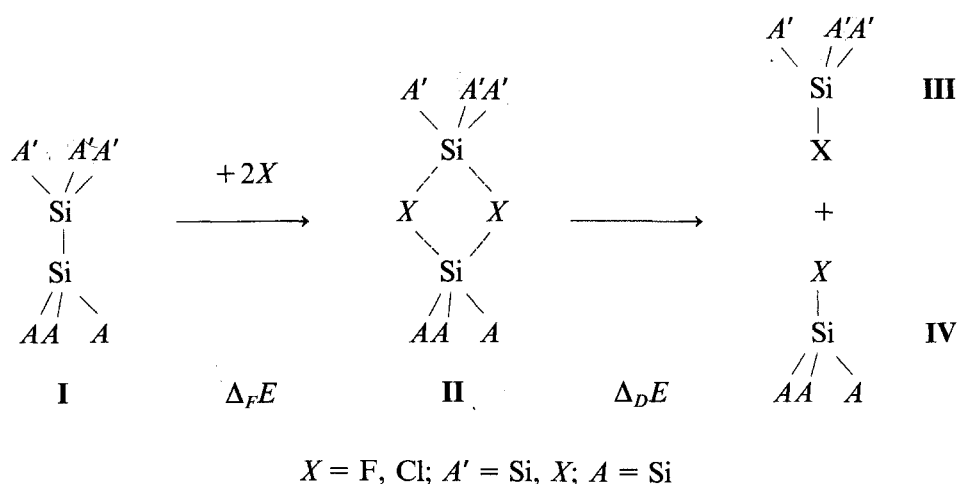
Essential processes during the etching are the weakening and breaking of Si-Si bonds. Possible intermediate structures could be silicon-halogen-silicon bridges (within reaction or corrosion layers).

There are many theoretical studies about silicon-oxygen-silicon bridges, e. g. [13–15]. Plans et al. have shown how oxygen breaks a covalent Si-Si bond and forms a local configuration similar to that of  $\text{SiO}_2$  [16].

Halogen bridges have been hardly investigated. Using molecular clusters and the MNDO method Barone et al. [17] have found that halogen bridges are the most stable position for the chemisorption of F, Cl, Br, and I on the Si(100) surface. Ignacio et al. [18] have obtained a minimum on the ab initio potential energy surface for the charged molecule  $\text{H}_3\text{Si-F-SiH}_3^+$  corresponding to a linear but very flexible symmetrical Si-F-Si bridge configuration. By local-density theory and ab initio pseudopotentials Van de Walle et al. [19] have demonstrated that insertion of F into a Si-Si bond becomes possible because of relaxed steric constraints in the near-surface region. The lowest-energy configuration occurs for a F atom symmetrically located between two Si atoms, with a Si-F distance of about 1.9 Å.

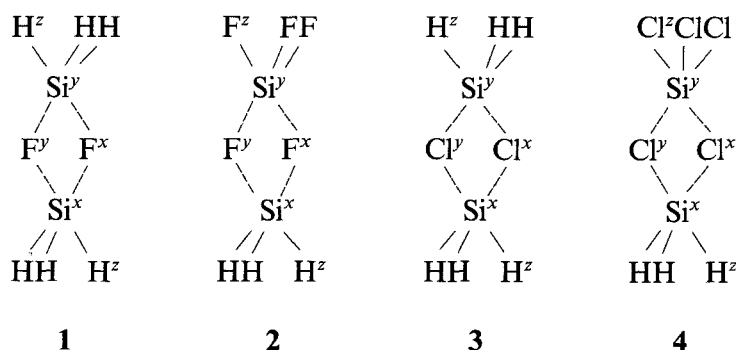
A more favourable position for fluorine atoms should be found outside of the Si-Si bond. The formation of such nonlinear bridges requires smaller steric relaxation of the surrounding Si atoms. Double bridge structures have also not been regarded till now. They allow to explain the dissociative chemisorption, e. g. of halogen molecules, as a local process at a Si-Si bond.

Assuming a double bridge model the breaking mechanism of a Si-Si bond can be represented by the following reaction:



If  $A$  and  $A'$  are silicon atoms, then structure I is a model for a bulk Si-Si bond. If  $A$  is Si and  $A'$  is a F or Cl atom, then the structure I represents a simple model for a surface  $\text{SiF}_3$  or  $\text{SiCl}_3$  group and  $\text{SiF}_4$  or  $\text{SiCl}_4$  is being desorbed, respectively.

In this study the geometry and the stability of the molecular clusters **1**–**4** are investigated using an ab initio pseudopotential method:



<sup>x</sup>, <sup>y</sup>, and <sup>z</sup> are marks for distinction of the atoms. These clusters are presented in the starting geometries. The real geometries result from the optimizations.

In order to reduce the computational expense the bonds directed from Si atoms to other Si bulk atoms are saturated by hydrogen atoms. These ensure that every Si atom has its proper atomic coordination. This is a standard technique for modelling local structures of solids [13–18, 20].

Within the last part of this study the results of the calculations are interpreted in connection with the silicon etching processes.

## Methods

Because the real structure of the clusters is not known from the beginning, one has to assume that strong bonds and weak bonding interactions can occur. The geometry of strong bonds is well described within the HF-SCF level. This is also a possible approximation for the geometry of weakly interacting strongly polar systems. Because of the high electronegativity differences between Si and F as well as Si and Cl the electrostatic forces are dominant in comparison to the dispersion and induction forces. However, for the calculation of binding energies the dispersion and induction energy should be considered by the correlation energy [21].

Using the LP-31 G split valence basis set and an effective core potential procedure [13, 22, 23] the geometry parameters of the reactant **I**, intermediate **II**, and product **III** and **IV** molecules were completely optimized. For comparison, in some cases, the geometry optimization was also executed using the 3-21 G basis set [24, 25].

The ab initio calculation of the energies of formation  $\Delta_f E$  and dissociation  $\Delta_D E$  requires the consideration of the electron correlation. The correlation energy was estimated by means of second-order Møller-Plesset perturbation theory (MP2) [28]. For these calculations the basis sets of the non-hydrogen atoms were supplemented by a set of d polarization functions with exponents of 0.39 (Si, Cl) [27] and 0.8 (F) [23] (LP-31 G\*). The basis set superposition error of  $\Delta_D E$  was estimated by the counterpoise correction method [28]. The ab initio calculations were performed by the GAUSSIAN 80 [23] and HONDO 7.0 [29] program systems.

## Results and Discussion

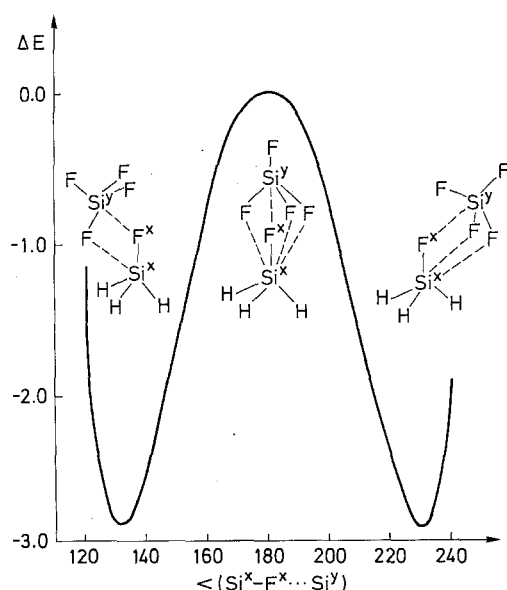
The essential geometry parameters, the energies of formation, and the energies of dissociation of the optimized bridge structures **II** are presented in the Tables 1–4. The data of the structures **I**, **III**, and **IV** may be ordered from the author.

### Geometries

A special procedure is employed for the structure **2**,  $\text{H}_3\text{SiF}_2\text{SiF}_3$ . The geometry optimization with the LP-31 G basis set provides a linear single bridge ( $\langle \text{Si}^x\text{-F}^x\text{...Si}^y \rangle = 180^\circ$ ). Investigations of disiloxane have shown that oxygen d functions are necessary for obtaining a reasonable Si-O-Si bond angle [13, 14]. Therefore, the dependence of the energy upon the  $\text{Si}^x\text{-F}^x\text{...Si}^y$  angle (see Fig. 1) was calculated using additionally d polarization functions on F and Si atoms (LP-31 G\* basis set). For these calculations the other geometry parameters were fixed at the values of the LP-31 G geometry. Two minima, one for the double and one for the triple bridge, were found at about  $131^\circ$  and  $229^\circ$ , respectively. The linear bridge ( $180^\circ$ ) is a saddle point with an energy about  $3 \text{ kcal mol}^{-1}$  higher than the minima. The complete optimization using the 3-21 G basis set provides  $137.9^\circ$  and  $224.5^\circ$ . The MP2/LP-31 G\* and the SCF/3-21 G energies show that the double bridge is more stable by 0.3 and  $0.4 \text{ kcal mol}^{-1}$  than the triple bridge. For the further discussions the geometry and energies of the double bridge structure are used.

The geometry optimizations of the structures **1**–**4** lead to asymmetrical double bridges (with the above-mentioned exception of the LP-31 G basis set). Each bridge consists of one strong (short) Si-X and one weak (long) Si...X bond. The clusters are van der Waals-like cyclic dimers. The  $\text{H}_3\text{SiX}_2\text{SiH}_3$  clusters change from  $C_s$  to  $C_i$  symmetry.

For the fluorine clusters **1** and **2** the geometry parameters can also be compared with results obtained by an all electron method. The ab initio pseudopotential values agree relatively well with the 3-21 G data.



**Fig. 1.** Dependence of the relative energy  $\Delta E$  [ $\text{kcal mol}^{-1}$ ] upon the  $\text{Si}^x\text{-F}^x\text{...Si}^y$  angle [degrees] of structure **2** using the LP-31 G\* basis set

**Table 1.** Calculated distances (AB) [ $\text{\AA}$ ], angles (ABC), torsion angles (ABCD) [degrees], energies of formation  $\Delta_F E$  and dissociation  $\Delta_D E$  (with the correction of the basis set superposition error  $\Delta_D E^{\text{CC}}$ ) [ $\text{kcal mol}^{-1}$ ] for  $\text{H}_3\text{SiF}_2\text{SiH}_3$  (**1**)

	(Si <sup>x</sup> F <sup>x</sup> )	(Si <sup>x</sup> F <sup>y</sup> )	(Si <sup>x</sup> Si <sup>y</sup> )	(Si <sup>x</sup> F <sup>x</sup> Si <sup>y</sup> )	
3-21 G	1.652	2.806	3.833	116.2	
LP-31 G	1.628	2.807	3.799	115.3	
	(Si <sup>x</sup> H <sup>z</sup> )	(Si <sup>x</sup> H)	(F <sup>x</sup> Si <sup>x</sup> H <sup>z</sup> )	(F <sup>x</sup> Si <sup>x</sup> H)	(Si <sup>y</sup> F <sup>x</sup> Si <sup>x</sup> H)
3-21 G	1.482	1.472	105.5	110.4	62.7
LP-31 G	1.470	1.461	105.3	109.6	62.3
	$-\Delta_F E$	$\Delta_D E$	$\Delta_D E^{\text{CC}}$		
3-21 G	147.6	11.5			
LP-31 G	150.9	9.5			
LP-31 G*	198.0	4.9	1.7		
MP2/LP-31 G*	260.9	7.1	1.6		

**Table 2.** Calculated data (see Table 1) for  $\text{H}_3\text{SiF}_2\text{SiF}_3$  (**2**)

	(Si <sup>y</sup> F <sup>y</sup> )	(Si <sup>x</sup> F <sup>x</sup> )	(Si <sup>x</sup> F <sup>y</sup> )	(Si <sup>y</sup> F <sup>x</sup> )	(Si <sup>x</sup> Si <sup>y</sup> )	(Si <sup>x</sup> F <sup>x</sup> Si <sup>y</sup> )
3-21 G	1.610	1.684	2.936	2.016	3.454	137.9
LP-31 G	1.586	1.656	3.691	1.889	3.545	180.0
	(Si <sup>y</sup> F <sup>z</sup> )	(Si <sup>x</sup> F)	(F <sup>y</sup> Si <sup>y</sup> F <sup>z</sup> )	(F <sup>y</sup> Si <sup>y</sup> F)	(Si <sup>x</sup> F <sup>y</sup> Si <sup>y</sup> F)	
3-21 G	1.606	1.593	99.4	116.3	73.1	
LP-31 G	1.596	1.586	98.1	118.0	76.3	
	(Si <sup>x</sup> H <sup>z</sup> )	(Si <sup>x</sup> H)	(F <sup>x</sup> Si <sup>x</sup> H <sup>z</sup> )	(F <sup>x</sup> Si <sup>x</sup> H)	(Si <sup>y</sup> F <sup>x</sup> Si <sup>x</sup> H)	
3-21 G	1.470	1.468	104.9	107.1	60.8	
LP-31 G	1.456	1.456	104.9	104.9	60.0	
	$-\Delta_F E$	$\Delta_D E$	$\Delta_D E^{\text{CC}}$			
3-21 G	161.7	17.1				
LP-31 G	160.7	19.2				
LP-31 G*	199.1	13.6	7.4			
MP2/LP-31 G*	266.1	17.6	5.8			

**Table 3.** Calculated data (see Table 1) for  $\text{H}_3\text{SiCl}_2\text{SiH}_3$  (**3**)

	(Si <sup>x</sup> Cl <sup>x</sup> )	(Si <sup>x</sup> Cl <sup>y</sup> )	(Si <sup>x</sup> Si <sup>y</sup> )	(Si <sup>x</sup> Cl <sup>x</sup> Si <sup>y</sup> )	
LP-31 G	2.143	3.622	4.673	105.4	
	(Si <sup>x</sup> H <sup>z</sup> )	(Si <sup>x</sup> H)	(Cl <sup>x</sup> Si <sup>x</sup> H <sup>z</sup> )	(Cl <sup>x</sup> Si <sup>x</sup> H)	(Si <sup>y</sup> Cl <sup>x</sup> Si <sup>x</sup> H)
LP-31 G	1.464	1.458	105.5	107.4	61.0
	$-\Delta_f E$	$\Delta_D E$	$\Delta_D E^{\text{CC}}$		
LP-31 G	77.9	4.9			
LP-31 G*	110.8	2.5	1.8		
MP2/LP-31G*	146.3	4.8	3.1		

**Table 4.** Calculated data (see Table 1) for  $\text{H}_3\text{SiCl}_2\text{SiCl}_3$  (**4**)

	(Si <sup>y</sup> Cl <sup>x</sup> )	(Si <sup>x</sup> Cl <sup>x</sup> )	(Si <sup>x</sup> Cl <sup>y</sup> )	(Si <sup>y</sup> Cl <sup>x</sup> )	(Si <sup>x</sup> Si <sup>y</sup> )	(Si <sup>x</sup> Cl <sup>x</sup> Si <sup>y</sup> )
LP-31 G	2.081	2.138	3.759	3.634	4.864	112.2
	(Si <sup>y</sup> Cl <sup>z</sup> )	(Si <sup>y</sup> Cl)	(Cl <sup>y</sup> Si <sup>y</sup> Cl <sup>z</sup> )	(Cl <sup>y</sup> Si <sup>y</sup> Cl)	(Si <sup>x</sup> Cl <sup>x</sup> Si <sup>y</sup> Cl)	
LP-31 G	2.080	2.070	107.3	110.6	62.1	
	(Si <sup>y</sup> H <sup>z</sup> )	(Si <sup>y</sup> H)	(Cl <sup>y</sup> Si <sup>x</sup> H <sup>z</sup> )	(Cl <sup>y</sup> Si <sup>x</sup> H)	(Si <sup>y</sup> Cl <sup>x</sup> Si <sup>x</sup> H)	
LP-31 G	1.461	1.461	106.5	107.0	60.2	
	$-\Delta_f E$	$\Delta_D E$	$\Delta_D E^{\text{CC}}$			
LP-31 G	62.8	3.7				
LP-31 G*	107.4	1.8	0.9			
MP2/LP-31G*	146.7	5.5	3.4			

### Energies

All the bridge formation reactions are exothermic. The  $\Delta_f E(\text{MP2/LP-31 G}^*)$  increase in the order

$$2 < 1 \ll 4 \approx 3.$$

The dissociation energies within the HF-SCF level decrease in the order

$$2 > 1 > 3 > 4.$$

The consideration of the correlation energy (containing induction and dispersion energy) by MP2 method leads to a stronger stabilization of the halogenated clusters **2** and **4**. Therefore, the sequence changes to

$$2 \gg 1 > 4 > 3.$$

The additional correction for the basis set superposition error calculated by the counterpoise method leads to  $[\Delta_D E^{CC}(\text{MP2/LP-31 G}^*)]$

$$2 > 4 > 3 > 1.$$

The largest corrections are necessary for the fluorine clusters, especially for **2**. The result is a drastic reduction of the dissociation energies and of the differences between the dissociation energies. However, the structure **2** is the most stable one within all levels of approximation. One has also to consider that the counterpoise method overestimates the basis set superposition error so that the true dissociation energies are higher than the corrected values  $\Delta_D E^{CC}$  [21].

### *Interpretation of the Results*

The increase of the Si-Si distance during the bridge formation is considerably larger for chlorine than for fluorine. Therefore, by reason of sterical constraints, chlorine atoms form bridges at the surface whereas fluorine atoms can form bridges below the surface preferentially [6, 10].

The energy released during the bridge formation by fluorine is considerably higher than that by chlorine. Therefore, because of different local heating, the fluorine etch rate is higher than that of chlorine. For efficient etching by chlorine, external heating is necessary.

Highly fluorinated structures (as **2**) are more stable than corresponding chlorinated structures (as **4**) so that the desorption of  $\text{SiCl}_4$  is easier than that of  $\text{SiF}_4$ . This fact is in agreement with experimental findings. Thermal desorption spectra of halogenated surfaces present the lowest temperature desorption peaks near 450 K ( $\text{SiCl}_4$ ) [10] and 550 K ( $\text{SiF}_4$ ) [7, 8].

### **Acknowledgement**

I would like to thank Prof. Dr. H.-J. Köhler and Dr. G. Peinel, University Leipzig for making available the program systems.

### **References**

- [1] Steinfeld J. I. (1989) Chem. Rev. **89**: 1291
- [2] Pelletier J. (1987) J. Phys. **D20**: 858
- [3] Jenichen A., Johansen H. (1988) Surf. Sci. **203**: 143
- [4] Winter H. F., Coburn J. W., Chuang T. J. (1983) J. Vac. Sci. Technol. **B1**: 469
- [5] Ibbotson D. E., Mucha J. A., Flamm D. L., Cook J. M. (1984) J. Appl. Phys. **56**: 2939
- [6] McFeely F. R., Morar J. F., Himpsel F. J. (1986) Surf. Sci. **165**: 277
- [7] Engstrom J. R., Nelson M. M., Engel T. (1988) Phys. Rev. **B37**: 6563
- [8] Engstrom J. R., Nelson M. M., Engel T. (1989) Surf. Sci. **215**: 437
- [9] Sanders F. H. M., Kolfshoten A. W., Dieleman J., Haring R. A., Haring A., De Vries A. E. (1984) J. Vac. Sci. Technol. **A2**: 487
- [10] Jackman R. B., Ebert H., Foord J. S. (1986) Surf. Sci. **176**: 183
- [11] Jackman R. B., Price R. J., Foord J. S. (1989) Appl. Surf. Sci. **36**: 296
- [12] Whitman L. J., Joyce S. A., Yarmoff J. A., McFeely F. R., Terminello L. J. (1990) Surf. Sci. **232**: 297
- [13] Ernst C. A., Allred A. L., Ratner M. A., Newton M. D., Gibbs G. V., Moskowitz J. W., Topiol S. (1981) Chem. Phys. Lett. **81**: 424

- [14] Grigoras S., Lane T. H. (1987) *J. Comput. Chem.* **8**: 84
- [15] Russo N., Toscano M., Barone V., Lej F. (1985) *Phys. Lett. A* **113**: 321
- [16] Plans J., Diaz G., Martinez E., Yndurain F. (1987) *Phys. Rev.* **B35**: 788
- [17] Barone V., Lej F., Russo N., Toscano M. (1986) *Solid State Commun.* **59**: 433
- [18] Ignacio E. W., Schlegel H. B., Bicerano J. (1986) *Chem. Phys. Lett.* **127**: 367
- [19] Van de Walle C. G., McFeely F. R., Pantelides S. T. (1988) *Phys. Rev. Lett.* **61**: 1867
- [20] Sauer J. (1989) *Chem. Rev.* **89**: 199
- [21] Hobza P., Zahradník R. (1988) *Chem. Rev.* **88**: 871
- [22] Kahn L. R., Baybutt P., Truhlar D. G. (1976) *J. Chem. Phys.* **65**: 3826
- [23] Binkley J. S., Whiteside R. A., Krishnan R., Seeger R., DeFrees D. J., Schlegel H. B., Topiol S., Kahn L. R., Pople J. A. (1980) *GAUSSIAN 80. QCPE* **13**: 406
- [24] Binkley J. S., Pople J. A., Hehre W. J. (1980) *J. Am. Chem. Soc.* **102**: 939
- [25] Gordon M. S., Binkley J. S., Pople J. A., Pietro W. J., Hehre W. J. (1982) *J. Am. Chem. Soc.* **104**: 2797
- [26] Møller G., Plesset M. S. (1934) *Phys. Rev.* **46**: 618
- [27] Collins J. B., Schleyer P. R., Binkley J. S., Pople J. A. (1976) *J. Chem. Phys.* **64**: 5142
- [28] Boys S. F., Bernardi F. (1970) *Mol. Phys.* **19**: 553
- [29] Dupuis M., Watts J. D., Villar H. O., Hurst G. J. B. (1987) *HONDO Version 7.0*. Kingston

*Received March 1, 1991. Accepted May 28, 1991*