Disilene, silylsilylene and their cations

K. Somasundram, R. D. Amos and N. C. Handy

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, Great Britain

An accurate examination of features of the ground state surfaces of Si_2H_4 and $Si_2H_4^+$ is reported; they are compared to C_2H_4 and $C_2H_4^+$. For the neutral species, accurate SCF calculations show disilene to be planar, but silylsilylene has the lower energy, whereas at the correlated (CI, MP2, MP3, MP4(SD)) levels disilene becomes trans bent and has the lower energy by ≈ 6 kcal/mol. In view of a recent theoretical suggestion that this value should be 23 kcal/mol, we have used large basis sets in these investigations. Our calculations cannot support this large value. Similar investigations are reported for the cation, where the planar disilene structure is predicted to be the most stable. It may be very slightly twisted at high accuracy CI, but it is much lower in energy than the silylsilylene structure. Vibrational frequencies and infra-red intensities are also reported. Theoretical photoelectron spectra of C and Si systems are presented and compared with experiment.

Key words: Disilene — Silylsilylene

1. Introduction

In this paper, we study the lowest singlet potential surface of Si_2H_4 and the lowest doublet surface of $Si_2H_4^+$. It is now clear [1] from calculations and experiments that the neutral molecule has a different ground state surface to C_2H_4. We know from calculation that the triplet ethylidene ($H_3C{-}CH$) has an energy at least 50 kcal/mole above ethylene [2]; it is doubtful if singlet ethylidene has a barrier to rearrangement to ethylene [3]. Best calculations [1] on Si_2H_4 show that the disilene structure may be planar or slightly trans bent at the SCF level, but that silylsilylene, (SiH_3SiH), has the lower energy by ≈ 1 kcal/mol. At a correlated

level *ab initio* calculations find disilene trans bent, and that it has a lower energy by 5-7 kcal/mol than silylsilylene. Very recently however, Ho et al. [4] have suggested that disilene should be lower by 23 kcal/mol; they base this on the inclusion of empirical correction factors to *ab initio* calculations which make up for basis set and correlation deficiencies.

Krogh-Jesperson [1] has reviewed both the theoretical and experimental situation of the Si_2H_4 surface. It appears that there has been successful isolation of heavily substituted disilenes, which proves the existence of the $Si=Si$ double bond [5]. Also he reports that the formation of silylsilylene has been postulated in the pyrolysis of trisilane [6]. The reader is referred to [1] for more references on the experimental evidence for the existence of both forms of Si_2H_4.

Ethylene radical cation has been much studied [7] recently. Detailed examination of the photoelectron spectra of C_2H_4 has shown that $C_2H_4^+$ in its ground state is slightly twisted (angle of twist is 27°, with a barrier to planarity of the order of 100 cm^{-1}). This is a very demanding problem for the *ab initioist*; SCF calculations with (sp) basis sets predicting it to be planar, but the MP2 calculations at this level making it twisted [8]. With polarization functions added, SCF and nearly all correlated calculations predict planarity [8], but the trend of such calculations suggest a very flat surface in this region of the minima. There appears to be no reported calculations on the structure of $Si_2H_4^+$, and there is also no experimental evidence. However, in view of the great difference obtained above between C_2H_4 and Si_2H_4, it is interesting to examine the difference in structure between $C_2H_4^+$ and $Si_2H_4^+$.

The purpose of this paper is to perform as detailed calculations as current methodology and computer allowance will permit, on the singlet surfaces of Si_2H_4 and the doublet surface of $Si_2H_4^+$. In particular we wish to see if there is any support for Ho et al.'s [4] large empirical correction for the disilene-silylsilylene energy difference. We shall therefore use large basis sets and also optimize geometries at the correlated level of calculation. Besides minima, we shall report the frequencies of the molecule, and some infra-red intensities which may be useful in the ultimate identification of this species. In Sect. 2 some computational details are given. The Si_2H_4 surface is discussed in Sect. 3 and $Si_2H_4^+$ in Sect. 4. In Sect. 5, the vibrational frequencies are reported, together with theoretical photoelectron spectra for C_2H_4 and Si_2H_4, the former being compared with experiment.

2. Computational details

The basis sets used in the optimizations in this study were of DZ + P and DZ + 2P quality. These were constructed using the $6s,4p$ basis for Si given by Dunning and Hay [9] with the $3s$ Dunning basis for hydrogen [10]. The polarization function exponents in the DZ + P basis where $\alpha_d = 0.4$ and $\alpha_p = 1.0$. This gives a total of 72 basis functions. In the DZ + 2P set the polarization functions were $\alpha_d = 0.8$, 0.2 and $\alpha_p = 1.5$, 0.5, giving a total for 96 basis functions.

Some single point calculations were performed with larger basis sets. The first of these had the d-functions in the DZ+2P basis replaced by a set of three with exponents, 1.6, 0.4 and 0.1, giving 108 functions in total. For the largest basis the silicon s and p functions were replaced by a $9s,6p$ contraction of the Huzinaga [11] $12s,8p$ primitive set. This gives a genuine triple-zeta quality set with 114 functions.

Restricted Self Consistent Field calculations were performed using our *ab initio* package CADPAC [12]; this package calculates SCF and MP2 gradients and second derivatives analytically, and therefore automatic location and characterization of minima and transition structures is possible. Attached to CADPAC is our configuration interaction module, which besides allowing Multi Reference
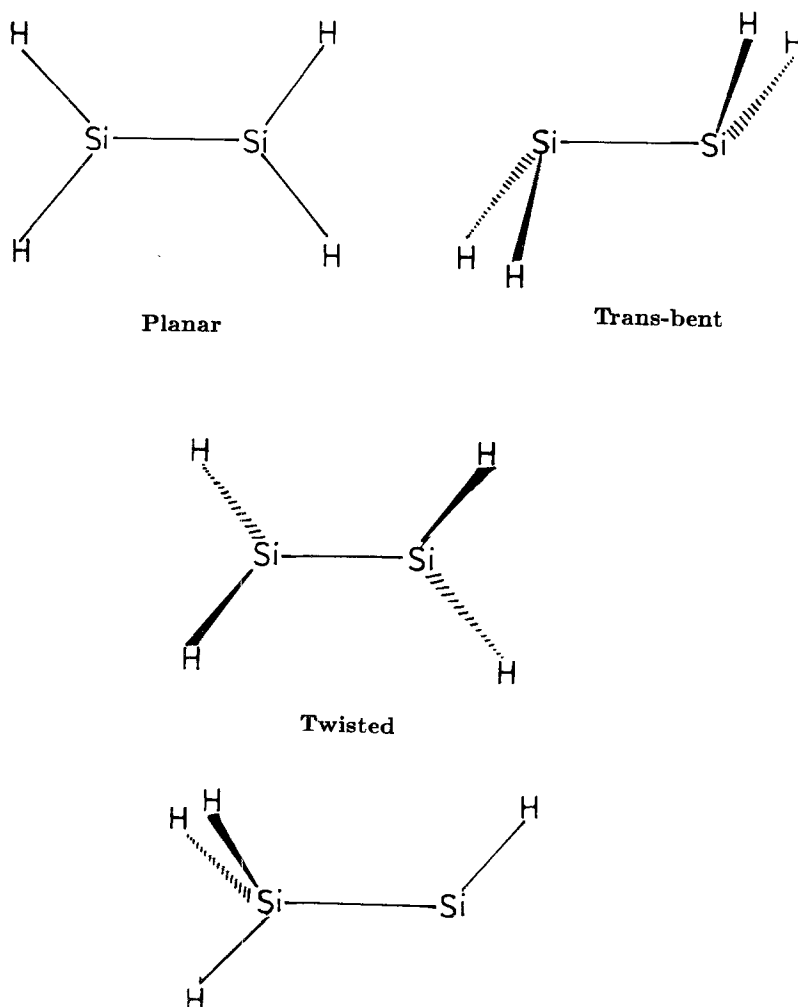
Planar   Trans-bent

Twisted

Fig. 1. Possible structures for Si_2H_4

Configuration Interaction Singles and Doubles (MRCISD) calculations, also allows the evaluation of energy gradients [13] at this level of calculation, and hence again the automatic location of stationary points. The structures examined are shown in Fig. 1.

3. Disilene and silylsilylene

The first *ab initio* calculation on Si_2H_4 was by Synder and Wasserman [14] in 1979, at the SCF level using a 4-31G basis. They found disilene to be trans bent, $I(b)$ with a rocking angle α (we define this as the angle between the HSiH bisector and the Si—Si axis) of 13°; with a 6-31G basis, Krogh-Jesperson [1] reports an angle of 22.5°. The addition of polarization functions in the basis reduces α. For example Lischka and Kohler [15] with a DZ basis plus *d*-polarization on Si predicted α to be 3°. Krogh-Jesperson with a similar basis (6-31G*) found the optimum α to be 11.2°, but states that the energy difference between $I(b)$ and $I(a)$ is only 0.01 kcal/mol. All calculations at the SCF level make the silylsilylene structure $I(d)$ have the lowest energy. For example Krogh-Jesperson [1], at the 6-31G* level, reports that it is 2.8 kcal/mol below the trans bent structure.

The optimized RHF geometries from our best DZ+2P calculations are shown in Fig. 2. The twisted form $I(c)$ and the trans bent form $I(b)$ collapsed to the planar form $I(a)$. The energies of the structures are given in Table 1. The present
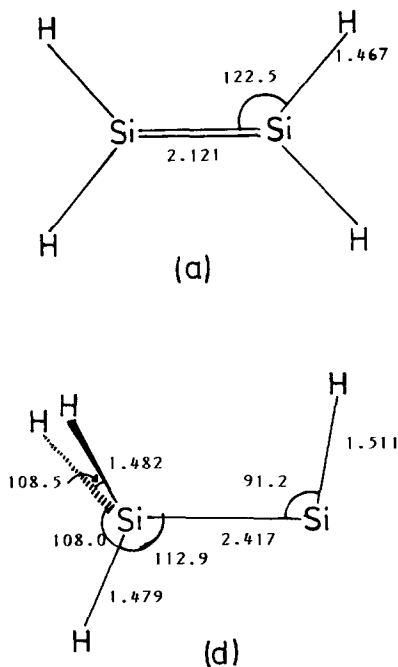

Fig. 2. Optimized geometries for Si_2H_4 at the RHF/DZ+2P level

Table 1. Total energies (in hartrees) of Si_2H_4 and $Si_2H_4^+$, using the RHF, CI and MP2 methods outlined in the paper

Method	$(SiH_2)_2$ (planar)	$(SiH_2)_2$ (trans bent)	SiH_3SiH	$(SiH_2)_2^+$ (planar)	SiH_3SiH^+
[a] RHF/DZP	−580.088951	—	−580.091661	−579.839486	−579.825808
[a] RHF/DZ+2P	−580.097571	—	−580.099208	−579.851034	−579.834227
[a,b] SDCI	−580.278191	−580.279864	−580.27256	−580.004704	
[a,b,c] SDCI (D.C)	−580.300099	−580.302849	−580.29248	−580.020732	
[a,b] MRCISD		−580.287559			
[a,b,c] MRCISD (D.C)		−580.319620			
[b,d] SDCI (ext)	−580.307594	−580.308435	−580.303297	−580.032823	
[b,c,d] SDCI (ext D.C)	−580.332864	−580.334664	−580.326687	−580.051815	
[a] MP2/DZP	−580.412583	−580.413821	−580.402852		
[a] MP2/DZ+2P	−580.447827	−580.448676	−580.438867		
[e] SDCI//RHF/DZP				−580.033024	−580.015294

[a] Geometry optimized
[b] DZP basis set
[c] Davidson correction
[d] Single point calculations at previous CI optimized geometries, with 10 frozen core and 10 frozen virtual orbitals (42 orbitals)
[e] Single point CI calculation, one reference, 42 virtual orbitals, at the RHF/DZP optimized geometry

calculations with both the DZP and DZ+2P basis sets predicted disilene to have a planar minimum (as checked by frequency calculation). With the DZP basis a change in energy of 0.01 kcal/mol is associated with a change in α of 10°. Very careful optimization is thus required. Earlier calculations reported above did not use as large basis sets (in various ways) as we have done.

The relative energies with respect to H_3SiSiH, $I(d)$ are given in Table 2. In line with earlier calculations, the DZ+2P calculations shows H_3SiSiH is ≈ 1 kcal/mol lower in energy than disilene at this SCF level.

Table 2. Relative energies (in kcal/mol) of Si_2H_4 and $Si_2H_4^+$ at the SCF and correlated levels

Method	$(SiH_2)_2$ (planar)	$(SiH_2)_2$ (trans bent)	SiH_3SiH	$(SiH_2)_2^+$ (planar)	SiH_3SiH^+
[a] RHF/DZP	+1.7	—	0	−8.6	0
[a] RHF/DZ+2P	−1.02	—	0	−10.5	0
[a] RHF/DZ+2P+ZPVE					
[a,b] SDCI	−3.5	−4.6	0		
[a,b] SDCI (D.C)[c]	−4.8	−6.5	0		
[a,b] SDCI (ext)	−2.7	−3.2	0		
[a,b] SDCI (ext D.C[c])	−3.9	−5.0	0		
[a] MP2/DZP	−6.1	−6.9	0		
[a] MP2/DZ+2P	−5.6	−6.1	0		
[e] SDCI//RHF/DZP				−11.1	0

[a,b,c,d,e] As for Table 1

The effect of electron correlation is now recognized to be important for the energy difference ΔE, between disilene and silylsilylene. Krogh-Jesperson [1] reported that at the MP3/6-31G** // 6-31G** level, ΔE was 5.0 kcal/mol. Luke et al. [2] predict ΔE to be 6.2 kcal/mol at the MP4SDTQ/6-31G* // 3-21G* level (including zero-point energies). Olbrich [16] reports ΔE to be 8.0 kcal/mol using the CPF method with a DZ + P basis (again including ZPE – this lowers ΔE by about 0.5 kcal/mol); his geometries were not completely optimized. Using MP2/6-31G** optimized geometries, and single point MP4(SDTQ) with an extended basis (McLean–Chandler) and one set of polarization functions, ΔE was predicted to be 6.4 kcal/mol by Gordon et al. [17]. They also performed some small single point MCSCF calculations which gave ΔE to be 3.9 kcal/mol. Finally Ho et al. [4] calculated an *ab initio* value for Δ of 6.5 kcal/mol, at the MP4/6-31G** // 6-31G* level. However Ho et al. argue that empirical correction factors must be added (which are a function of the Si—Si bond lengths, and Si—H bond lengths) to take account of "systematic errors arising from the truncated wavefunctions and incomplete basis sets". They then predict ΔE to be 23 kcal/mol, and say that this is because the short Si=Si distance requires a greater correction factor. There is therefore clearly room for investigation into these "systematic errors".

Our calculations, which included electron correlation, commence at the configuration interaction level. At the DZP level, most appropriate would be SDCI, using excitations from 6 doubly occupied valence orbitals to 42 virtual orbitals, i.e. freezing 10 core and 10 virtual orbitals. This CI generated too many CSF's (20 377 in C_s symmetry) for the CI gradient program, so we were forced to reduce it to SDCI for 6 doubly occupied orbitals with the lowest 30 virtual orbitals (4207 CSF's in C_{2h}, 8554 CSF's in C_s symmetry). These CI(DZP) optimized geometries are shown in Fig. 3. From Table 1, it is seen that disilene has a trans bent form and is lower in energy than silylsilylene. The angle α was 17°, and the CI/DZP calculation gave the energy difference to be 4.6 kcal/mol, with a barrier to planarity for disilene of 1.1 kcal/mole. The addition of the Davidson correction [18] further stabilizes the trans bent disilene to give a value of 6.5 kcal/mol for ΔE. For the geometry changes, we note CI increased the bond length of disilene by 0.04 Å, and in silylsilylene by 0.02 Å.

Analysis of the CI wavefunctions shows that for H_3SiSiH, it is dominated by one CSF, whereas in H_2SiSiH_2, there is a second CSF which is important, a double excitation from the HOMO b_u to the LUMO a_g (in the planar structure this corresponds to a π^2 to π^{*2} replacement). A two reference MRCISD (same virtual space) was therefore performed, and the geometry optimized for disilene (8189 CSF's). The rocking angle α increased to 20.5°. From Table 2 it is seen that our best value for the energy difference was 5.0 kcal/mol. It is worth noting that a two-configuration SCF calculation also predicts a bent structure which is very similar to the CI structure. This indicates the qualitative importance of the second configuration.

To support these calculations, we also optimized the geometries of these structures at the Moller-Plesset second order perturbation theory level of accuracy, (using our recent extension of CADPAC to calculate MP2 gradients [19]). In Table 1,
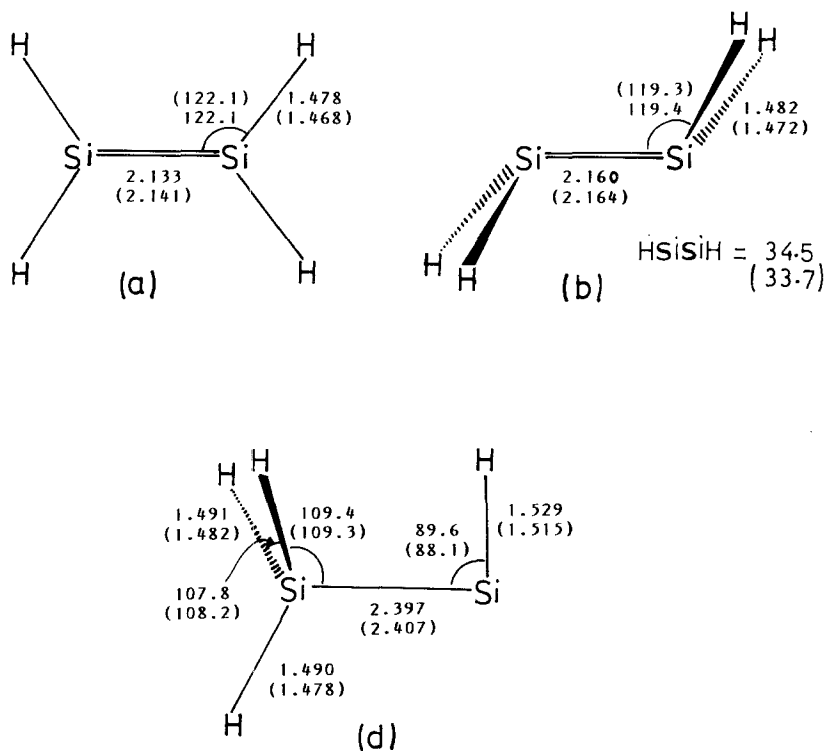
Fig. 3. CI(DZ+P) and MP2(DZ+2P) (shown in parenthesis) optimized structures of Si_2H_4

the energies are given for the MP2/DZP and MP2/DZ+2P structures (all orbitals involved, no frozen core or frozen virtual). The MP2/DZ+2P structures are given in Fig. 3 in parenthesis. It will be seen that there is very little difference in the CI and MP2 structures. The MP2/DZ+2P energies give the energy difference of disilene and silylsilylene as 6.1 kcal/mol.

The MP2/DZ+2P optimized geometries reported in Fig. 3 may be compared with the MP2/6-31G** optimized geometries reported by Gordon et al. [17]. For H_2SiSiH_2, our Si=Si bond is 0.0005 Å shorter. For H_3SiSiH, our Si—Si bond is 0.017 Å longer. If anything these results indicate some saturation of the basis as far as polarization functions are concerned.

To investigate further the energy separation ΔE between H_2SiSiH_2 and SiH_3SiH the larger basis sets were used in conjunction with Moller-Plesset perturbation theory. Various levels of perturbation theory were investigated, along with various choices of the active space. MP2 calculations were made correlating only the valence shell (i.e. with 10 core orbitals frozen), and with only the Si 1s core orbitals frozen. In addition, with the valence shell calculation, the third order energy and the contribution of the single and double excitations in the fourth order expression were evaluated.

The results are given in Table 3, and show little change for those obtained with

Table 3. Total and relative energies of H_2SiSiH_2 and SiH_3SiH using very large basis sets. Basis set (1) Si: $9s\ 6p\ 2d$, H: $3s\ 2p$. Basis set (2) Si: $6s\ 4p\ 3d$, H: $3s\ 2p$

Method	H_2SiSiH_2	SiH_3SiH	ΔE (kcal/mol)
(1) $(9s\ 6p\ 2d/3s\ 2p)$ basis			
SCF	−580.133073	−580.135818	+1.7
MP2[a]	−550.603537	−580.593132	−6.5
MP2[b]	−580.352940	−580.341956	−6.9
MP3[b]	−580.388953	−580.381077	−4.9
MP4-SD[b]	−580.401623	−580.393798	−4.9
(2) $(6s\ 4p\ 3d/3s\ 2p)$ basis			
SCF	−580.098414	−580.102188	+2.3
MP2[a]	−580.474319	−580.464683	−6.0
MP2[b]	−580.316278	−580.305506	−6.7
MP3[b]	−580.353003	−580.344820	−5.1
MP4-SD[b]	−580.365733	−580.357427	−5.2

[a] With 2 core orbitals frozen
[b] With 10 core orbitals frozen

smaller basis sets. At the SCF level, SiH_3SiH is lower in energy by 1–2 kcal/mol; with MP2, H_2SiSiH_2 is lower by 6–7 kcal/mol, regardless of the choice of basis set and active space. The use of MP3 or MP4-SD reduces the separation. It is unfortunate that we could not include the triple excitations at the MP4 level, however, the calculations of Gordon et al. (using basis set intermediate in size between our DZP and DZ + 2P sets) found that the triple excitations lowered the H_2SiSiH_2 energy by about 2 kcal/mol relative to H_3SiSiH. This would simply cancel out the other 3rd and 4th order terms and restore the energy difference to that calculated at the MP2 level. It is entirely possible that the effects of the triple excitations will be greater than this with larger basis sets; but not by an order of magnitude. Accordingly we can see no justifications for the suggestion by Ho et al. [4] that the energy difference ΔE is 23 kcal/mol. Indeed we would be surprised if ΔE exceeded 10 kcal/mol. Our summary of these calculations is that the addition of extra basis functions, more complete geometry optimization and a more complete study of correlation effects has not changed the picture of the H_2SiSiH_2, H_3SiSiH surface. At the best levels of calculation, disilene is lower in energy than H_3SiSiH by 6–7 kcal/mol. This returns us to the claim of Ho et al. that a Si=Si bond correction factor of 23 kcal/mol is in order for deficiencies in the *ab initio* calculation. Other than the fact the correction factor idea of Melius and Binkley [20] works well for hydrocarbon species, it is difficult to find theoretical support for this. The *ab initioist* ought to be able to find some indication of such a high deficiency; our basis set size increase in particular ought to show it. It did not.

4. The cations of disilene and silylsilylene

The geometries of $H_2SiSiH_2^+$ and H_3SiSiH^+ were first optimized at the restricted SCF level with the DZP and DZ + 2P basis sets. The results are in Fig. 4 for the
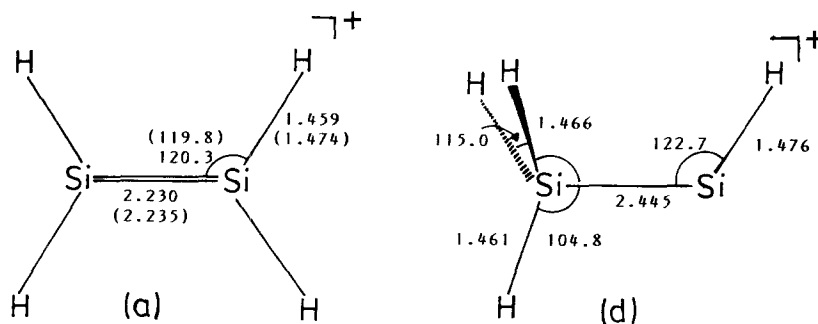
Fig. 4. RHF/DZ+2P optimized geometries for $Si_2H_4^+$ with the CI/DZ+P values in parenthesis

DZ+2P basis. The energies are given in Table 1. It is seen from Table 2 that the disilene cation is lower by 8.1 kcal/mol at the DZP level; this increases to 10.6 kcal/mol at the DZ+2P level. We note that on ionization the Si—Si bond lengthened by 0.1 Å and the Si—H bond shortened by 0.008 Å.

Electron correlation was included by the CISD method. Single point calculations at the DZP level (i.e. CISD/DZP//RHF/DZP) with 10 frozen core and 10 frozen virtual orbitals, gave an energy difference of ≈ 11 kcal/mol between the two minima, strongly indicating the stability of disilene cation. Because the qualitative aspects of these results are consistent at the RHF and CI level and the two minima are separated by a large amount of energy, H_3SiSiH^+ was not optimized at the CI level.

$H_2SiSiH_2^+$ was optimized using the restricted virtual space CISD described for H_2SiSiH_2, and the geometry is given in Fig. 4, with the values in parenthesis. It will be recalled from the introduction that the *ab initio* determination of the structure of $C_2H_4^+$ (twisted or planar) was very difficult. We performed a CISD calculation on $Si_2H_4^+$ using a 6-31G basis, to optimize the twisted structure, but it collapsed to the planar structure. A similar calculation on $C_2H_4^+$ showed that it remains twisted. This suggests (but see below) that $Si_2H_4^+$ might be planar.

5. Frequencies, intensities and photoelectron spectra

The frequencies and infra-red and Raman intensities of disilene, its cation and deuterated derivatives, calculated at the RHF/DZ+2P level of accuracy, are given in Tables 4 and 5. Herzberg [21] notations are used to assign the frequencies. For comparison purposes the frequencies of C_2H_4 and $C_2H_4^+$, calculated [22] at RHF/TZ+2P basis set level of accuracy are also included. Our frequencies for disilene agree reasonably well with those of Ho et al. which were calculated with a 6-31G* basis.

There are several comments to make from these SCF calculations, all at D_{2h} symmetry. We note that earlier discussion shows that D_{2h} is not necessarily the structure of the systems, and that therefore the values of some of the small frequencies should be treated with caution. The ν_8 frequency corresponds to the

Table 4. Harmonic frequencies of $(SiH_2)_2$, $(SiD_2)_2$, $(SiH_2)_2^+$ and $(SiD_2)_2^+$ at the RHF/DZ+2P optimized (i.e. D_{2h} planar) geometry, compared with those for C_2H_4 and $C_2H_4^+$ (RHF/TZ+2P basis [11])

Mode[a]	$(SiH_2)_2$	$(SiD_2)_2$	$(SiH_2)_2^+$	$(SiD_2)_2^+$	C_2H_4	$C_2H_4^+$
ν_1	2376	1700	2409	1722	3292	3291
ν_2	1034	782	1023	760	1819	1693
ν_3	641	592	557	525	1477	1362
ν_4	598	423	421	297	1139	473
ν_5	2380	1722	2443	1771	3347	3396
ν_6	650	501	650	497	1346	1336
ν_7	637	466	632	462	1086	1100
ν_8	174	134	449	343	1102	1220
ν_9	2388	1730	2450	1776	3374	3412
ν_{10}	390	278	389	277	892	898
ν_{11}	2365	1689	2406	1717	3273	3281
ν_{12}	952	689	931	674	1593	1589

[a] Herzberg notation [21]

molecule's deformation from planar D_{2h} to trans bent C_{2h} form. The very small value (174 cm^{-1}) for $(SiH_2)_2$ is to be compared with 1102 cm^{-1} for C_2H_4. This is the greatest contrast between these two molecules. The ν_4 mode is the twisting vibration. Its relatively small value (473 cm^{-1}) for $C_2H_4^+$, when compared to 1139 cm^{-1} for C_2H_4 indicates that $C_2H_4^+$ may have the tendency to twist. We see that the corresponding values for $Si_2H_4^+$ and Si_2H_4 are 421 cm^{-1} and 598 cm^{-1}.

It is possible to comment on some details of the photoelectron spectra $Si_2H_4 \rightarrow Si_2H_4^+$. For completeness, and to supplement our earlier discussion [22], we shall also discuss the photoelectron spectra for $C_2H_4 \rightarrow C_2H_4^+$, and compare it with experiment.

Table 5. Infrared intensities (km/mol) and Raman intensities (A^4/amu) for $(SiH_2)_2$, $(SiH_2)_2^+$ at the RHF/DZ+2P level

Mode	Infra-red		Raman
	$(SiH_2)_2$	$(SiH_2)_2^+$	$(SiH_2)_2$
ν_1	0	0	321
ν_2	0	0	11
ν_3	0	0	127
ν_4	0	0	0
ν_5	0	0	169
ν_6	0	0	5
ν_7	5	35	0
ν_8	0	0	67
ν_9	140	7	0
ν_{10}	29	20	0
ν_{11}	103	3	0
ν_{12}	126	109	0

The photoelectron spectra will be dominated by those vibrations ν_2, ν_3 in which the X atoms (X = C, Si) move significantly, because of the increase in the X—X bond length in the cation.

For these two a_g vibrations we use the Herzberg notation [21]:
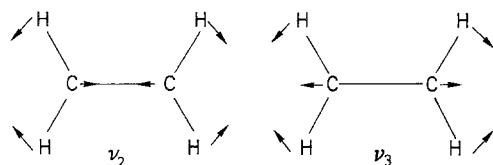
ν_2 usually being called the X—X stretch, and ν_3 being called the H—X—H scissors vibration.

If Q_i are normal coordinates, and q are mass weighted cartesian displacements, then straightforward theory shows that the maximum displacements of the X atom's coordinates x_j in the ν_i vibration are given by $x_j = c_{ji}/\sqrt{m_X \omega_i}$, where $q_j = \sum_i c_{ji} Q_i$. These maximum displacements are given in Table 6 for $C_2H_4^+$, $C_2D_4^+$, $Si_2H_4^+$, and $Si_2D_4^+$, and these are compared with the neutral systems. We see that only for C_2H_4, C_2D_4 and $C_2D_4^+$ the maximum displacement for ν_2 is greater than that for ν_3. These results also suggest that the ν_3 progression in the photoelectron spectra of C_2H_4, Si_2H_4 and Si_2D_4 will be more prominent than the ν_2 progression.

It is possible to calculate the Franck–Condon intensity factors $|R(v', v)|^2$,

$$R(v', v) = \langle H_{v'}(Q') | H_v(Q) \rangle \tag{1}$$

where (v', Q') refer to the vibrations of the upper state and (v, Q) to the lower state. Formulae for $R(v', 0)$ are given by Smith and Warsop [23] and Chau [24].

The key to the analysis is the relation between the normal coordinates Q', Q and geometries of the two states. One can proceed by considering S', S symmetry coordinates for the two states; if R is the change in equilibrium geometry, we can write

$$S' = S + R \tag{2}$$

Furthermore if $S' = L'Q'$, then it follows that

$$Q' = AQ + d \tag{3}$$

where

$$d = (L')^{-1} R \tag{4}$$

Table 6. Maximum X atom (X = C or Si) displacements in ν_2 and ν_3 vibrations

Mode	C_2H_4	$C_2H_4^+$	C_2D_4	$C_2D_4^+$	Si_2H_4	$Si_2H_4^+$	Si_2D_4	$Si_2D_4^+$
ν_2	0.048	0.032	0.045	0.048	0.013	0.012	0.032	0.026
ν_3	0.028	0.044	0.013	0.020	0.055	0.059	0.045	0.054

d is required for the evaluation of (1). We have used the program SPECTRA to complete this analysis [24].

In Fig. 5, we have compared our theoretical intensities for the photoelectron spectra for $C_2H_4 \rightarrow C_2H_4^+$ with the experimental spectra of Pollard et al. [7]. The height and position of the theoretical intensities are scaled such that the (000) ← (000) coincides with experiment. It is seen that the resulting scaled values, for ν_3, agree nicely for (001) ← (000), (002) ← (000), (003) ← (000) and also for (010) ← (000). (Recall that Pollard et al. [7] misassigned ν_2 and ν_3, hence our change in the labels of Fig. 5). In Fig. 6 a similar picture is presented for $C_2D_4 \rightarrow C_2D_4^+$ (using the photoelectron spectra from Cvitaš et al. [26]). It is seen that the positions and relative heights of the peaks are in good agreement.

There are no photoelectron spectra for $Si_2H_4 \rightarrow Si_2H_4^+$ and $Si_2D_4 \rightarrow Si_2D_4^+$, and so Fig. 7 shows our theoretical predictions. Note that for both of these the principle progression corresponds to ν_3.

The infra-red and Raman intensities are obtained using analytic evaluation of the dipole moment and polarizability derivatives, as implemented in CADPAC
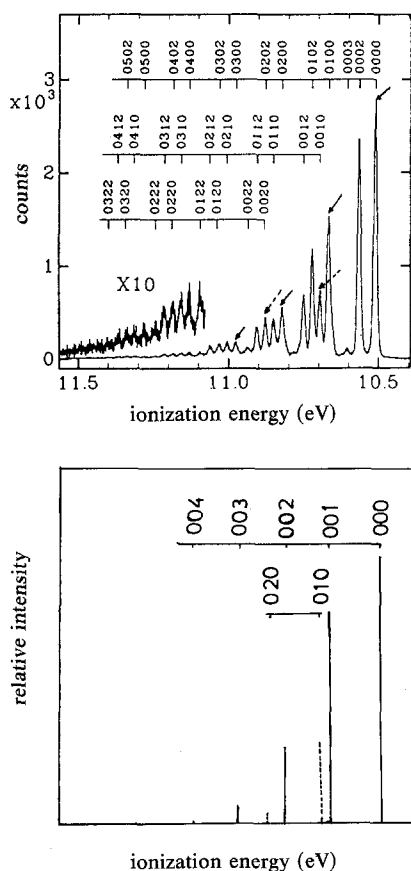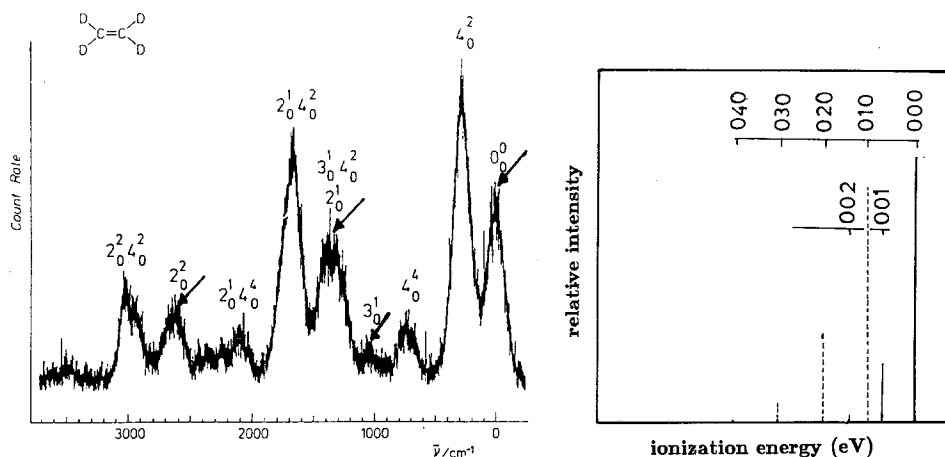

Fig. 5. Comparison of theoretical and experimental photoelectron spectra for $C_2H_4 \rightarrow C_2H_4^+$. (Experimental photoelectron spectra from Pollard et al. (1984) J Chem Phys 81:5302). In the experimental spectra ν_2 and ν_3 should be interchanged (see text)

Fig. 6. Comparison of theoretical and experimental photoelectron spectra for $C_2D_4 \to C_2D_4^+$. (Experimental photoelectron spectra from Cvitaš et al. (1979) J Chem Phys 70:57)

[27, 28]. With the basis set used the qualitative features of the intensities should all be correct, however truly quantitative results probably cannot be obtained at the SCF level, even with much larger basis sets and a correlated approach will be required [29, 30].

6. Conclusion

In this paper we have examined in detail features of the ground state potential surface of Si_2H_4 and $Si_2H_4^+$. Our principal conclusions are that

(a) the trans bent disilene structure is 6–7 kcal/mol lower in energy than silylsilylene structure. We can find no evidence to support the empirically corrected value from Ho et al. [4] of 23 kcal/mol.

(b) $Si_2H_4^+$ is of disilene form, either planar or slightly twisted, but it is much lower in energy than the H_3SiSiH^+ structure.
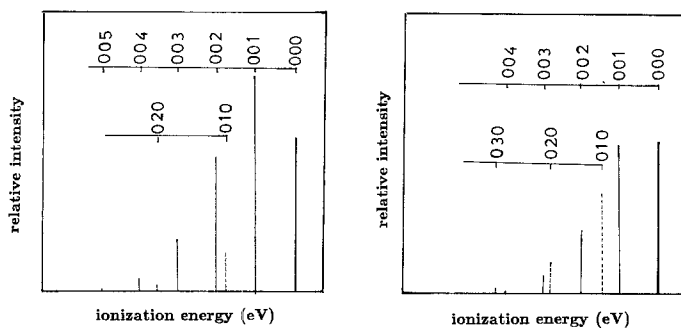

Fig. 7. Theoretical photoelectron spectra for Si_2H_4 and Si_2D_4

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