

Geometry, Chemical Bonding, and Electronic Spectra of Si_n and Si_n -Glycine ($n = 3-5$) Complexes

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Structures and spectra are calculated for Si_n and Si_n -Gly ($n = 3-5$) complexes. Relative stability differences of Gly conformers are magnified by interactions with the Si_n cluster, so that one conformer of Si_n -Gly is stabilized. Significant charge transfer occurs from the amino group in Gly to a Si atom in the cluster. Interactions with Gly are predicted to shift the excitation energies of Si_n significantly to the blue to 2.1–2.7 eV, although they are still lower than in a Si cluster passivated by hydrogen.

I. Introduction

Much attention has been given to the structures and the electronic (absorption and emission) spectra of silicon clusters.^{1–13} Recently it was observed that porous silicon may emit strong photoluminescence in the visible (blue to orange-red, depending on the size and the porosity). Although porous silicon is usually presumed to be passivated by hydrogen atoms, the detailed structure is not unambiguously known. For example, there may exist dangling bonds on some Si atoms, depending on the experimental conditions. The luminescence is known to depend quite sensitively on the surface conditions. Exposing the porous silicon to air leads to a redshift of the photoluminescence by as much as 1 eV, and this was attributed to the trapping of an electron by Si–O bonds on the surface. The nature of the Si–O bonds giving rise to the redshift is, however, somewhat speculative, being described as Si=O or Si–O–Si bonds, or both.^{14–19} Interactions with heteroatoms such as oxygen and/or functional groups may change the properties of the silicon nanoclusters. Besides providing useful insights into the nature of electronic processes, studying the effects of “doping” with various chemical agents may help in designing clusters with specific electrical and the optical properties.

In this work, we study the functionalization of clusters with a biomolecule. Much effort has been directed at taking advantage of the high flexibility of biomolecules, for example, by functionalizing carbon nanotubes (CNT)^{20,21} or inorganic surfaces^{22–24} to change the physicochemical properties of nanomaterials. Glycine (Gly) is one of the simplest biomolecules, and several studies have focused on the Gly–Si surface. Shemesh et al.²⁵ studied the dynamics of photoionization of Gly on a Si surface, employing the semiempirical PM3 method in an on-the-fly molecular dynamics simulations. The structures of Gly on Si have been modeled as a passivated Si cluster–Gly system by Lopez et al.²⁶ and Qu et al.²⁷

Here, we present calculations for the geometry, chemical bonding and the electronic excitations of Si_n and Si_n -Gly ($n = 3-5$) complexes as a prototypical model of an inorganic

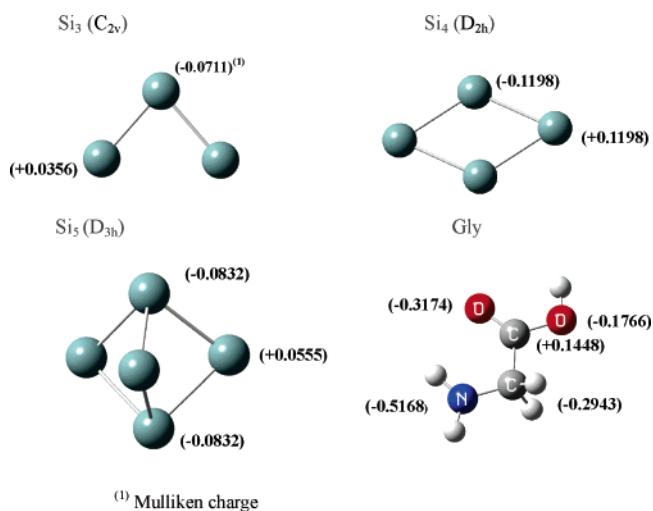


Figure 1. Geometry of Si_n ($n = 3-5$) and Gly.

cluster–biomolecule system, focusing on the effects of the Si_n -Gly interactions on the structures of Gly and on the electronic transitions of Si_n . We employ density functional theory (DFT) and time dependent density functional theory (TDDFT). We predict a notable splitting in the relative energies of glycine conformers caused by interaction with Si_n . The electronic transitions (1.4–2.7 eV) in Si_n ($n = 3-5$) are calculated to be of much lower energy than in fully hydrogenated silicon clusters as the results of dangling bonds. The interactions with Gly are predicted to shift the electronic excitations of Si_n significantly (by 0.5–0.8 eV) to the blue from to 2.1–2.7 eV.

II. Computational Methods

We employ DFT and TDDFT as implemented in Gaussian03.²⁸ Becke’s three parameter hybrid method²⁹ and the correlation functional by Lee, Yang, and Parr³⁰ are used with the 6-311++G** and the aug-cc-pVTZ basis set. Stationary structures are obtained by verifying that all the harmonic frequencies are real. Default criteria are employed for all optimizations. No symmetry constraints are imposed for optimizing the Si_n -Gly ($n = 3-5$) complexes.

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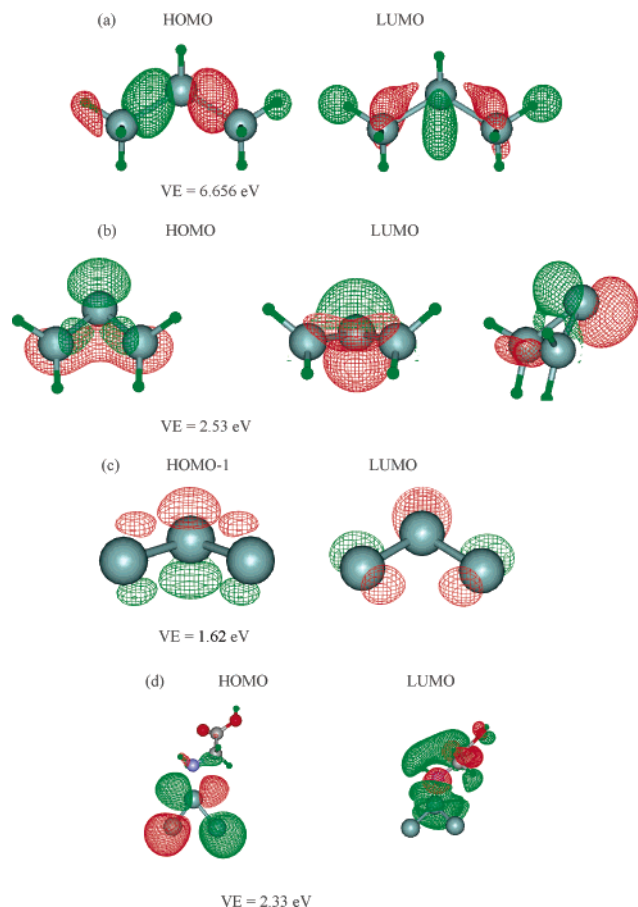


Figure 2. Dominant single-electron Kohn-Sham transitions in (a) Si_3H_8 , (b) Si_3H_4 , (c) Si_3 , and (d) $\text{Si}_3\text{-Gly}$.

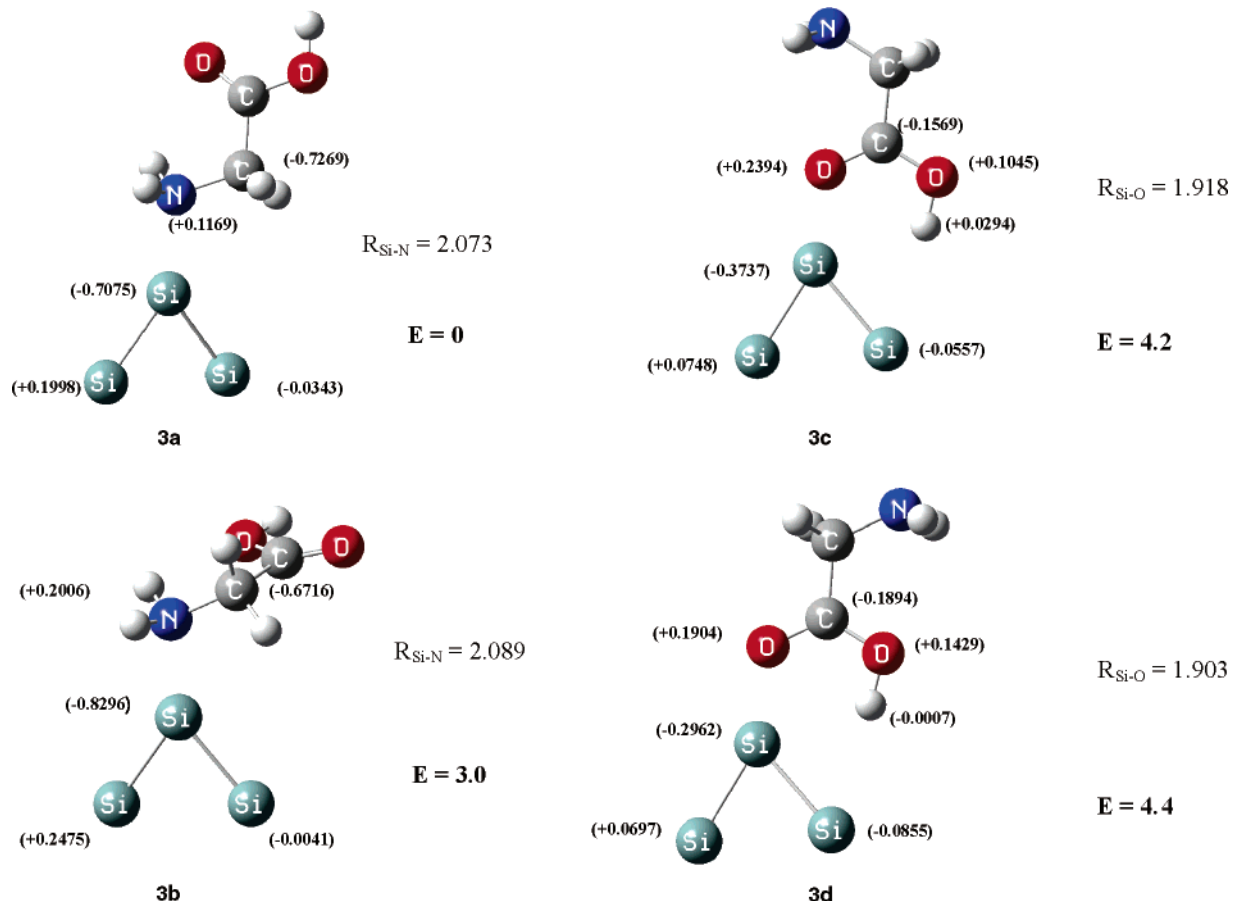


Figure 3. Geometry of $\text{Si}_3\text{-Gly}$ complex (relative energy in kcal/mol, and bond lengths in Å).

TABLE 1: Electronic Excitation Energy (eV) of Si_n ($n = 3-5$)

	exp ^a	exp ^b	this work	
Si_3			1.43 ^c (1.36) ^d	$^1\text{B}_2 \leftarrow \text{X } ^1\text{A}_1$
Si_4	1.59	1.67	1.62 (1.58)	$^1\text{B}_1 \leftarrow \text{X } ^1\text{A}_1$
Si_5	2.14		2.04 (1.99)	$^1\text{A}_1 \leftarrow \text{X } ^1\text{A}_1$
	2.37		2.23 (2.22)	$^1\text{B}_1 \leftarrow \text{X } ^1\text{A}_1$
	1.34	1.37	1.51 (1.44)	$^1\text{B}_{3u} \leftarrow \text{X } ^1\text{A}_g$
			1.63 (1.61)	$^1\text{B}_{2g} \leftarrow \text{X } ^1\text{A}_g$
			2.23 (2.17)	$^1\text{B}_{1g} \leftarrow \text{X } ^1\text{A}_g$
	2.66		2.70 (2.67)	$^1\text{A}_u \leftarrow \text{X } ^1\text{A}_g$
			2.21 (2.20)	$^1\text{E}'' \leftarrow \text{X } ^1\text{A}_1'$
			2.21 (2.20)	$^1\text{E}'' \leftarrow \text{X } ^1\text{A}_1'$
			2.58 (2.60)	$^1\text{E}' \leftarrow \text{X } ^1\text{A}_1'$
			2.71 (2.71)	$^1\text{E}' \leftarrow \text{X } ^1\text{A}_1'$

^a 0-0 transition in neon matrix; ref 9. ^b Photoelectron spectroscopy; ref 10. ^c Vertical transition energy: B3LYP/6-311++G**. ^d Vertical transition energy: B3LYP/aug-cc-pvtz.

III. Results

III.1. Si_n ($n = 3-5$). We first calculate the structures^{31,32} and the excitation energies of Si_n ($n = 3-5$) clusters for comparison to experiment. The lowest energy structures of the Si_n ($n = 3-5$) clusters are calculated to be of C_{2v} , D_{2h} , and D_{3h} symmetry, respectively, in agreement with experimental observations.³² The charge distribution seems to be quite uniform in Si_n as the silicon atoms are more or less neutral. The Mulliken charges in Gly are also presented in Figure 1. Note the significant negative charge on the nitrogen (-0.52). Later we compare these partial charges with those in $\text{Si}_n\text{-Gly}$.

Although the ground states of Si_n clusters have been examined extensively, the properties of the electronically excited states are not well-known. We therefore calculate the vertical electronic excitation energies of Si_n ($n = 3-5$) clusters and compare

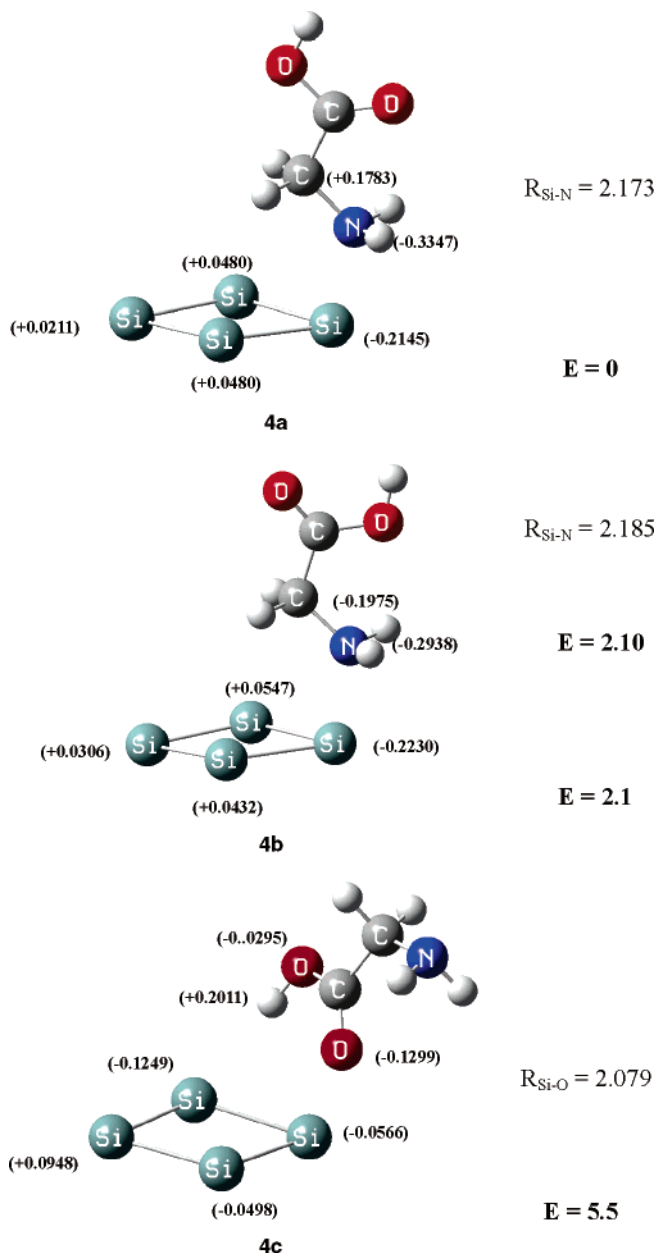


Figure 4. Geometry of Si₄–Gly complex (relative energy in kcal/mol, and bond lengths in Å).

with the experimental observations by Maier and co-workers (Table 1).⁹ The transition energy to the first excited state (¹B₂) of Si₃, which was not observed experimentally due to very small oscillator strength, is calculated to be 1.43 eV. The calculated transition energies (1.62, 2.04, 2.23 eV) to the three higher excited states (¹B₁, ¹A₁, and ¹B₁) compare well with the experimental values (1.59, 2.14, 2.37 eV). For Si₄, the transition to the first excited state is assigned as ¹B_{3u} ← X ¹A_g, both in our calculations and in the experiment by Maier and co-workers.⁹ Transitions to the ¹B_{2g} and ¹B_{1g} states, calculated to be accessible from the ground state by the excitation energy of 1.63 and 2.23 eV, respectively, are not observed experimentally. The calculated vertical excitation energy (2.70 eV) for the ¹A_u ← X ¹A_g transition is in excellent agreement with the experimental measurement (2.66 eV). Calculations with the larger aug-cc-pVTZ basis set give similar but bit better excitation energies.

These excitation energies to the lower excited states of Si_n (*n* = 3–5) in the range of 1.4–2.7 eV (red to green) are much lower than for small silicon clusters that are fully passivated

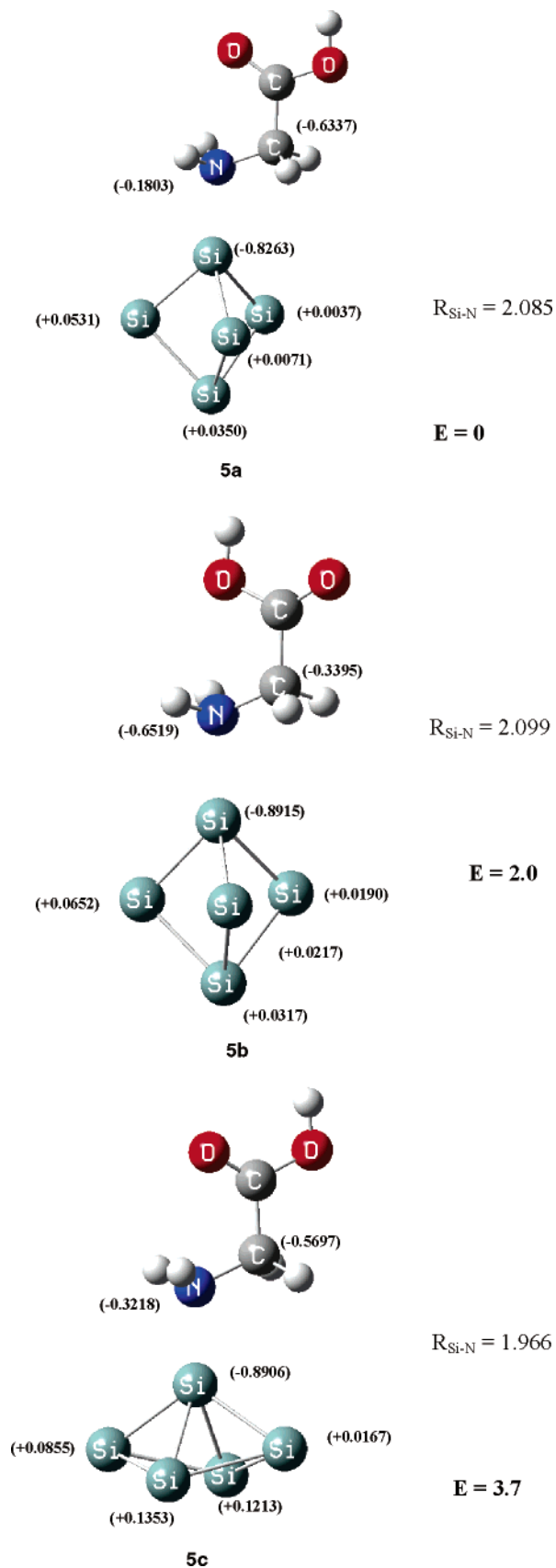


Figure 5. Geometry of Si₅–Gly complex (relative energy in kcal/mol and bond lengths in Å).

with hydrogen atoms (usually larger than 6 eV; for example, the vertical transition energy to the first excited state of Si₃H₈ is calculated to be 6.66 eV; see Figure 2). To understand these differences we depict in Figure 2 the dominant transitions for

TABLE 2: Electronic Energy (E), Zero Point Energy (ZPE), Interaction Energy (IE), Vertical Transition Energy (VE), and Oscillator Strength (f) to the Low Excited States of Si_n and $\text{Si}_n\text{-Gly}$ ($n = 3\text{--}5$)^a

	E (hartree)	ZPE	IE	VE (eV)	f
Si_3	-868.429	1.8		1.43, 1.62, 2.04, 2.23	0.0000, 0.0019, 0.0014, 0.0090
3a	-1152.978	53.5	-15.0 ^b (-13.3) ^c	2.33, 2.46, 2.51, 2.56	0.0006, 0.0063, 0.0017, 0.146
3b	-1152.973	53.4	-12.9 (-10.9)	2.25, 2.45, 2.48	0.0005, 0.0064, 0.0156
3c	-1152.969	52.0	-10.9 (-9.3)	2.15, 2.36, 2.54, 2.58	0.0000, 0.0001, 0.0004, 0.0080
3d	-1152.968	51.9	-10.4 (-8.8)	2.13, 2.35, 2.58	0.0000, 0.0001, 0.0003
Si_4	-1157.976	2.9		1.51, 1.63, 2.23, 2.70	0.00105, 0.0000, 0.0000, 0.0000
4a	-1442.527	54.8	-16.1 (-14.1)	2.36, 2.45, 2.71, 2.77	0.0002, 0.0248, 0.0011, 0.0002
4b	-1442.524	54.8	-14.2 (-12.5)	2.38, 2.44, 2.67	0.0046, 0.0219, 0.0010
4c	-1442.516	53.5	-10.5 (-8.9)	2.42, 2.47, 2.73	0.0085, 0.0120, 0.0004
Si_5	-1447.492	4.2		2.21, 2.21, 2.58, 2.71	0.0001, 0.0000, 0.0000, 0.0000
5a	-1732.039	55.9	-13.8 (-11.5)	2.72, 2.83, 2.83, 2.86	0.0000, 0.0026, 0.0028, 0.0006
5b	-1732.036	55.9	-11.9 (-9.5)	2.72, 2.79, 2.79	0.0000, 0.0023, 0.0012
5c	-1732.034	56.2	-10.4 (-8.1)	1.92, 2.46, 2.71	0.0000, 0.0002, 0.0003

^a ZPE and IE in kcal/mol. ^b IE = $E(\text{Si}_n\text{-Gly}) - E(\text{Si}_n) - E(\text{Gly})$, ZPE-corrected. ^c IE corrected for BSSE by the counterpoise method.

a series of silicon clusters: Si_3H_8 , Si_3H_4 , and Si_3 . Although they do not describe the collective electronic excitation processes, these transitions may be useful for pictorially describing the nature of electronic transitions. The dominant contribution in the transition (VE = 6.66 eV) to the first excited state of the fully hydrogenated Si_3H_8 is from a HOMO to a LUMO, which, as depicted in Figure 2 (a), are both σ orbitals, indicating that the electronic excitation in Si_3H_8 is mainly a $\sigma\text{-}\sigma^*$ transition. On the other hand, the dominant transitions for the partially hydrogenated Si_3H_4 (VE = 2.53 eV) and Si_3 (VE = 1.62 eV) are found to be $\pi\text{-}\pi^*$, as shown in Figure 2, parts b and c, respectively. Note that the excitation energies decrease progressively from Si_3H_8 to Si_3 , with increasing degree of unsaturation in the Si-Si bonds. Therefore, the lower excitation energies in the partially hydrogenated Si_3H_4 and the unpassivated Si_3 are due to the dangling bonds.

III.2. Structures of $\text{Si}_n\text{-Gly}$ ($n = 3\text{--}5$). In Figures 3–5 the structures of $\text{Si}_n\text{-Gly}$ ($n = 3\text{--}5$) complexes are presented along with their relative energies. In the lowest energy conformers, the amino group interacts with Si, while the carbonyl oxygen bonds with Si in some higher energy conformers. This is different from the structure of a Gly on a Si surface, where the carboxyl oxygen rather than the nitrogen atom binds to Si to form the O-Si bond, with the hydrogen atom of the OH group in Gly transferred to Si surface. In contrast, in the $\text{Si}_n\text{-Gly}$ complexes studied here, the Gly moiety remains “intact” to influence the electronic transitions in Si_n .

The calculated relative energies of the $\text{Si}_n\text{-Gly}$ complexes exhibit an interesting pattern that is not seen in bare Gly. One of the conformers lies much lower in energy than the other conformers. For example, the energies of **3b**, **3c**, and **3d** in Figure 3 are calculated to be 3.0, 4.2, and 4.4 kcal/mol, respectively, relative to the lowest energy structure (**3a**). Similarly, the higher lying conformers of $\text{Si}_4\text{-Gly}$ and $\text{Si}_5\text{-Gly}$ complexes are more than 2 kcal/mol higher in energy than the lowest energy conformers (**4a** and **5a**). This is in contrast with bare Gly that has several closely spaced conformers^{33,34} (six conformers³⁵ within 2 kcal/mol). Therefore, the lowest energy conformers (**3a**, **4a**, and **5a**) of $\text{Si}_n\text{-Gly}$ will be overwhelmingly observed in the low temperature gas phase environments, in contrast with the observation of at least three conformers of Gly in matrix isolation spectroscopy.³⁶ It is noted that the difference between **3a** and **3b** is mainly the orientation of the carboxyl group with respect to the rest of the complex, which implies that the difference in the position of the functional group, although it is not directly involved in chemical bonding, may also be important for the interaction with Si_n . The Mulliken charges of the Si and the atom (O or N) directly interacting

with it give useful insight into the nature of the chemical bonding in the complexes. The nitrogen atom in bare Gly is highly negative with a partial charge of -0.52 in Si_3 (Figure 1), but it has a positive charge (+0.12) in **3a** (Figure 3). The almost neutral Si atom in Si_3 now becomes very negative (-0.71) when forming the complex with Gly, indicating that a significant amount of negative charge has been transferred from N to Si. Similarly, the partial charges of Si and N change from -0.23 to -0.83, and from -0.52 to -0.18, respectively, when Si_5 interacts with Gly in complex **5a**, again suggesting a large degree of charge transfer. Such changes are less noticeable (-0.33 for Si and +0.19 for N) in $\text{Si}_4\text{-Gly}$ complex **4a**, possibly accounting for the larger $R_{\text{Si-N}}$ bond length (2.173 Å) in **4a** as compared with those in **3a** and **5a** (2.073 and 2.085 Å). The interaction energies (10–16 kcal/mol) also given in Table 2 indicate that the Si-N and Si-O bonds are weak with partial ionic character.

III.3. Electronic Excitation in $\text{Si}_n\text{-Gly}$ ($n = 3\text{--}5$). Table 2 lists the vertical transition energies of the $\text{Si}_n\text{-Gly}$ ($n = 3\text{--}5$) complexes along with the oscillator strengths. Strong blue shifts of the transition energies in the complexes from the corresponding silicon cluster Si_n are predicted. The excitation energies, which are in the range of 1.4–2.3 [1.5–2.7] eV in Si_3 [Si_4], change to 2.1–2.6 [2.3–2.8] eV for the $\text{Si}_3\text{-Gly}$ [$\text{Si}_4\text{-Gly}$] complexes. Transitions to the first excited states in Si_3 and Si_4 are predicted to shift to a larger degree (0.8–0.9 eV), whereas those to higher excited states are calculated to change by about 0.5 eV. The blue shift is a bit smaller in (**5a**), with excitation energies that are calculated to be 2.7–2.9 eV as compared with 2.2–2.7 eV in Si_5 .

Several studies have predicted that the excitation energies of the oxygen-doped porous silicon modeled as small silanones¹⁵ $\text{Si}_n\text{O}_m\text{H}_k$ ($n \leq 4$, $m \leq 5$) (VE = 3.3–6.0 eV) and $\text{Si}_n\text{OH}_{2n}$ (VE > 4 eV)¹⁶ would red-shift from those (VE > 6 eV) of hydrogen-passivated silicon clusters due to the contributions of the p orbitals in the Si=O bond.¹⁷ In the present case, interactions between the Si_3 moiety and Gly lead to the reallocation of the electron density to Gly, giving rise to the blue shift by lowering the ground state or lifting the excited state. In the dominant transition in the excitation (VE = 2.33 eV) of the $\text{Si}_3\text{-Gly}$ cluster **3a** (Figure 2d), the HOMO is mostly localized in the Si_3 moiety, whereas the electron density is extensively reallocated to the Gly moiety in the LUMO. Another notable feature of the electronic excitations presented in Table 2 for the $\text{Si}_n\text{-Gly}$ ($n = 3\text{--}5$) complexes is that transitions that are very weak or symmetry forbidden in Si_n may now exhibit finite oscillator strengths and could therefore be observed. Finally, the excited states of the $\text{Si}_n\text{-Gly}$ complexes have an emission Stokes

redshift of 0.5–1.0 eV relative to the absorption frequencies in Table 2 due to vibrational relaxation.¹⁴

IV. Conclusion

The good agreements of the calculated vertical transition energies of small silicon clusters with the experimental observations are quite encouraging, and the TDDFT methods could be employed for bigger silicon clusters interacting with a variety of biomolecules. Experiments on this interesting system will also be highly desirable.

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