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Ab-initio Theoretical Investigations of the Electron Spin Resonance of the SiH_2^+ cation radical and the $SiH_2^+…H_2$ complex

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Abstract

The structure and the isotropic hyperfine coupling constants (iHFCCs) of the SiH_2^+ cation radical and the $SiH_2^+…H_2$ complex have been calculated using coupled cluster theory CCSD and CCSD(T) together with the Dunning *et al.* cc-pVXZ and aug-cc-pVXZ (X=2, 3, 4) basis sets. The calculated geometry and iHFCCs are in good agreement with experimental values. In fact, the calculated iHFCC for hydrogen from $SiH_2^+…H_2$ is in better agreement with the experimental value (41.7 G) than is the value calculated for the SiH_2^+ not complexed with H_2. This H_2 complex radical might be the stable form of the SiH_4^+ species.

الخلاصة

استخدمت نظرية التشويش ونظرية ازدواج العناقيد التي تتظمن كل الاثارات الاحاديه والثنائية في CCSD وكذلك الثلاثية في CCSD(T) وهي من طرق ميكانيك الكم المتقدمة جدا مع دوال داننغ واخرين cc-pVXZ و aug-cc-pVXZ (X=2, 3, 4) لحساب التركيب الجزيئي وثوابت الازدواج الفوق الدقيقة في مطيافية e.s.r (iHFCCs) للجذر الموجب SiH_2^+ والمعقد $SiH_2^+…H_2$ وكانت النتائج متفقة بصورة جيدة مع النتائج التجريبية . وكانت قيم (iHFCCs) المحسوبة من المعقد $SiH_2^+…H_2$ باتفاق افضل مع القيمة التجريبية (G 41.7) من تلك المحسوبة من الجذر الموجب SiH_2^+ . يعتقد انه من الممكن ان يمثل هذا المعقد $SiH_2^+…H_2$ الشكل المستقر للايون SiH_4^+.

Introduction

Very little is known about the SiH_2^+ cation radical, which contains only five valence electrons. Apparently, the only spectroscopic measurements involve laser photofragment studies of the $A^2 B_1 \leftarrow x^2 A_1$ absorption in the 567-659 nm region by monitoring the appearance of Si^+ or SiH^+ fragment ions.[1] In related studies, the total cross section for the reaction $Si^+ + H_2 \rightarrow SiH^+ + H$ has been obtained as a function of collision energy.[2] The neutral species SiH_2 molecule has a singlet ground state unlike CH_2, which is X_3B_1.[3] Plasma techniques used to deposit silicon layers in the fabrication of microelectronic devices and solar cells often involve SiH_4 and a complete understanding of the various intermediate ions involved is important for generating computer models of such processes. The identification of silicon containing molecules in discharge environment has been investigated by a variety of methods.[4]

The generation of SiH_2^+ from SiH_4 at 4K for trapping in a solid neon matrix as an isolated ion is described by Knight *et. al.*[5] This work presented a complete interpretation of the first ESR (electron spin resonance) measurements for this small open-shell ion. Careful ESR searches were also made for the presence of SiH_4^+ but apparently this parent cation is unstable under the generation conditions employed. The SiH_2^+ cation and other highly reactive species are extremely difficult or impossible to study in the gas phase with sufficient resolution for obtaining the nuclear hyperfine interactions-parameters that reveal considerable electronic structure information. Given The "simplicity" of the SiH_2^+ radical, it is an excellent candidate for extensive comparison between experimental results and *ab-initio* theoretical calculations at the post Hartree-Fock level. In this regard, it is an important prototype for evaluating the accuracy of calculated one electron properties based on the energy criterion and should provide useful insights for future studies of small silicon radicals. Fortunately the ESR spectrum of SiH_2^+ is sufficiently well resolved in the neon matrix at 4 K to allow a complete determination of the molecular g tensor and the nuclear hyperfine A tensors for ^{29}Si ($I = ½$) and H. The observed A_{iso} for ^{29}Si is (-300.8 G) and for hydrogen (41.7 G).[5] Negative A values correspond to positive spin density in the Si (3s and 3p) orbitals since the magnetic moment for ^{29}Si ($I = ½$) is negative.

The optimized geometry for SiH_2^+ has been calculated at the SCF levels with different basis sets.[6,7,8] Dyke *et al.* [8] report an energy of -289.71378 hartrees with a bond angle of 120.1° and bond length of 1.465 Å compared to experimental values of 119° and 1.49 Å[1] In their calculations the silicon basis set [11s, 7p] was contracted to (6s, 4p) with a diffuse *p* function and two d polarization functions. The hydrogen basis set was Huzinaga's [4s] contracted to (2s) with a p polarization function.[9] Pople and Curtiss[10] determined the geometry at the Hartree-Fock SCF level using the 6-31G basis set to give an energy of -289.709 83 hartrees at 1.46 Å and 119.8°. Evaluation of the energy at this geometry using Møller-Plesset theory (MP4) with a larger basis set yielded a final energy of -298.80551 hartrees. In this same paper they also calculate the geometry of SiH_4^+ and find the global minimum geometry to be a structure having C_s symmetry with SiH_2^+ weakly bound to H_2 in a donor-acceptor complex. Frey and Davidson's extensive treatment of SiH_4^+ confirms this structure as the minimum energy geometry.[11]

In this work we present a detailed theoretical treatment of the structure and isotropic HFCCs of SiH_2^+ radical cation and for the species $SiH_2^+ \ldots H_2$ at the CCSD and CCSD(T) level.

Computational Details:

All calculations were performed with the ACES II[12] program system using spherical d, f, and g functions.

Geometries were fully optimized using coupled cluster theory with singles and doubles CCSD and non-iterative triples with CCSD(T) with correlation consistent basis sets of Dunning *et al.*[13]

cc-pVXZ and aug-cc-pVXZ (X=2, 3, 4). Later on, these will be abbreviated as XZ and AXZ. The frozen core (fc) approximation was used.

The isotropic hyperfine coupling constants (iHFCCs) of molecules provide a direct measure of the net spin density at the various nuclei in a molecule. The isotropic HFC constant $A_{iso}(N)$ at a magnetic nucleus N is determined by the Fermi contact interaction and is given in units of the magnetic flux required to obtain resonance by

$$A_{iso}(N)=\frac{8\pi}{3}\left(\frac{g_e}{g_0}\right)g_N\beta_N\langle\delta(r_N)\rangle_{spin} \quad ...(1)$$

where g_e and g_0 are the g values of the electron in the radical and the free electron. For most organic free radicals the ratio (g_e/g_0) may be taken unity. The nuclear g factor g_N and nuclear magneton β_N are known constants. The essential quantity to be calculated is therefore $\langle\delta(r_N)\rangle_{spin}$ which is the electronic spin density at a point in space **r**. In atomic units this is the effective number of unpaired electron spins per cubic bohr, which is simply given by

$$\langle\delta(r_N)\rangle_{spin}=\frac{1}{n}\left[\rho_\alpha(r)-\rho_\beta(r)\right] \quad ......(2)$$

where $\rho_\alpha(\mathbf{r})$ and $\rho_\beta(\mathbf{r})$ are the separate densities of α and β spin electrons, respectively, and n is the net number of unpaired electrons ($n_\alpha - n_\beta$). The subscript "spin" indicates averaging over the unpaired spin density.

In this work the isotropic hyperfine coupling constants (iHFCCs) are calculated from analytic spin densities using the coupled cluster theory with singles and doubles CCSD and non-iterative triples with CCSD(T) and the Dunning *et al.* up to cc-pVQZ . To describe the electron density at the hydrogen nucleus, we have developed new basis sets especially designed for highly accurate calculations of the isotropic hyperfine constants (iHFCCs). In a previous work[14] we have developed and tested new basis sets especially designed by adding n tight s primitives to the cc-pVXZ parent basis set by multiplying the largest s exponent of the previous cc-set by a constant (4 in our case). These basis sets are named cc-pVXZ-sn and aug-cc-pVXZ-sn.[15]

$^{29}SiH_2^+$

The optimized geometries and corresponding energies calculated at the CCSD-fc level and the DZ, ADZ, TZ and ATZ basis sets are shown in Table 1. These values are in essential agreement with the earlier published results.[6-8] Our results in (Table 1) show very little change in geometry on going to a richer basis set or on adding diffuse functions. However, the CCSD-fc/ATZ calculations (f, g) polarization functions plus diffuse functions gives the lowest energy and (Si-H = 1.49Å; and H-Si-H =120.1°) in good agreement with experimental values.

Table 1: Calculated structure of SiH_2^+ radical cation. Bond lengths in Angstroms, bond angles in degrees, and energies in Hartree.

Basis set	Method	θ(H-Si-H)	r(Si-H)	Energy
DZ	CCSD-fc	120.3	1.494	-289.8106
ADZ	CCSD-fc	120.3	1.497	-289.8140
TZ	CCSD-fc	120.1	1.484	-289.8366
ATZ	CCSD-fc	120.1	1.485	-289.8380
Expt.		119.0	1.49	

We calculated the isotropic hyperfine coupling constants (iHFCCs) of SiH_2^+ radical cation at the CCSD-fc and CCSD(T)-fc levels of theory with a variety of basis sets and using the two optimized geometries from CCSD-fc/DZ and CCSD-fc/TZ calculations. The results given in Tables 2 and 3 indicate little change in the iHFCCs of both Si and H as function of “method/basis set/geometry”. However, the best agreement of the iHFCCs of Si and H with experiment is the values from CCSD(T)-fc/TZ//CCSD-fc/ATZ calculation Si: (-262.9 G); H:(60.6 G). The iHFCCs calculated from our newly developed basis sets for hydrogen tend to give higher values than those from the corresponding parent cc- basis sets. (c. f. Tables 3 and 4). A full CISD calculations by Knight *et. al.*[5] gave iHFCCs, Si (-289.8 G) and H (56.8 G).

Table 2: Isotropic Hyperfine Coupling Constants (in Gauss) of SiH_2 at CCSD-fc/DZ optimized geometry. [a, b]

Basis set		Method	iHFCCs	
Si	H		Si	H
DZ	DZ	CCSD-fc	-255.8	58.9
TZ	TZ	CCSD-fc	-267.1	62.0
QZ	QZ	CCSD-fc	-256.9	63.4
ADZ	ADZ	CCSD-fc	-256.3	57.6
DZ	DZ-s5	CCSD-fc	-256.1	69.0
ADZ	ADZ-s5	CCSD-fc	-256.7	67.8
DZ	DZ	CCSD(T)-fc	-254.8	58.7
TZ	TZ	CCSD(T)-fc	-265.6	61.7
ADZ	ADZ	CCSD(T)-fc	-255.3	57.3
DZ	DZ-s5	CCSD(T)-fc	-255.1	68.8
ADZ	ADZ-s5	CCSD(T)-fc	-255.6	67.5

[a] Experimental iHFCC: Si: (-300.8 G); H:(41.7 G). [b] A full CISD calculations by Knight *et. al.*[5] gave iHFCCs, Si (-289.8 G) and H (56.8 G).

Table 3: Isotropic Hyperfine Coupling Constants (in Gauss) of SiH_2^+ at CCSD-fc/TZ optimized geometry.[a]

Basis set		Method	iHFCCs	
Si	H		Si	H
DZ	DZ	CCSD-fc	-256.5	67.8
TZ	TZ	CCSD-fc	-267.6	62.0
ATZ	ATZ	CCSD-fc	-264.5	60.9
TZ	TZ-s4	CCSD-fc	-267.7	67.5
DZ	DZ	CCSD(T)-fc	-255.5	67.5
TZ	TZ	CCSD(T)-fc	266.0	60.9
ATZ	ATZ	CCSD(T)-fc	-262.9	60.6

[a]Experimental iHFCC: Si:(-300.8 G); H:(41.7 G).

$SiH_2^+ \ldots H_2$

In the light of the calculations by Pople and Curtiss[10], Frey and Davidson[11], and Knight et al.[5] We have calculated the geometry and the hyperfine parameters for the species $SiH_2^+ \ldots H_2$. (See Figure 1 for a description of the r's (based on the numbered H atoms and theθ's). This H_2 complex radical might be the stable form of the SiH_4^+ species. The calculations are made at the CCSD-fc level of theory with the basis set of Dunning *et al.*[13] cc-pVTZ (f,g) and aug-cc-pVDZ with diffuse functions. We have also calculated the geometry and hyperfine structure for the $SiH_2^+ \ldots H_2$ complex with the H_2 rotated 90º from the most stable geometry so that the two hydrogen atoms are equivalent on reflection in the x-z plane. The energy of this structure is about 700-800 cal/mol higher than the global minimum geometry. It has been suggested that tunneling through such a low barrier is feasible for a variety of internal rotation and other molecular arrangements.[5,15,16] The TZ basis set gives the lowest energy for both conformations and the geometry is very close to experimental values (c.f. Table 4). The longer Si-H distance r_3 is less sensitive to basis set than r_4, but when H_2 molecule was twisted by 90º r_3 became shorter by (~ .031Å).

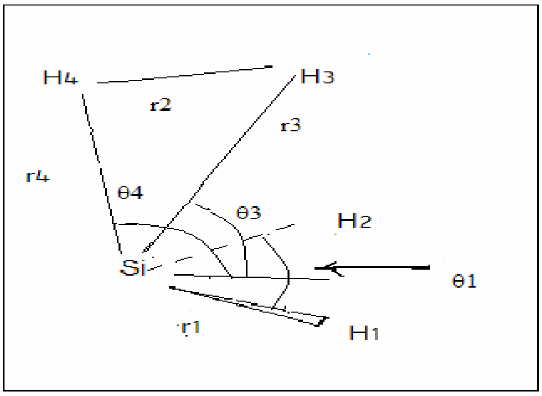

Figure 1: Angles, distances and atomic numbering used in the text are shown for the complex, $SiH_2^+ \ldots H_2$. (Numbering based on the numbered H atoms and the θ's).

Table 4: Calculated energy and structure of $SiH_2^+ \ldots H_2$. Bond length in Angstroms, bond angles in degrees, and energies in Hartree. See Figure 1 for a description oh the *r's* (based on the numbered H atoms) and the *θ's*.

Basis sets	Method	r_1	$θ_1$	r_3	$θ_3$	r_4	$θ_4$	Energy
ADZ[a]	CCSD	1.485	121.5	1.941	64.7	1.885	88.7	-291.0001
TZ	CCSD	1.485	121.5	1.941	64.8	1.905	88.8	-291.0315
ADZ[b]	CCSD	1.489	119.9	1.952	91.2	1.952	91.2	-290.9989
TZ[b]	CCSD	1.477	119.9	1.921	91.3	1.921	91.3	-291.0303
D95 (DZ)[c]	SCF	1.471	120.6	2.512	82.3	2.426	99.5	-290.8138
D95** (DZP)[c]	SCF	1.405	120.3	1.983	87.4	1.949	109.6	-290.8572
D95** (DZP)[c]	MP2	1.467	121.1	1.910	87.9	1.866	111.4	-291.0125
D95** (DZP)[d]	SCF	1.467	119.6	1.999	95.6	1.999	95.6	-290.8567

[a] H-H distance = 0.7979 Å ; [b]H2 twisted 90° so that H_2 lies above SiH_2, approximately in the xy plane; this conformation is about 700-800 cal/mol higher in energy. [c]Ref. 5; [d]Ref. 5 (twisted).

The calculated hyperfine parameters are given in Tables 5 and 6. For hydrogen we have used the newly developed basis sets[14] together with the corresponding parent basis sets for silicon. As we have indicated above, the calculated hyperfine parameters given in Tables 2 and 3 show little change in the iHFCCs values for silicon and the bonded hydrogens but a substantial reduction is indicated in the iHFCCs for the H_2 hydrogen as shown in tables 5 and

6. The results given in Tables 5 and 6 show that, the nearby H_2 molecule should perturb the SiH_2^+ unpaired spin density to a measurable degree. In particular, the Si (iHFCC) value is greater than in SiH_2^+ while the H (iHFCC) value is smaller. In fact, the calculated iHFCC for hydrogen is in better agreement with the experimental value (41.7 G) than is the value calculated for the SiH_2^+ not complexed with H_2.The iHFCCs values are obviously sensitive to the geometry.

Table 5: Isotropic Hyperfine Coupling Constants (iHFCCs) (in Gauss) of H_2…SiH_2 [H_2 - parallel to symmetry axis].

Basis set		Method	geometry	iHFCCs			
Si	H			Si	H_1[a]	H_3	H_4
DZ	DZ-s5	CCSD-fc	CCSD-fc/ADZ	-263.9	37.9	22.1	-11.2
TZ	TZ-s4	CCSD-fc	CCSD-fc/ADZ	-274.3	38.1	22.6	-10.4
DZ	DZ-s5	CCSD-fc	CCSD-fc/TZ	-262.9	35.5	23.1	-11.4
TZ	TZ-s4	CCSD-fc	CCSD-fc/TZ	-272.9	35.8	23.6	-10.5

[a] See Figure 1 for an assignment of the H atoms.

Table 6: Isotropic Hyperfine Coupling Constants (in Gauss) of H_2…SiH_2 [H_2 - perpendicular to symmetry axis].

Basis set		Method	geometry	iHFCCs			
Si	H			Si	H_1	H_3	H_4
DZ	DZ-s5	CCSD-fc	CCSD-fc/ADZ	-275.9	47.9	-0.535	-0.535
TZ	TZ-s4	CCSD-fc	CCSD-fc/ADZ	-276.0	46.0	-0.582	-0.582
DZ	DZ-s5	CCSD-fc	CCSD-fc/TZ	-287.6	47.6	-0.0202	-0.0202
TZ	TZ-s4	CCSD-fc	CCSD-fc/TZ	-287.3	45.8	-0.0821	-0.0821

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