On the Structure of the SiH_4^+ Cation and its Potential Energy Surface for Rearrangement and Dissociation: An *Ab Initio* M.O. Study

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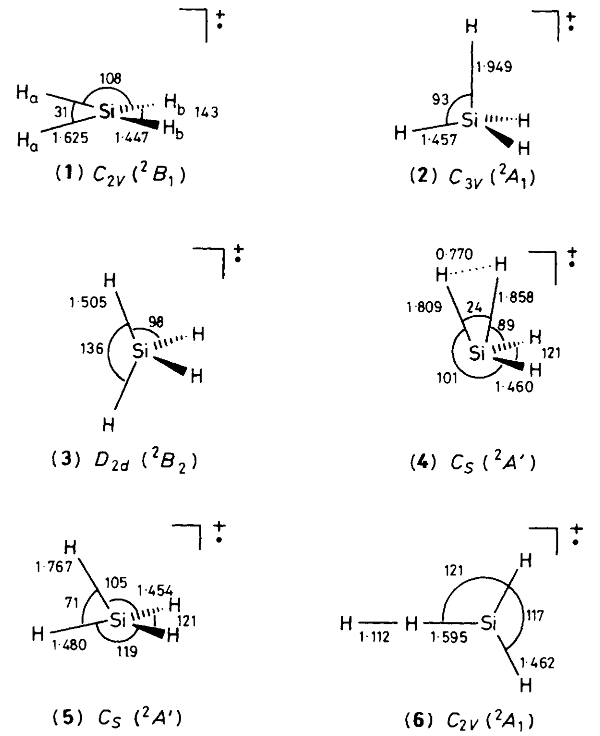
An *ab initio* M.O. study of the SiH_4^+ potential energy surface reveals, in contrast with previous studies, that its most stable structure has C_s symmetry, and that a C_{2v} transition structure interconverts equivalent C_s structures; the C_s form should easily dissociate, giving SiH_2^+ and H_2, rather than SiH_3^+ and H; higher energy C_{3v} and D_{2d} minima were also located but are predicted to have only evanescent existence.

Electron loss from the triply degenerate t_2 orbital of methane or silane produces the corresponding cation radical in the $^2T_2$ ground state which, according to the Jahn–Teller theorem,[1] is unstable with respect to distortions that eventually lead to structures having D_{2d}, C_{3v}, C_{2v}, and C_s symmetry. Although the potential energy surface for the electronic ground state of the CH_4^+ cation is fairly well understood,[2—4] and consists of a single stable structure of C_{2v} ($^2B_1$) symmetry and two transition structures of C_s symmetry that interconvert equivalent C_{2v} structures, the same cannot be said of the SiH_4^+ potential energy surface. The photoelectron (p.e.) spectrum of SiH_4 has been interpreted in terms of the SiH_4^+ cation having a ground state D_{2d} ($^2B_2$) geometry.[5] Two recent *ab initio* M.O. studies on the SiH_4^+ cation, using the unrestricted Hartree-Fock (UHF) method and rather small basis sets, 4-31G in one study,[6] and 6-21G (supplemented by configuration interaction, CI) in the other,[7] both indicate that C_{3v} and C_{2v} structures have lower energies than the D_{2d} form, with the C_{3v} structure having the lowest energy. A more recent *ab initio* study[8] reverses the relative stabilities of the C_{3v} and C_{2v} structures, but did not investigate the D_{2d} form. Unfortunately none of these studies determined whether any of these structures actually correspond to genuine minima on the SiH_4^+ energy surface. Herein, we communicate the results of our investigations that reveal features of the SiH_4^+ energy surface quite different from those previously supposed.

Stationary points on the SiH_4^+ energy surface were located (subject to symmetry constraints) using second order Møller–Plesset theory[9] and the 6-31G** basis set[10] (*i.e.*, UMP2/6-31G**).† Single point fourth order Møller–Plesset calculations,‡ using the 6-31G** basis set, on the UMP2/6-31G** optimized geometries [UMP4(SDTQ)/6-31G**//UMP2/6-31G**] were also carried out. Harmonic frequency calculations were carried out on the optimized geometries in order to obtain zero-point energies (Z.P.E.s) and to ascertain whether the structures correspond to minima or to first order saddle points (*i.e.*, transition structures). Energies of the structures are given in Table 1, the UMP2/6-31G** optimized geometries are shown in Figure 1, and a schematic (vibrationless) energy surface at the UMP4(SDTQ)6-31G**//UMP2/6-31G** level is shown in Figure 2. All energies quoted below refer to the UMP4(SDTQ)/6-31G**//UMP2/6-31G** calculations.

Six optimized structures, (**1**)—(**6**), for SiH_4^+ were located.§ The geometries of (**1**) {C_{2v}($^2B_1$)}, (**2**) {C_{3v} ($^2A_1$)}, and (**3**) {D_{2d} ($^2B_2$)}, are similar to those previously calculated,[6—8] although the H_a–Si–H_a and H_b–Si–H_b bond angles of (**1**) differ substantially from the reported UHF values of 65 and 123°, respectively.[6,7] Structure (**2**) may be regarded as a weak complex between a hydrogen atom and SiH_3^+, even though the unique Si–H bond is about 0.4 Å shorter than the optimized UHF value. Two novel structures, (**4**) and (**5**), each having C_s ($^2A'$) symmetry were also found. Interestingly, (**4**) has a lower energy than any of the structures of higher symmetry.

UMP2 harmonic frequency calculations revealed that only (**2**), (**3**), and (**4**) are genuine minima (*i.e.* they have no imaginary frequencies), and that (**4**) is the global minimum, lying 80.1 kJ mol^{-1} below (**2**) (68.5 kJ mol^{-1}, including Z.P.E. correction) and 126.6 kJ mol^{-1} below (**3**) (126.1 kJ mol^{-1}, including Z.P.E. correction). Structures (**1**), (**5**), and (**6**) have one imaginary frequency each, and are therefore transition structures. The calculated adiabatic ionization potentials (I_a) of SiH_4 for the formation of (**2**), (**3**), and (**4**) are respectively, 11.34, 11.94, and 10.63 eV (including Z.P.E. corrections scaled[12] by a factor of 0.93). Assuming that these values are



(**1**) C_{2v} ($^2B_1$)

(**2**) C_{3v} ($^2A_1$)

(**3**) D_{2d} ($^2B_2$)

(**4**) C_s ($^2A'$)

(**5**) C_s ($^2A'$)

(**6**) C_{2v} ($^2A_1$)

Figure 1. UMP2/6-31G** optimized geometries of SiH_4^+ (bond lengths in Å, angles in degrees). Other optimized geometries are: SiH_4 (r = 1.473 Å); SiH_3^+ (r = 1.455 Å); SiH_2^+ (r = 1.469 Å, H–Si–H = 120°); H_2 (r = 0.734 Å).

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† All orbitals were used in the correlation. The GAUSSIAN 82[11] suite of programs was used in all calculations.

‡ Only valence orbitals were used in the correlation.

§ Other structures, having D_{2d} (^2E), C_{4v} (^2E), and D_{4h} ($^2B_{1g}$) symmetries were also located at the UHF/6-31G** level, but were not investigated further because each structure has at least two imaginary frequencies.

Table 1. Negatives of the total energies (hartrees[a]) and zero point energies (Z.P.E.)

Molecule		Symmetry		MP2/6-31G**	MP4(SDTQ)/6-31G**[b] //MP2/6-31G**	Z.P.E./ kJ mol^{-1}
SiH_4^+	**(1)**	C_{2v}	($^2B_1$)	290.94072[c]	290.95549	78.65
SiH_4^+	**(2)**	C_{3v}	($^2A_1$)	290.93132	290.94247	69.47
SiH_4^+	**(3)**	D_{2d}	($^2B_2$)	290.90790	290.92474	80.53
SiH_4^+	**(4)**	C_s	($^2A'$)	290.95651	290.97298	81.04
SiH_4^+	**(5)**	C_s	($^2A'$)	290.92963[c]	290.94192	68.78
$H_2 \cdots SiH_2^+$	**(6)**	C_{2v}	($^2A_1$)	290.90769[c]	290.92032	58.86
SiH_4^{+d}		T_d	($^2T_2$)	290.88747	290.90074	
SiH_4		T_d	($^1A_1$)	291.34986	291.36559	86.04
SiH_2^+		C_{2v}	($^2A_1$)	289.78209	289.78927	34.09
SiH_3^+		D_{3h}	($^1A_{1g}$)	290.42414	290.43468	61.42
H_2		$D_{\infty h}$	($^1\Sigma_g$)	1.15766	1.16457	27.58
H·		K_h	(^2S)	0.49823	0.49823	

[a] 1 hartree = 2625 kJ mol^{-1}. [b] Single point energies UMP4(SDTQ)/6-31G** (frozen core) calculated using UMP2/6-31G** optimized geometries. [c] One imaginary frequency (transition structure). [d] Energy calculated based on the corresponding ground state SiH_4 T_d optimized geometry.

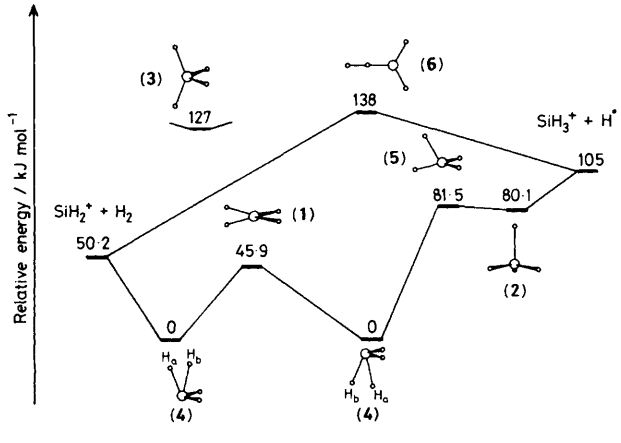

Figure 2. UMP4(SDTQ)/6-31G**//UMP2/6-31G** (vibrationless) energy surface for the rearrangment and dissociation of SiH_4^+. Relative energies in kJ mol^{-1}.

reliable (to within 0.3 eV)¶, then the experimental I_a value of 11.60 eV[5] is consistent with its assignment to the $^2B_2$ band arising from the D_{2d} structure (**3**).[5] However our results suggest that the '$^2B_2$' band of the photoelectron (p.e.) spectrum of SiH_4 may actually be a composite of bands arising from two or more of the structures (**2**), (**3**), and (**4**).††

The geometry of (**4**) is quite remarkable, since it has all four Si–H bonds lying within one hemisphere. Two of the Si–H bonds are fairly long, with the terminal hydrogen atoms lying only 0.770 Å apart (*cf.* 0.734 Å for H_2, see caption to Figure 1). This geometry, together with the calculated charge densities and unpaired spin distribution, suggests that (**4**) is best regarded as a complex of SiH_2^+ ($^2A_1$) and H_2. Indeed, (**4**) is very fragile, requiring only 50.2 kJ mol^{-1} (30.9 kJ mol^{-1}, including Z.P.E.) for decomposition into SiH_2^+ ($^2A_1$) and H_2.§§

Structure (**1**) corresponds to the transition state for the interconversion of equivalent C_s structures (Figure 2), which results in the scrambling of the hydrogen atoms marked H_a and H_b. The activation energy for this process is 45.9 kJ mol^{-1} (43.5 mol^{-1}, including Z.P.E.). However, such a process should not be observed since the activation energy for the scrambling reaction is 12.7 kJ mol^{-1} (including Z.P.E.) above that for dissociation of (**4**) into SiH_2^+($^2A_1$) and H_2.

The C_{3v} structure (**2**) exists in a very shallow well and is converted into (**4**), *via* transition structure (**5**), with an activation energy of less than 2 kJ mol^{-1}. It is therefore unlikely that (**2**) could be capable of anything other than fleeting existence, even at 4 K [tunnelling will further lower the barrier to the formation of (**4**)], and it should decompose into SiH_2^+($^2A_1$) and H_2 [the combined energies of these two molecules being lower than the energy of (**2**)]. The combined energies of SiH_3^+ and hydrogen atom are 54.9 kJ mol^{-1} (54.7 kJ mol^{-1} including Z.P.E.) greater than the combined energies of SiH_2^+ ($^2A_1$) and H_2. Thermal decomposition of (**4**) [and (**2**)] should therefore give exclusively SiH_2^+ and H_2. The reaction of an H atom with SiH_3^+ is predicted to give H_2 and SiH_2^+ ($^2A_1$) *via* (**2**) and (**4**) without activation.§§ An alternative pathway, involving the C_{2v} transition structure (**6**), is energetically less favourable. Decomposition and rearrangement pathways for the D_{2d} structure (**3**) have not yet been delineated. Preliminary calculations, however, suggest the evanescent nature of (**3**) since its conversion into the lower energy structure (**2**) is predicted to involve an activation barrier of less than 4 kJ mol^{-1}.

In summary, the global minimum for the ground state SiH_4^+ cation is predicted to be (**4**) of C_s ($^2A'$) symmetry. It should undergo ready dissociation into SiH_2^+ ($^2A_1$) and H_2 and it is hardly surprising, therefore, that the SiH_4^+ cation is not observed in the mass spectrum of silane[13] except under special conditions,[14] since the T_d ($^2T_2$) SiH_4^+ cation, generated by vertical ionization of SiH_4, lies 189.6 kJ mol^{-1} above (**4**) (see Table 1). However, (**4**) should be stable in a neon matrix at

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¶ The good agreement between the observed (12.82 eV[5]) and calculated (12.65 eV, Table 1) $(t_2)^{-1}$ vertical ionization potentials of SiH_4 lends credence to this assumption.

†† The lack of any ionizations below 11.6 eV in the p.e. spectrum of SiH_4,[5] predicted for transitions into the lowest vibrational states of (**3**), could be due to the very different geometries of SiH_4 and (**3**). Consequently, Franck–Condon factors for these transitions could be small enough to render the transition intensities below the limits of experimental detection.

§§ We were unable to locate any barriers to the addition of H_2 to SiH_2^+ ($^2A_1$) to form (**4**), or to the addition of an H atom to SiH_3^+ to form (**2**); in each case, it was possible to find an energy path that fell continuously and smoothly from reactants to product.

4 K and therefore amenable for study by e.s.r. spectroscopy. Under these conditions, the fluxional behaviour of (**4**), unlike that of the CH_4^+ cation,[2,3] should not be apparent and its e.s.r. spectrum therefore should reflect a C_s structure.

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