International Conference on Industrial Technology and Management Science (ITMS 2015)

Potential Energy Surface for Si -H2 System

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ABSTRACT: The first three-dimensional potential energy surface (PES) of Si-H_2 system is calculated by the coupled cluster singles-and-doubles with noniterative inclusion of connected triple [CCSD (T)] level of theory. The computations involve full counterpoise corrections and large basis sets including midbond functions. The 198 *ab initio* points on the PES are fitted to a 96-parameter algebraic form with an average absolute error of 0.3425% and amaximum error less than 4.0072%. The characteristics of the fitted PES are compared with those of previous surfaces. Unlike the older surfaces, our PES has the anisotropy thought to be required for a proper description of experimental data.

KEYWORD: potential energy surface; Si-H_2 system; CCSD (T)

1 INTRODUCTION

Hydrides of Group IV elements are a major subject of concern and have been investigated extensively from the theoretical as well as from the experimental point of view. Silicon dihydride SiH_2 is one of the simplest Si-containing compounds and is known to be a reactive intermediate species in chemical-vapor deposition process in the silicon semiconductor manufacturing process. SiH_2 appears as an important intermediate during decomposition reactions of silane, which have attracted much attention because of their importance in manufacturing amorphous silicon. SiH_2 can undergo further dissociation SiH +H or Si+H_2.The dissociation processes of the low-lying electronic states of SiH_2 have been studied experimentally and theoretically. [1-7]

The spectra in the SiH_2 stretching region have already been reported [8-9] In this work, Considered the electron correlation which requires basis sets of much larger size than necessary for Hartree-Fock calculations and is rather expensive when a large number of geometries have to be, We calculated the interaction potential covering a large range in the distance *R* between the two subsystems. As far as we know, all the PESs calculated before for this title system are either semiempirical or obtained by fitting preexisting but old *ab initio* calculations. In the present work we decide to improve previous theoretical results using more accurate basis sets to gain an accurate *ab initio* PES for the SiH_2 complex. In the following section, we present the results of the CCSD (T) interaction energy calculations and the corresponding fits to analytical functions. Section III deals with the evaluation, results, and 3D view of the interaction potential for Si-H_2 complex at $r = r_e$

2 BASIS SETS AND THE PES FIT

We use aug-cc-pCVTZ basis sets on Si and aug-cc-pVTZ basis sets on H. We treated electron correlation by using the CCSD (T) method as implemented in G09 for our basis set test calculations. We calculated 198 *ab initio* points on the PES and fitted the points to a 96-parameter algebraic form with an average absolute error of 0.3425% and amaximum error less than 4.0072%.

3 COMPUTATIONAL METHOD AND PES CHARACTER

In Figure 1.From ten different anglers we show the behavior of the potential as a function of the Si-H_2 separation for a number of relative orientations for H_2 fixed at equilibrium distance. We can see that in the long range for all angles the interaction energy almost converges to the same asymptotic value.

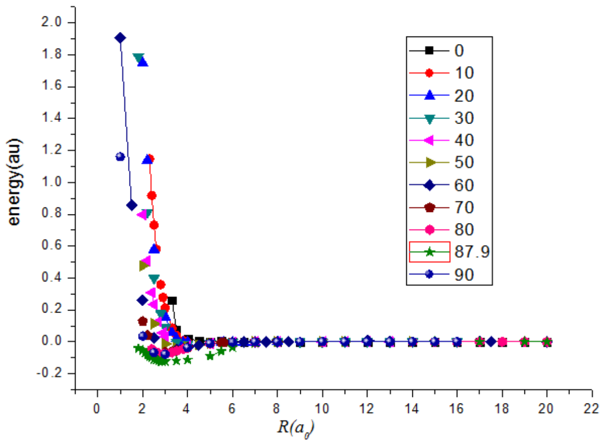

Figure 1. Orientation features of the PES of Si-H_2

When **$R<4a_0$** , as the R increasing induces the potential energy reducing, the potential is mainly of repulsion, while for the **$R>4a_0$** potential energy surface change leveled off. We can clearly see that the well is at θ=87.9° which is the same as the experimental data θ =92.1°, at R=2.86a_0 .The depth is 0.12339 cm^{-1}. The results fit well with the experiment results; we put the results listed in the table 1.

Table 1. The comparison of the experimental data

Parameters	Experimental data	Our results
$R_{Si\text{-}H}(a_0)$	2.8654[10]	$R_{Si\text{-}H} = 2.86$
θ(deg)	92.1[10]	92.1
D_e （cm^{-1}）	0.12035[11]	0.12339

In Figure.2 we show the contour plots of the new PES for the Si-H_2 complex. The figure shows that the PES presents mainly isotropic interactions and weak anisotropy. The depth is shallower than the others; the reason may be the lack of a proper correction for BSSE and the smaller basis sets used in their calculations.

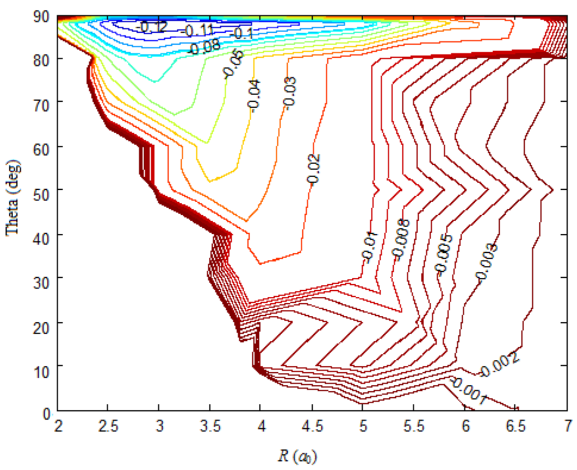

Figure 2.Contour plots of the potential for Si-H_2 complex at $r = r_e$ .Contours are labeled in cm^{-1}

In Figure.3 the potential energy surface shows a mostly shallow attractive van der Waals minimum, which is due to electron correlation effects resulting in dispersion forces that cannot be examined at the Hartree-Fock level. In the intermediate region, Hartree-Fock repulsion and dispersion attraction are of about the same magnitude but opposite in sign.

In order to more detailed study of the potential energy surface details we draw the close shot in Figure 4.One can easily see the mainly isotropic interaction and the well-defined molecular core identified by the repulsive regions which show vanishing angular dependence for this very weakly bound Van der Waals complex. The interaction energy potential well position clearly displayed.

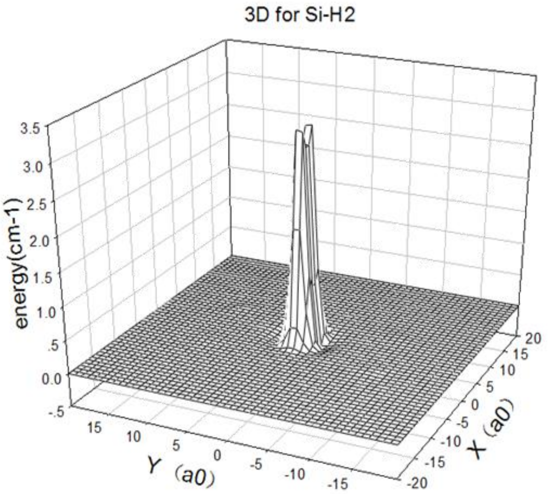

Figure 3.3D view of the interaction potential for Si-H_2 complex at $r = r_e$

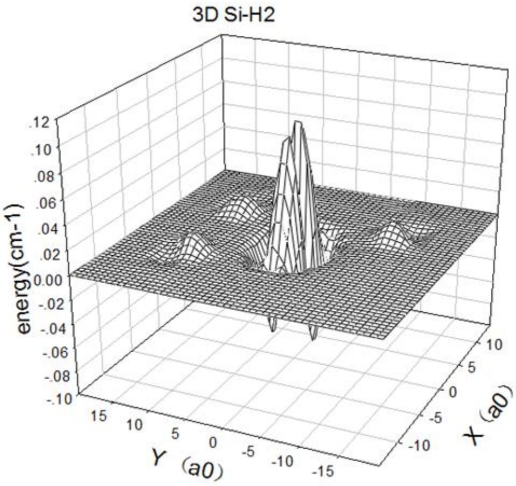

Figure 4.The close shot for the three-dimensional potential energy surface

4 CONCLUDING REMARKS

An ab initio potential energy surface for the interaction of rigid H_2 with Si has been calculated using CCSD (T) theory, with full counterpoise corrections and a large basis set including bond functions. The 198 *ab initio* points on the PES are fitted to a 96-parameter algebraic form with an average absolute error of 0.3425% and a maximum error less than 4.0072%.

A comparison of the characteristics of our fitted CCSD (T) surface with previous ones indicates that it seems to satisfy the criteria believed [12] necessary to obtain agreement with a wide variety of experimental data pertaining to beam scattering, transport phenomena, and relaxation phenomena. Extensive tests will be required to determine whether this is so. We think that our CCSD (T) surface is unlikely to differ from the true PES by more than 10% over the range of intermolecular distances ($2a_0$–$6a_0$) sampled in this work. We invite further work to test this assertion; therefore this work should provide useful information for further experimental and theoretical studies.

5 ACKNOWLEDGMENTS

This work is supported by the Natural Science Foundation of Anhui educational committee (Grant KJ2013B303).

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