Accurate Multireference Electronic Structure Calculations on the Si_3 Molecule

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Introduction

The properties of small silicon clusters have been discussed since the last century. The interest started from astrophysics research concerning the spectra of carbon-rich stars[1] and chemical vapor decomposition processes[2,3]. Nowadays they are important for semiconductor devices and optoelectronic nanomaterials[4-6].

The Si_3 system, in particular, has shown quite a challenge since even its ground state is difficult to determine, and the literature is not yet in consent[7-13]. Although many theoretical works agree with experimental results, the symmetry of the ground state is still in discussion, balancing between the singlet C_{2v} group and the triplet D_{3h} one. Oyedepo et al.[13] recently performed multireference correlation consistent composite approach (MR-ccCA) calculations of Si_3, predicting geometries, total atomization energy (TAE) and the singlet-triplet gap (S-T Gap). They showed that this system have a strong multireference (MR) character.

Even the Si_2 potential energy surface (PES) has many low lying electronic states, with several crossings between them. Therefore, molecular dynamics simulations of the $Si(^3P)+Si_2$ collision will have a myriad of states interfering in the reaction process. The electronic profile of Si_3, including its excited states and geometries, using high accurate MR methods is the main subject of this work.

Methods

All calculations were carried out with the MOLPRO 2012 package[14], using the Multireference Configuration Interaction, MRCI(Q), with the Davidson correction[15,16]. We use the correlation-consistent basis, aug-cc-pVQZ[17,18]. All geometry optimization were carried out under the complete active space self-consistent field (CASSCF) with the same basis, using the quadratic steepest descent method.

The frequencies were obtained using CASSCF level of theory, with the aug-cc-pVQZ basis due to the high computational cost.

Results and Discussion

To test the accuracy of our calculations, we compare our results with the most recent theoretical results of the literature, using single or multireference methods, and the available experimental data. Table 1 shows the comparison of the geometries and frequencies, total atomization energy (TAE) and the S-T Gap.

Oyedepo *et al.*[13] exposed that both singlet and triplet forms have a strong multirefrence (MR) character. A system with strong MR effects shows a C_0^2 (the magnitude of the SCF configurations to the CASSCF wave functions) value less than 0.90 while the T_1 and D1

Table 1. Comparison of the present methodology with experimental results and most recent theoretical values for the Si3 two lowest states. Energies are given in kJ/mol, frequencies (ω) in cm−1, bond lengths in Å, and bond angles (θ) in degrees.

		Ref. 12	**Ref. 13**	**Experimental Ref. 7,10,19**	**This work**
	TAE	719	710	705±16	700.863
	S-T gap	0.8	0.8	4.19?	3.675
Singlet	RS_i-S_i		2.21	2.177	2.207
	θ		79.7	78.10	79.71
	ω_{sy}	549		550.6	528.9
	ω_{as}	524		525.1	518.4
	ω_b	180		*	175.8
Triplet	RS_iS_i		2.31		2.322
	θ		60.0		60.00
	ω_{sy}	502		501±10	482.6
	ω_{def}	324		337±10	302.4
	ω_{def}	325		337±10	302.4

Only the most accurate coupled cluster result from Tam et al12 is given. * Ref. 19 gives two possible values, 146.2 and 153.2 cm^{-1}.

diagnostics20-22 are larger than the generally accepted cutoff of 0.02 and 0.05. The Si_3 singlet state parameters are C_0^2=0.822, T1 = 0.032 and D1 = 0.082, therefore not properly described by a single-reference method by any of those criterion. The triplet state with C_0^2=0.843, T1 = 0.031 and D1 = 0.082 also fails the tests.

Tam *et al.*12 most accurate calculations used single reference coupled cluster with the large aug-cc-pVXZ basis expanded with tight d-functions, extrapolated to the complete basis set limit (CBS), including scalar relativistic, core-valence and spin-orbit corrections. Their best result for TAE (719 kJ/mol) deviates from the experimental value more than Oyedepo et al.13 (710 kJ/mol), probably because of the strong MR character of this molecule.

We made, instead of MR composite approach of Oyedepo *et al.*[13], full MRCI(Q) calculations, with the large aug-cc-pVQZ basis. Our result, 700.863 kJ/mol, considering the zero point energy (ZPE), is closer to the experiment than Oyedepo's. All our geometries are in excellent agreement with experiments, but our frequencies were systematically below experimental values, probably due to the lower level of theory in the calculations.

If the interest is to study the collisions that lead to Si_3, there will be a myriad of electronic states involved. The Si_2 molecule has two nearly degenerate states, $^3\Pi u$ and $^3\Sigma_g^-$, and they alternate for the ground state with the distance. Figure 1 shows the PES of the Si_2 molecule, including some low-lying excited states that may not be accessible under normal circumstances, but are still below the dissociation limit.

Exploring a "T shaped" profile of the system, in which a silicon atom approaches the Si_2 molecule perpendicular to the bond axis and in its center-of-mass, one can have a preliminary insight of the collision reaction. Figure 2 shows the PES for singlet and triplet two-state calculations in C_{2v} symmetry for each wave function A_1, B_1, B_2 and A2. The Si_2 bond distance is fixed at its equilibrium value of 2.17 Å. It can be seen several attractive states that will lead to a barrierless collision, and all of them are important to the cross sections and rate constants of reactive events23-25. In the dissociation limit the surfaces merge to two separated energies, and this separation gap, 4.5 kJ/mol, is very close to the one observed between the two lowest states of Si_2 molecule, 4.9 kJ/mol.

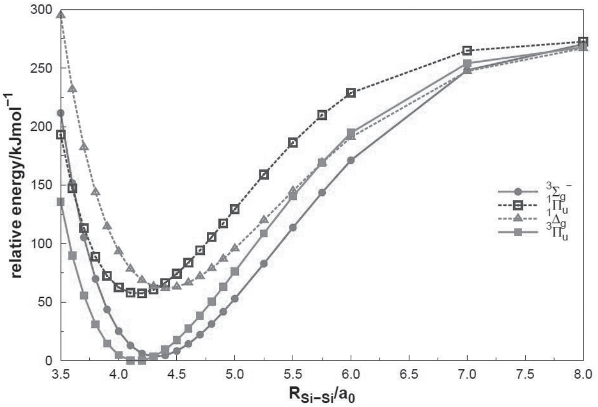

Figure 1. T-shaped atom-diatom interaction profile. Dashed lines represent the respective excited states; The Si2 separation is fixed at 2.17 Å.

Conclusions

We report new values for geometry, TAE, frequencies and S-T Gap for the singlet and triplet states of Si3 molecule, using a high accuracy MRCI(Q) with a large basis, since it is known that this system has a strong MR character. The first 16 lowest PES are also calculated showing several attractive states that lead to a barrierless collision, which means that they all contribute to cross sections and rate constants of reactive events. If one is aiming to study the dynamics of Si_3 molecule, all these non-barrier channels should be considered.

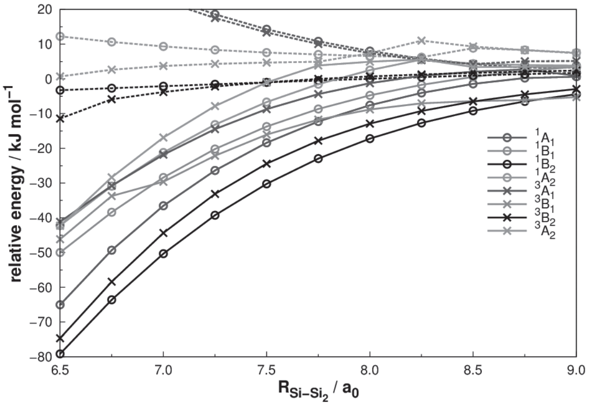

Figure 2. T-shaped atom-diatom interaction profile. Dashed lines represent the respective excited states; The Si_2 separation is fixed at 2.17 Å.

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