

Positive ions of SiH_4 : Jahn-Teller-like distortions for SiH_4^+ and eventually molecular collapse on further ionisation.

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Abstract We have recently studied by quantum-chemical calculations some fifteen tetrahedral and octahedral molecules. These seemingly disparate numerical tabulations were, it was demonstrated, pulled together by comparison with model semiclassical scaling laws for (i) nuclear–nuclear repulsion energy at the equilibrium geometry and (ii) total energies likewise. Here, we again appeal to such model scaling predictions, but now for positive ions of SiH_4 . We then report Hartree-Fock equilibrium geometries and MP2 corrections. For SiH_4^+ , we assumed the symmetry to be C_{2v} , by analogy with CH_4^+ for which experimental confirmation of this symmetry is available. Larger distortions, but still for C_{2v} symmetry, are found from our quantum-chemical studies in the case of SiH_4^{2+} . But for SiH_4^{3+} there is a marked tendency to return to a configuration quite close to tetrahedral symmetry. But non-convergence is found for SiH_4^{4+} . Finally relations to the admittedly simplistic semiclassical geometry scaling predictions of Lawes and March are conjectured.

Keywords Jahn-Teller distortions · Ionisation · Molecular collapse

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1 Introduction

In this journal Li et al. [1] have very recently reported quantum-chemical calculations of the isolated silane molecule. These authors utilized the MP2 method with a 6-311++G(3df,3pd) basis set and their finding was a tetrahedral configuration (T_d symmetry) with a Si–H bond length of 1.47 Å. This is in pretty good accord with experimental data by Kattenberg and Oskam [2], who report a bond length of 1.4606 ± 0.0008 Å and by Willets and Jones [3], who give 1.482 Å. Later the linear fitting prediction data (see Duncan et al. [4]) resulted in the value 1.479 ± 0.003 Å.

Quite independently of Ref. [1], but using essentially the same quantum-chemical approach, we have reported equilibrium geometries of some 15 or so neutral tetrahedral and octahedral [T and O] molecules [5] including SiH_4 . These seemingly separate molecular calculations were there pulled together by comparison with, and then some necessary modification of, model scaling laws [6,7] for (i) nuclear-nuclear repulsion energy at the equilibrium geometries [8] and (ii) total energy likewise [5].

The current work is closely related to Ref. [6], which utilized an admittedly oversimplified semiclassical spherical model of neutral T and O molecules, and which was then solved, at least partially analytically, self-consistently using the forerunner of modern density functional theory [9], namely the Thomas-Fermi statistical method [10]. Positive ions were also treated using the same approach by Lawes and March [11].

In Sect. 2 below, we summarize the extension of scaling properties derived in Ref. [6] and utilized in Ref. [5] for neutral T and O molecules, given by Lawes and March [11]. However, we must emphasize that, as was already noted in Ref. [11], that the retention of spherical geometry there for positive ions neglected Jahn-Teller (JT) distortions. A major aim of the present study is to report, by quantum-chemical calculations referred to already, such JT distortions in the equilibrium geometry of the singly charged positive ion of silane. This is set out in Sect. 3. But we have also thought it of interest to study how the removal of further electrons, as in SiH_4^{2+} and SiH_4^{3+} , would affect the equilibrium geometry. Our conclusions on this matter are recorded in Sect. 4. The penultimate Sect. 4.1 brings these numerical quantum-chemical studies into contact with the (model-dependent) scaling predictions of [11] referred to above. Section 5 constitutes a summary, together with some proposals for future work which should prove fruitful.

2 Scaling properties of the march results for the Thomas-Fermi semi-classical model of positive octahedral and tetrahedral molecular cations

Lawes and March [11] generalised the scaling properties for the March [6] Thomas-Fermi semiclassical model for tetrahedral and octahedral molecules, to apply to positive molecular ions. Here our interest is in SiH_4^{n+} , $n=1-3$, but first let us summarize the general scaling relationships for the above model. However, as Lawes and March emphasize, the molecular positive ions would, in fact, become Jahn-Teller (JT) distorted on ionisation from the neutral tetrahedral molecules. This is suppressed in the Lawes-March modelling.

Given that restriction, the purpose of this brief section is to summarize the Lawes-March scaling relations in this spherical model. As in Ref. [6], Z_e denotes the charge on the central nucleus ($Z = 14$ for SiH_4 ions therefore) while ne is the total charge on the outer (surface charge spread) nuclei, where $n = 4$ for the silane ions. N always denotes the total number of electrons in the molecular ion under consideration.

Then the first important scaling relation of the Lawes-March (LM) model is for the (single, when no JT distortion is allowed) equilibrium bond length R_e : (See Ref. [11]; eqn.(3.6))

$$R_e = Z^{-\frac{1}{3}} f(N/Z, n/Z) \quad (1)$$

Evidently, for the silane ions under discussion, Z and n are fixed ($Z = 14$, $n = 4$) and hence in the present application Eq. (1) becomes

$$R_e = \text{constant } F(N) \quad (2)$$

We will return to Eq. (2) in Sect. 5, after we report quantum chemical calculations transcending the TF approximation and, of course, allowing JT distortions from T symmetry. It is attractive, however, that (see also for a wide variety of neutral T and O molecules [8]) R_e is predicted to depend on the total number of electrons N and this will be confronted with our quantum-chemical findings in Sect. 5 below.

Lawes and March [11] also predict in their admittedly over-simplistic spherical model, by utilizing the result (1) above for the equilibrium radius R_e , that the nuclear-nuclear repulsion energy at equilibrium, denoted by U_{nn}^{equil} , has the scaling behaviour according to the semiclassical TF model that

$$U_{nn}^{equil} = \frac{ne^2(Z + cn)}{Z^{-\frac{1}{3}} f(N/Z, n/Z)} \quad (3)$$

where $c = 3\sqrt{6}/32$ [6] for tetrahedral molecules. Evidently, by simple manipulation, Eq. (3) then corresponds to the scaling property

$$U_{nn}^{equil} = Z^{7/3} g(N/Z, n/Z) \quad (4)$$

In spite of the simplistic character of the LM model, it proves possible to make sensible contact with Eq. (4) above and the quantum-chemical numerical results for spherically SiH_4^+ and SiH_4^{3+} . For the doubly charged ion SiH_4^{2+} , it turns out, to our surprise we confess, that the JT distortion is too large to invoke the LM scaling recorded in Eqs. (1) and (2).

To conclude this section, it is of interest to note that LM also discuss the scaling properties of the chemical potential for the positive molecular ions focussed on here.

Table 1 Hartree-Fock plus MP2 prediction for the positive ions of SiH₄ at equilibrium

	SiH ₄ ⁺		SiH ₄ ²⁺		SiH ₄ ³⁺	
R(1,2)	1.455		1.472		1.923	
R(1,3)	1.455		1.472		1.923	
R(1,4)	1.569		1.897		1.902	
R(1,5)	1.569		1.897		1.902	
A(2,1,3)	125.0		153.8		123.6	
A(4,1,5)	55.65		24.03		25.65	
A(2,1,4)	114.1		102.8		117.6	
HF energy	-290.8564		-290.3105		-289.3394	
MP2 contribution	-0.1001		-0.8991		-0.6242	
Nuclear repulsion	21.0274		19.5340		16.9261	
Orbital energies	α	β	α	β	α	β
	-69.10	-69.10	-69.47		-69.79	-69.79
	-6.44	-6.44	-6.81		-7.11	-7.11
	-4.55	-4.55	-4.91		-5.22	-5.22
	-4.55	-4.55	-4.91		-5.21	-5.21
	-4.55	-4.54	-4.91		-5.21	-5.21
	-1.06	-0.98	-1.30		-1.52	-1.50
	-0.83	-0.78	-1.14		-1.35	-1.30
	-0.77	-0.77	-1.06		-1.29	
	-0.71					

Geometry (bond lengths R in Å, angles A in degrees), energies in au

3 Results for equilibrium geometry and energy components from Hartree-Fock and MP2 calculations on SiH₄⁺.

As already mentioned in the abstract, for the singly charged positive ion of silane we assumed the symmetry at equilibrium to be C_{2v}. This we did by rather direct analogy with CH₄⁺, for which case experimental confirmation of this symmetry is available, as we summarize below with appropriate references.

As reviewed by Frey and Davidson [12] early ab-initio work on CH₄⁺ predicted both D_{2d} and C_{3v} equilibrium geometries. But as Frey and Davidson stress, molecular ions are, in general, difficult to study experimentally. CH₄⁺ has been observed in mass-spectroscopic experiments, but direct spectroscopic measurements in the gas phase confront the difficulty of the short lifetime of CH₄⁺ (see, e.g. [13] and [14]). Subsequently Knight et al. [15] reported experimental evidence for a C_{2v} (²B₁) ground-state assignment for CH₂D₂⁺. They used neon-matrix electron-spin resonance (ESR) results, but CH₄⁺ was determined as fluxional with four equivalent protons. Reeves and Davidson [16] some years later commented that the above experimental findings could be, at least qualitatively, understood by assuming that CH₄⁺ was fluctuating among C_{2v}

Table 2 MP2 prediction for the positive ions of SiH₄ at equilibrium

	SiH ₄ ⁺		SiH ₄ ²⁺		SiH ₄ ³⁺	
R(1,2)	1.451		1.475		1.925	
R(1,3)	1.451		1.475		1.925	
R(1,4)	1.637		1.890		1.900	
R(1,5)	1.637		1.890		1.900	
A(2,1,3)	142.9		153.9		121.4	
A(4,1,5)	31.47		24.34		25.89	
A(2,1,4)	107.8		102.8		118.5	
HF energy	−290.8572		−290.3104		−289.3394	
MP2 contribution	−0.1047		−0.9000		−0.6250	
Nuclear repulsion	21.9040		19.5341		16.9737	
Orbital energies	α	β	α	β	α	β
	−69.10	−69.09	−69.47		−69.79	−69.79
	−6.44	−6.43	−6.80		−7.11	−7.11
	−4.56	−4.54	−4.91		−5.22	−5.22
	−4.55	−4.54	−4.91		−5.21	−5.21
	−4.54	−4.53	−4.91		−5.21	−5.21
	−1.10	−1.04	−1.30		−1.52	−1.50
	−0.87	−0.86	−1.14		−1.36	−1.30
	−0.78	−0.78	−1.06		−1.29	
	−0.59					

Geometry (bond lengths R in Å, angles A in degrees), energies in au

faster than the time scale of the ESR measurements. On the other hand, CH₂D₂⁺ can be anticipated to have a lower zero-point energy, and therefore would be expected to be less likely to fluctuate. Reeves and Davidson [16] also note that Coulomb explosion experiments are in support of a C_{2v} geometry.

This therefore led us to assume the C_{2v} symmetry for SiH₄⁺ and we record in Tables 1 and 2 our quantum-chemical findings for this molecular ion. These tables contain the appropriate equilibrium bond lengths and angles thereby determined. The expected JT distortion is clearly in evidence from the two different bond lengths 1.45 and 1.57 Å (Table 1, HF geometry) and 1.45 and 1.64 Å (Table 2, MP2 geometry).

In the lower part of the Tables, corresponding energy components are reported, together with one-electron eigenvalues for occupied states. Also the virial theorem 2T + V = 0 is found to be accurately obeyed in the Hartree-Fock plus MP2 calculations presented. The total kinetic energy T is 290.8 atomic units (au). The nuclear-nuclear repulsion U_{nn} referred to already in Sect. 2 is recorded separately as 21.0 au.

The one-electron eigenvalues are given for the two spin directions α and β . Of course, if we had, as in the Thomas-Fermi theory of Lawes and March summarized in Sect. 2 above, restricted ourselves to spherical symmetry, degeneracies would occur, which the JT distortions recorded in the Tables remove.

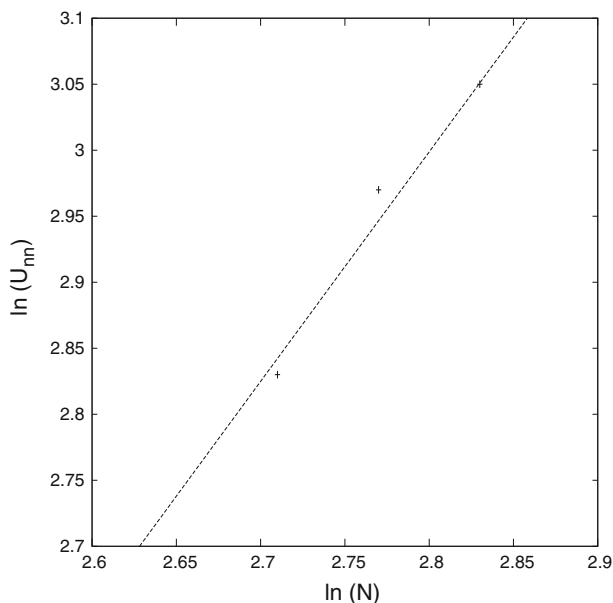


Fig. 1 Logarithmic plot of the nuclear–nuclear repulsion energy U_{nn} versus the total number N of electrons in three positive ions of SiH_4 calculated at the HF level of theory. The equation of the trend line is: 1.739×-1.870 . It is tempting to compare the value of the a -coefficient with the scaling index (but for Z now) of $7/3$ in semiclassical Eq. (4) which, however, neglects JT distortions (compare Table 1)

We shall refer again especially to the nuclear repulsion energy U_{nn} in the Tables. But before doing so, we thought it of interest in the following section to report similar theoretical studies we have carried out on the tabulated changes resulting from further ionization, as in doubly and triply charged positive ions of silane.

4 Results of further ionization for both SiH_4^{2+} and SiH_4^{3+} .

As indicated already, we have used the same quantum-mechanical approach to study the change induced by further ionization, our results being recorded in Tables 1 and 2.

What is surprising from the bond lengths $R(1,2)$ to $R(1,5)$ is the pronounced increase in the JT distortion as a second electron is removed from the originally neutral silane molecule.

As a result, the nuclear repulsion energy is reduced somewhat from that for SiH_4^+ : a matter to which we return in Sect. 5 below. As seen from the one-electron eigenvalues, we have eight non-degenerate electron eigenvalues for this spin-compensated molecular ion SiH_4^{2+} .

For the triply charged positive ion there is a dramatic increase in the equal bond lengths $R(1,2)$ and $R(1,3)$, resulting in a return to somewhere near spherical geometry. Because of these large bond lengths, the nuclear energy U_{nn} at equilibrium for SiH_4^{3+}

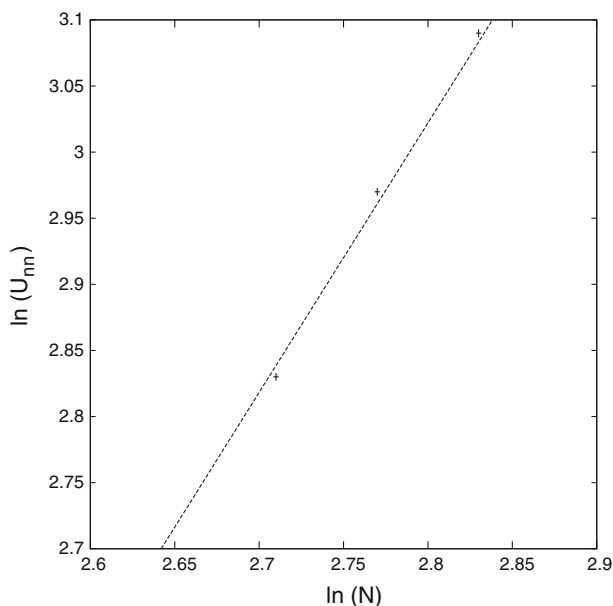


Fig. 2 Logarithmic plot of the nuclear–nuclear repulsion energy U_{nn} versus the total number N of electrons in three positive ions of SiH_4 calculated at the MP2 level of theory. The equation of the trend line is: 2.039×-2.687 . It is tempting to compare the value of the a -coefficient with the scaling index (but for Z now) of $7/3$ in semiclassical Eq. (4) which, however, neglects JT distortions (compare Table 1)

is markedly reduced from the values given in Tables 1 and 2. We shall return to this prediction of the HF plus MP2 studies in Sect. 5 immediately below.

4.1 Energy components and dependence on the number of electrons N .

To compare and contrast with the Lawes-March semiclassical Thomas-Fermi model for the positively charged molecular ions, we have first plotted in Figs. 1 and 2 the nuclear repulsion energy U_{nn} versus the total number of electrons N , in the three stable positive ions of silane predicted above (see Tables 1, 2). The possible relevance of the scaling exponent $7/3$ in Eq. (4) warrants more attention in subsequent studies.

5 Summary and further directions

The main numerical results of the present theoretical study are reported in Tables 1 and 2 plus Fig. 1. We believe, in the future, as has already been done for the singly charged positive ion of methane, that it should be possible to test the theoretical predictions in Tables 1 and 2. Coulomb explosion experiments plus ESR measurements, we believe, may well be motivated as a result of the predictions made in the present article.

As to further ionization, we have, as theorists, little insight into whether any related experiments on SiH_4^{2+} say, might be possible in the foreseeable future. Though we

have not reported results in the above text, we also ran CH_4^{3+} by H-Fock and MP2 studies and found no convergence, though CH_4^{2+} did exist in the present framework. Returning to the SiH_4 positive ions, we briefly studied also SiH_4^{4+} but starting from a geometry with the H atoms in the 'bonding' region it was found that the H atoms drifted away from the Si nucleus.

Finally, other molecular ions with different Z and n would, we believe, be worthy of study in the future by quantum-chemical procedures, in relation to the semiclassical scaling in Eqn. (4). We expect from our study of T and O neutral molecules in [5] that the $Z^{7/3}$ dependence will prove somewhat to strong.

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