Weak Interactions:

Hydrogen Bonds and

van der Waals Forces

Applications on the Fringe

by

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I. Introduction

In the realm of moderate strength chemical bonds and solid structures, where the electron density has an appreciable value, enhanced Hartree-Fock and density functional theory procedures now exist to successfully predict general system properties on the quantum level. However, for low electron density regimes containing van der Waals forces or hydrogen bonding, the traditional ab initio strategies encounter some unpredictable aberrations. Regions of low electron density for quantum chemistry purposes include: gas phase clusters, physisorption, solute-solvent interactions, protein-DNA coupling, and a wide range of intermolecular forces. During the course of this paper, the bonding nature will be explored in more detail, some advances on the theoretical front will be summarized, and a structure calculation involving physisorption will be presented.

II. Bonding Characteristics

Depending on the molecules involved, van der Waals forces can manifest themselves in three ways[1] as seen in figure 1. If both molecules have dipoles, opposing dipole orientations as in figure 1a would create a repulsive force ; while dipoles matching head to tail as in figure 1b would generate an attractive potential. In the case where one

molecule contains a dipole, the electric field created by the dipole will cause the electrons and nuclei of the other molecule to move in opposite directions, inducing an instantaneous dipole as in figure 1c. Even if neither molecule contains a dipole, the screening of the nuclei by the electron clouds is incomplete, so electric fields pass between molecules which induce instantaneous dipoles in both species, illustrated in figure 1d.

The last scenario where both molecules induce dipoles in the other was proposed by Fritz London and has become known as the London dispersion forces. As the molecules get heavier, the nuclei wield more charge for use in electric field exchange, amplifying van der Waals forces. Therefore, boiling points in liquids generally increase with molecular weight and/or dipole strength in accordance with van der Waals interactions. Among the three possible situations, the London dispersion forces tend to dominate, although strong permanent dipole interactions can upstage this natural order[2].

Van der Waals forces give physical significance to the $1/r^6$ term in the Lennard-Jones pair potential equation[1]:

$$u(r) = c_{12}/r^{12} - c_6/r^6$$

since all three of the van der Waals interactions are proportional to the distance, $r,$ to the

minus sixth power. Figure 2 illustrates a typical Lennard-Jones energy curve with the $1/r^{12}$ term representing repulsive forces and the $1/r^6$ term taking into account the van der Waals attractive forces.

Hydrogen bonding was discovered when looking at anomalies in boiling points of hydrides[3] as represented in figure 3. Because H_2O, HF, and NH_3 all have higher boiling points than other hydrides within the same group, progressing down the period, clearly some other phenomenon is influencing these compounds, beyond van der Waals type interactions. The strength and existence of the hydrogen bond tends to depend on the electronegativity difference between the H atom and the affiliated atom it bonds to. As such, $HF > H_2O > NH_3$ for a single hydrogen bond between each compound. Hydrogen favors coordination to the lone pairs of the recipient atom as depicted in figure 4.

Physisorption is a van der Waals type interaction involving a gas molecule's attraction to a surface, where no chemical reaction takes place between the two substituents. In contrast, chemisorption represents a chemical reaction between the incoming molecule and the surface, which is typically 10 to 20 times stronger than comparable physisorption bonds[1]. Figure 5 pictorially shows the difference between the two processes energetically as a function of distance between the surface and the molecule. In physisorption, the energy diminishes to zero at infinite distances, since the

molecule stays intact. For a singly bonded diatomic, it must sacrifice its molecular bond in order chemisorb on the surface as atoms. Upon desorption, the atoms may not reunite as a compound, so their combined energy is greater than the reference molecule level. In terms of distance, the chemisorbed state is dramatically shorter relative to the physisorbed state consistent with the energy difference. Once all the surface sites are saturated with adsorbate in a chemisorption situation, subsequent layers physisorb in a homogeneous fashion. If there is a large activation energy between physisorption and chemisorption, some molecules undergo a physisorption precursor, which may or may not overcome its ultimate barrier.

III. Numerical Considerations

There are various strategies in handling van der Waals forces in ab initio calculations. One of the most common pitfalls surrounds basis sets when using the supermolecular approach[4]:

$$\Delta E(r) = E^{AB}(r) - E^{A} - E^{B}$$

The interaction energy, $\Delta E(r)$, is comprised of the dimer energy at a distance, r, less the two monomer molecule potentials in their equilibrium geometry. Within the region of finite monomer separation, monomers have access to dimer molecular orbitals, which invokes a basis set superposition error, resulting in overbinding. To correct for the

monomer equilibrium geometry, the counterpoise technique uses dimer basis sets at the characteristic separation, r, to calculate monomer potentials[4]:

$$\Delta E^{CP}(r) = E^{AB}(r) - E^{A\{AB\}}(r) - E^{B\{AB\}}(r)$$

Alternatives to the counterpoise technique include using mammoth basis sets, to minimize basis set error within the supermolecular approach, or symmetry adapted perturbation theory, which can directly calculate the interaction energy without monomer potentials[4].

Even after counterpoise correction, some less systematic errors can arise due to the fact that there is no wavefunction overlap between the molecules in a dimer or the dispersion forces are not properly represented in the quantum chemical approach. To address the latter effect, theorists have tried different methods to handle London dispersion forces at different stages of the quantum hierarchy. One group does all the quantum chemical calculations first, then finds a macroscopic van der Waals force based on experimental data[5]. Another favors Hartree-Fock plus dispersion or density functional plus damped dispersion, where van der Waals forces are estimated on a microscopic scale in parallel with the ab initio scheme[6]. Perhaps the most ambitious strategy is to use time dependent density functional theory to model the instantaneous dipoles in real time[7]. All the techniques referenced above address the nonoverlapping wavefunction issue by introducing a damping function to cutoff the van der Waals forces

at close range, below the van der Waals radius.

IV. Structure Calculation

In the process of thin film deposition, many gas phase reactants are used to control the solidification process and improve film purity relative to more conventional physical vaporization approaches. In a paper by Gupta and coworkers, at North Carolina State University, the researchers focus their attention on the low temperature growth of amorphous silicon from silane and hydrogen reactant streams[8]. They want to calculate activation energies for two competing surface reactions:

monohydride abstraction by H

$$Si_4H_{10} + H \rightarrow Si_4H_9 + H_2$$

monohydride abstraction by SiH_3

$$Si_4H_{10} + SiH_3 \rightarrow Si_4H_9 + SiH_4$$
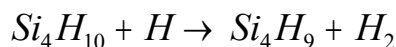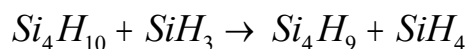
to compare reaction rates and look at potential energy surfaces to explore the possibility of a three body silyl physisorption precursor on a H-terminated silicon surface. Figure 5 illustrates the two abstraction reactions in more detail while figure 6 shows an example of a three body silyl physisorption precursor complex.

Interestingly enough, the Si_4H_{10} cluster is sufficient to model the H-terminated

silicon surface using *Gaussian98* to achieve the necessary chemical information without introducing plane waves. If you compare figure 5 to figure 6, the three body silyl precursor complex is an extension of a SiH_3 collision on the surface. In terms of methods, the authors look at Hartree-Fock self consistent field (HF-SCF), single parent configuration interaction (SP-CI), multi parent configuration interaction (MP-CI), density functional theory under the generalized gradient approximation (DFT-GGA: BLYP), and hybrid Hartree-Fock/ density functional approach (HF-DFT: B3LYP).

For monohydride abstraction by SiH_3, the activation energy barrier height ranges from 4.1 kcal/mol to 14.2 kcal/mol, for B3LYP and MP-CI, respectively. Because tunneling is more prevalent for monohydride abstraction by *H*, the effective activation energy falls between 0 kcal/mol to 7.2 kcal/mol, for B3LYP and MP-CI, respectively, which compares favorably with an experimental measurement of about 2 kcal/mol. Tables 1 and 2 summarize all the thermodynamic quantities achieved in the study for the two abstraction reactions. On the basis of activation energy barriers, it would appear that the *H* atom dominates the surface reaction environment compared to a silyl radical in the low temperature growth regime, 150 to 350 C. Figures 7 and 8 profile the potential energy surfaces for monohydride abstraction by SiH_3, for MP-CI and BLYP respectively. If a three body physisorption silyl precursor existed, a depression in the minimum energy path should occur somewhere near the saddle point. Within the

geometric limits imposed by this study, no such indentation could be found, bringing into question the three body reaction mechanism for amorphous silicon film growth[8].

V. Conclusion

Until van der Waals forces and hydrogen bonding can be better understood, the models used may have limited value. Clearly, weak interactions play important roles in many different systems of scientific interest from protein-DNA coupling to chemical vapor deposition. Now that the counterpoise method has become widely accepted to correct basis set errors, perhaps the next stage is to refine dispersion forces or look at systems where dipole interactions become significant.
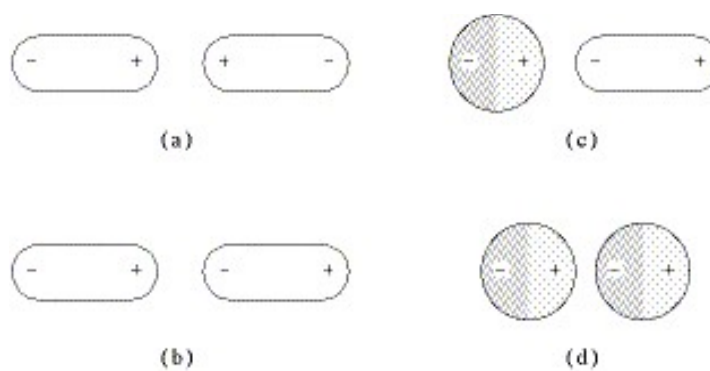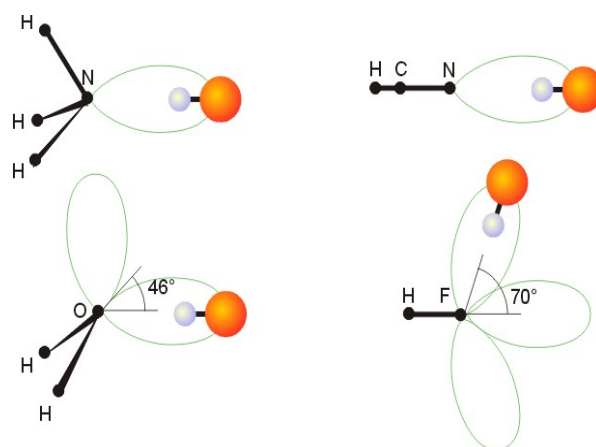
Figure 1: Van der Waals interactions for (a) opposing dipoles, (b) attracting dipoles (c) dipole-induced dipole, and (d) London dispersion.
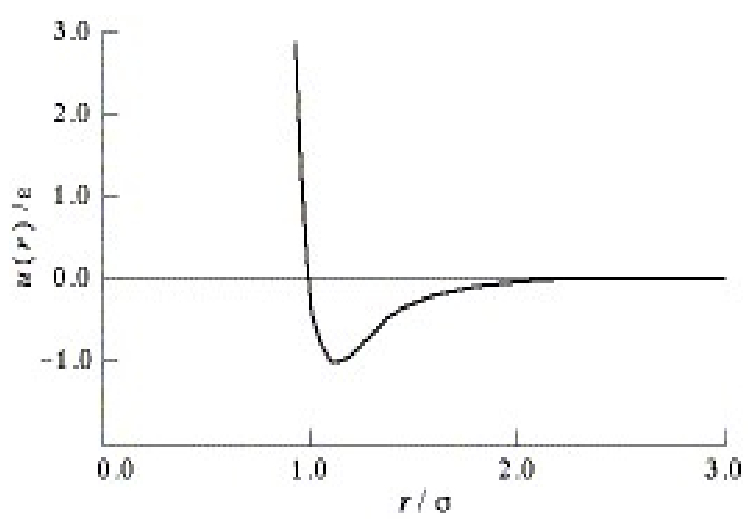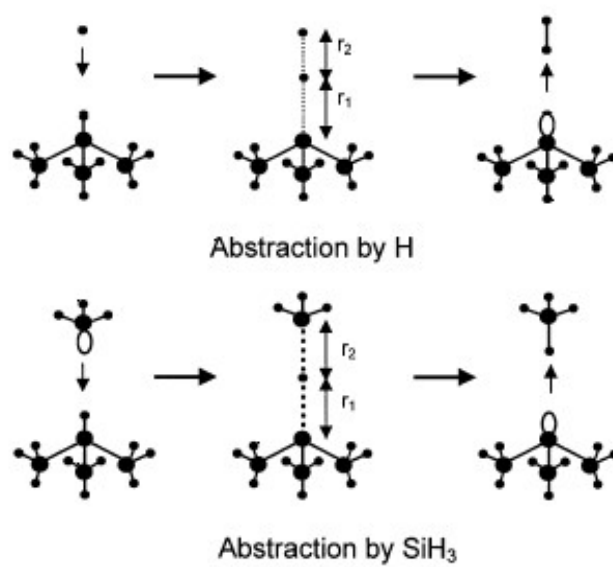
Figure 2: Lennard-Jones potential energy curve as a function of separation distance.
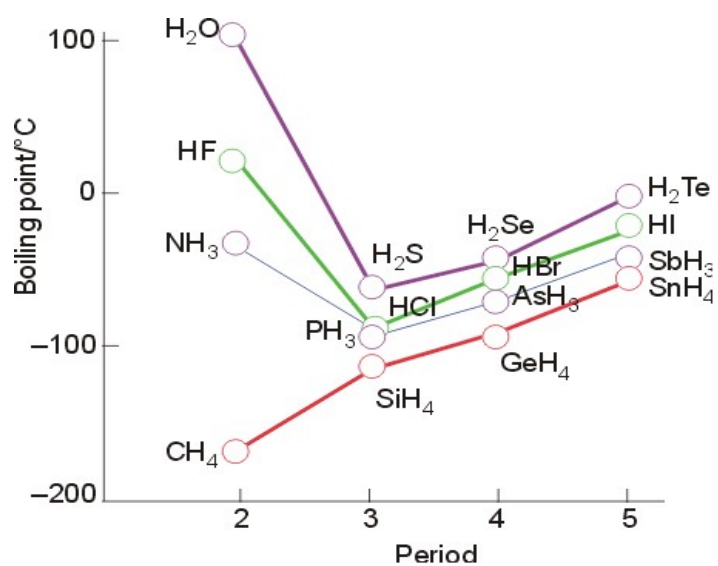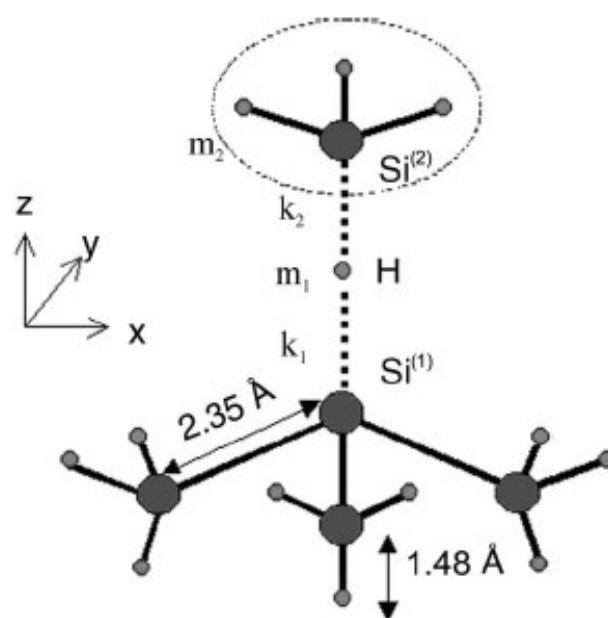
Figure 3: Boiling points of various hydrides.

Figure 4: HF coordination to other hydrogen bonding species.

Figure 5: Abstraction steps considered in structure calculation.

Figure 6: Model 3 body silyl physisorption precursor complex.

Table 1

Reaction: $SiH_{3(g)} + H-Si\equiv \rightarrow -Si\equiv_{(d.b.)} + SiH_{4(g)}$ H abstraction by SiH_3 radical

Calculation method	Basis set/functionals	Saddle point		ΔH_r (kcal/mol)	E_a (kcal/mol)	ω ($\times 10^{13}$ rad/s)	$P(E)$ (@ 250 °C)
		$Si^{(1)}-H$ (Å)	$H-Si^{(2)}$ (Å)				
HF-SCF	Dunning–Huzinaga	1.69	1.85	−5.33	18.62	1.35	1.49×10^{-8}
SP-CI	Dunning–Huzinaga	1.72	1.83	−4.42	15.08	1.19	5.16×10^{-7}
MP-CI	Dunning–Huzinaga	1.69	1.80	−4.69	14.16	1.13	1.29×10^{-6}
DFT-GGA	TZV/BLYP	1.65	1.95	−8.18	4.93	1.04	0.017
HF-DFT	6-311G/B3LYP	1.65	1.97	−6.26	2.82	0.73	0.1
HF-DFT	6-31G++(3d,2p)/B3LYP	1.65	1.99	−7.22	4.09	0.58	0.029

HF-SCF: Hartree–Fock self-consistent field.

SP-CI: single parent configuration interaction.

MP-CI: multi-parent configuration interaction.

DFT-GGA: Density functional theory under the generalized gradient approximation (BLYP functionals).

HF-DFT: Hybrid Hartree–Fock and density functional approach (B3LYP method).

$P(E)$: Wigner tunneling probability for surface H atom energy corresponding to a surface temperature of 250 °C ($kT = 0.6$ kcal/mol).

Table 2

Reaction: $H_{(g)} + H-Si\equiv \rightarrow -Si\equiv_{(d.b.)} + H_{2(g)}$ H abstraction by H radical

Calculation method	Basis set/functionals	Saddle point		ΔH_r (kcal/mol)	E_a (kcal/mol)	ω ($\times 10^{13}$ rad/s)	$P(E)$ (@250 °C)
		$Si^{(1)}-H$ (Å)	$H-Si^{(2)}$ (Å)				
MP-CI [9]	Dunning–Huzinaga	1.69	1.06	−12.7	7.2	1.07	0.0014
UHF-SCF [10]	6-31G*	1.7	1.1	−13.6	13	–	–
DFT-GGA [10]	6-31G*/BLYP	–	–	−26.3	0	–	–
HF-DFT	6-311G/B3LYP	–	–	−24.4	0	–	–
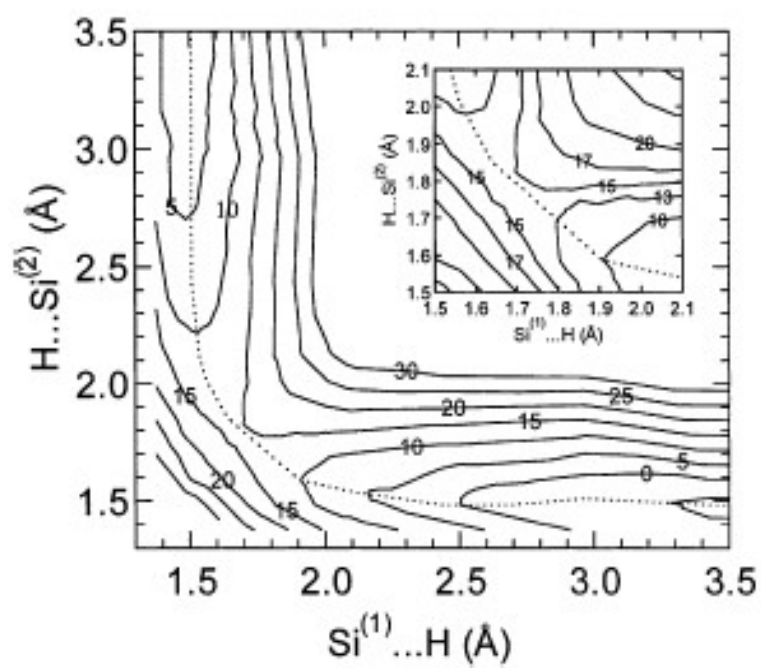
Figure 7: Potential energy surface for hydride abstraction by SiH_3 using MP-CI.
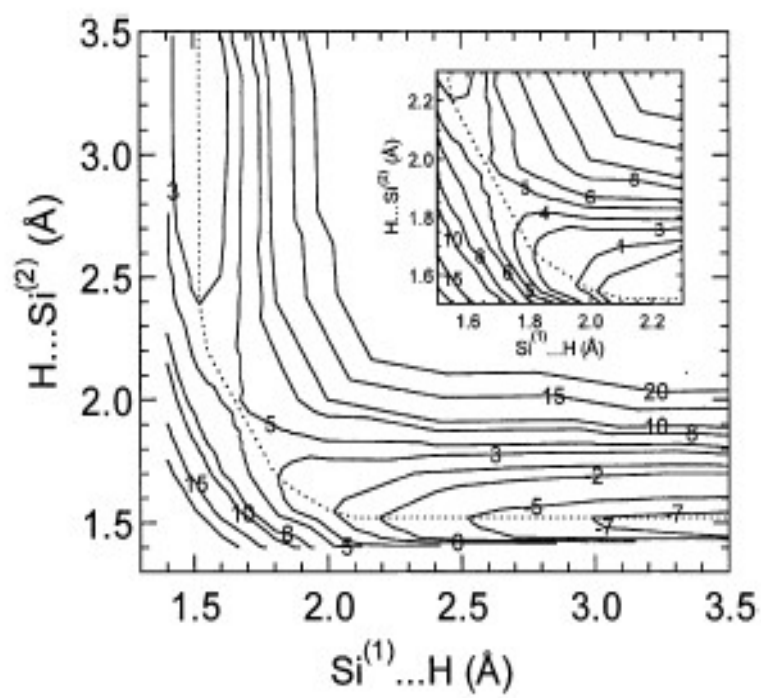
Figure 8: Potential energy surface for hydride abstraction by SiH_3 using BLYP.

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