Ab Initio Molecular Orbital Calculations on Silaethylene, $H_2Si{=}CH_2$. The Theoretical Infrared Spectrum

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Summary The i.r. spectra of silaethylene ($H_2Si{=}CH_2$) and [2,2,-$^2H_2$]-silaethylene ($H_2Si{=}CD_2$) are predicted by theoretical calculations.

RECENT reports have indicated that species containing a carbon–silicon double bond may exist as unstable reaction intermediates.[1–6] The carbon–silicon double bond appears to be strongly polarized ($\overset{+}{\text{Si}}$–$\overset{-}{\text{C}}$)[4] and has a π-bond energy about half that of the carbon–carbon double bond.[5] In addition, the 1,1-dimethyl-1-silaethylene obtained in the pyrolysis of 1,1-dimethyl-1-silacyclobutane probably exists as a closed shell (singlet) species and not as a biradical (triplet).[1,4a] Semi-empirical molecular orbital computations are consistent with these findings.[6]

In a low-temperature trapping experiment of the pyrolysis products of 1,1-dimethyl-1-silacyclobutane, Barton and McIntosh[3] observed an unstable substance which possesses a sharp band at 1407 cm^{-1} in the i.r. spectrum and which they tentatively assigned to the species $Me_2Si{=}CH_2$. We now report a theoretical i.r. spectrum of the parent compound $H_2Si{=}CH_2$, silaethylene.

TABLE 1. In-plane vibration frequencies for silaethylene[a]

Description	$H_2Si{=}CH_2$ unadjusted	$H_2Si{=}CH_2$ adjusted	$H_2Si{=}CD_2$ adjusted
1. asym CH(CD)str	3160	3160 (9)	2341 (1)
2. sym CH(CD)str	3096	3096 (18)	2260 (13)
3. asym SiH str	2483	2483 (80)	2484 (80)
4. sym SiH str	2479	2479 (46)	2480 (46)
5. CH_2bend, Si=C str	1590	1490 (19)	1238 (23)
6. Si=C str, SiH_2bend, CH_2bend	1151	1140 (14)	954 (11)
7. SiH_2bend	1061	993 (55)	1002 (50)
8. CH_2rock, SiH_2rock	969	777 (68)	700 (65)
9. SiH_2rock, CH_2rock	556	317 (10)	266 (5)

[a] Frequencies in cm^{-1}. Estimated (ref. 12) % absorption given in parentheses. (Strongest band adjusted to 80% absorption).

Wavefunctions were generated on an IBM 360/91 computer with the Gaussian 70 programme system.[7] Force constants were computed by the 'force' method,[8a] using a programme written in our laboratory.[8b] For a preliminary survey of the conformational hypersurface of the molecule, an STO-3G basis set with standard scale factors was used. More detailed calculations were then performed at the extended basis set level. The scale factors for the H and C valence shells were taken as those optimized for ethylene.[9] The silicon basis set was constructed from an STO-4G basis set with the contraction scheme altered to conform with the 4,4,3-1G extended basis sets for third period atoms. Standard scale factors were used for the silicon core shells, while the scale factors for the valence shells were optimized in silaethylene ($\zeta_{\text{inner}} = \zeta_{\text{outer}} = 1{\cdot}952$, constrained to be equal).

The examination of the energy surface at the STO-3G level indicated that the molecule was planar, with a partial positive charge on silicon and a partial negative charge on carbon, in agreement with Sommer *et al.*,[4] and the semi-empirical MO calculations.[6] Forces and force constants obtained with this minimal basis set were used to relax the geometry[8] to obtain a starting point for more detailed calculations. Geometry relaxation at the extended basis set level yielded the optimized structure of silaethylene (C_{2v} symmetry, Si=C 1·693 Å, Si–H 1·479 Å, C–H 1·074 Å, $<$ H–Si–C 122·9°, $<$ H–C–Si 122·7°; dipole moment 1·1 D, indicative of a highly polarized Si=C bond). Force constant calculations, using the same extended basis set, for ethylene and silane† agree well with other theoretical[10] and experimental[11] work. As noticed by Pulay,[10] bending force constants are systematically overestimated by 20%. However, with the basis set used in the present work stretching force constants are underestimated by *ca.* 5%† in contrast to other basis sets[10] which overestimate stretching force constants by 10%. Table 1 contains the fre-

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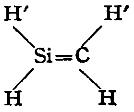
† Details will be presented in the full paper.

TABLE 2. L-Matrix elements for the in-plane vibrations of silaethylene.



	r_{C-Si}	r_{Si-H}	$r_{Si-H'}$	r_{C-H}	$r_{C-H'}$	<C–Si–H	<C–Si–H′	<Si–C–H	<Si–C–H′
1.	−0·000000	−0·010491	0·010491	−0·744114	0·744114	−0·052253	0·052253	0·080878	−0·080878
2.	−0·071652	0·006809	0·006809	0·721492	0·721492	0·003264	0·003264	0·038538	0·038538
3.	−0·000000	0·721819	−0·721819	−0·010510	0·010510	−0·031856	0·031856	0·018153	−0·018153
4.	−0·029918	0·711531	0·711531	−0·006847	−0·006847	0·006748	0·006748	0·009294	0·009294
5.	0·147543	0·010236	0·010236	−0·007139	−0·007139	−0·025931	−0·025931	−0·678972	−0·678972
6.	0·298996	0·000853	0·000853	0·022796	0·022796	−0·128709	−0·128709	0·128869	0·128869
7.	0·043365	0·014350	0·014350	0·000889	0·000889	0·494752	0·494752	−0·002443	−0·002443
8.	−0·000000	0·013954	−0·013954	−0·019968	0·019968	−0·419482	0·419482	0·576784	−0·576784
9.	−0·000000	−0·004309	0·004309	−0·013620	0·013620	0·369031	−0·369031	0·455222	−0·455222

quencies of the in-plane vibration modes calculated with the extended basis set force constants. The second column of Table 1 is obtained by reducing the diagonal bending force constants by 20%, as suggested in ref. 10. These adjusted frequencies are expected to be within 5—10% of the true values and their intensities have been estimated according to ref. 12. The associated normal co-ordinates are given in Table 2. The third entry of Table 1 lists the predicted spectrum for the C deuteriated analogue, assuming that the force constants are essentially unchanged.

A relatively high frequency Si–H stretch is found. This is attributed to the partial positive charge on silicon. The 1407 cm^{-1} band observed by Barton and McIntosh for $Me_2Si{=}CH_2$ most likely corresponds to the 1490 cm^{-1} band calculated for silaethylene. If this assignment is correct, a lowering of *ca.* 250 cm^{-1} would be expected for $Me_2Si{=}CD_2$.

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