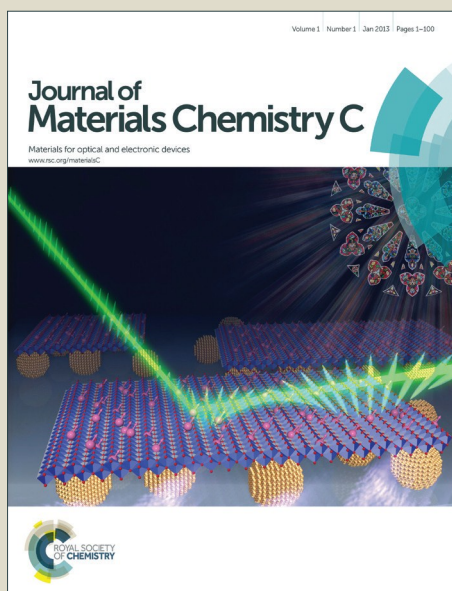


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Tunable optical absorption in silicene molecules

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Abstract

Two-dimensional materials with a tunable band gap that covers a wide range of the solar spectrum hold great promise for sunlight harvesting. For this reason, we investigate the structural, electronic, and optical properties of silicene molecules using time dependent density functional theory. We address the influence of the molecular size, buckling, and charge state as well as that of a dielectric environment. Unlike planar graphene molecules, silicene molecules prefer to form low-buckled structures with strong visible to ultraviolet optical response. We also identify molecular plasmons.

Keywords: Silicene, molecular plasmon, solar energy, TDDFT

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Silicene is a two-dimensional material with hexagonal honeycomb structure analogous to graphene. Its unusual electronic properties are attracting attention since several years [1–8]. While the stability of sp^2 bonded Si atoms is subject of a longstanding debate [9], theory has early predicted that freestanding silicene realizes a mixed sp^2 - sp^3 hybridization [10, 11] and shows a linear dispersion in the vicinity of the Fermi energy (massless Dirac Fermions). It is intriguing to study whether the concepts and applications suggested for graphene also apply to silicene, because its direct compatibility with current Si-based technologies would enable an easy integration into electronic devices, a great advantage over graphene. Silicene has been synthesized first on Ag [12] and subsequently on ZrB_2 [13] and Ir [14]. In each case the interaction with the substrate is strong so that the electronic states are perturbed significantly. Stability also has been predicted on substrates with weaker interaction, such as SiC and h-BN [15], but synthesis could not yet be realized.

Among the known methods to tune the electronic properties of a material, quantum confinement through nanostructuring turns out to be a very efficient approach. It therefore is not surprising that Si polymers have been identified as interesting materials a long time ago [16]. Their direct band gaps are useful for optoelectronic applications (crystalline Si has an indirect band gap) and show strong ultraviolet luminescence. Recently, time dependent density functional theory has been employed to study poly-silo-acenes, which are based on a linear arrangement of hexagonal Si rings (structure similar to poly-acenes but with buckling) [17]. Strong absorption is found in the visible to ultraviolet region of the electromagnetic spectrum. On the other hand, geometrical and electrical tuning of the optical response of poly-aromatic hydrocarbons (molecular form of graphene with H passivated edges) has been demonstrated both experimentally [20] and theoretically [21]. Synthesis of analogous silicene molecules may be demanding, but according to the results of the present work would be highly desirable due to promising material properties.

We study the properties of silicene molecules, taking into account the influence of the molecular size, buckling, and charge state as well as that of a dielectric environment. All calculations are performed using version 6.6 of the Turbomole software [22, 23]. We employ the BP86 generalized gradient approximation to the exchange correlation functional and an all-electron triple-zeta plus polarization basis set, both for the structure relaxation and the calculations within time dependent density functional theory. The same combination of functional and basis set has been employed previously to study the optical absorption of

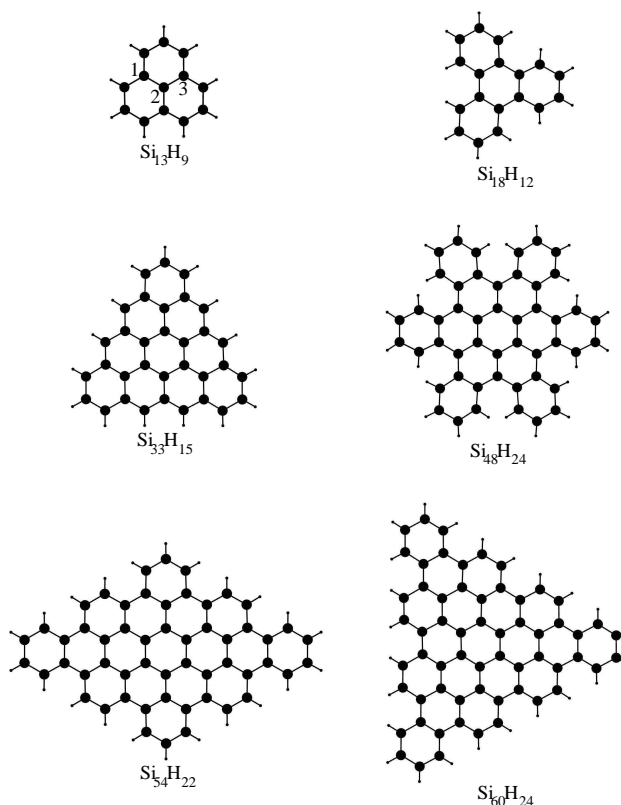


FIG. 1. Si molecules considered in this work. All edge Si atoms are saturated by H.

poly-silo-acenes [17]. We note that semilocal exchange correlation functionals can suffer from a red shift of the absorption spectrum of up to ~ 0.5 eV, while the shape of the spectrum is typically well reproduced [18, 19]. The multipole accelerated resolution of identity method is used for the Coulomb term and quadrature grids of m3 quality are employed. The dielectric environment is simulated by the conductor-like screening model of the Turbomole software [24], which previously has been used for several similar systems, see Ref. [25], for example. Generating 1000 roots is found to be sufficient to obtain absorption spectra up to an energy of 4 eV.

Structural relaxation shows that Si_{13}H_9 , $\text{Si}_{18}\text{H}_{12}$, $\text{Si}_{33}\text{H}_{15}$, $\text{Si}_{48}\text{H}_{24}$, $\text{Si}_{54}\text{H}_{22}$, and $\text{Si}_{60}\text{H}_{24}$ molecules, see Fig. 1, favor low-buckled structures, a tendency of silicene molecules that is known from previous theoretical studies [17, 26, 27]. We find that the buckling angle ($\angle 231$ in Fig. 1) varies between 39.6° and 43.7° , which is very similar to the range reported in Ref. [17] (between 38.9° and 42.9°) in the case of poly-silo-acenes. Diagonalization of the dynamical matrix in no case results in negative vibrational frequencies, which demonstrates that all low-buckled structures are dynamically stable. A spin-polarized calculation has been

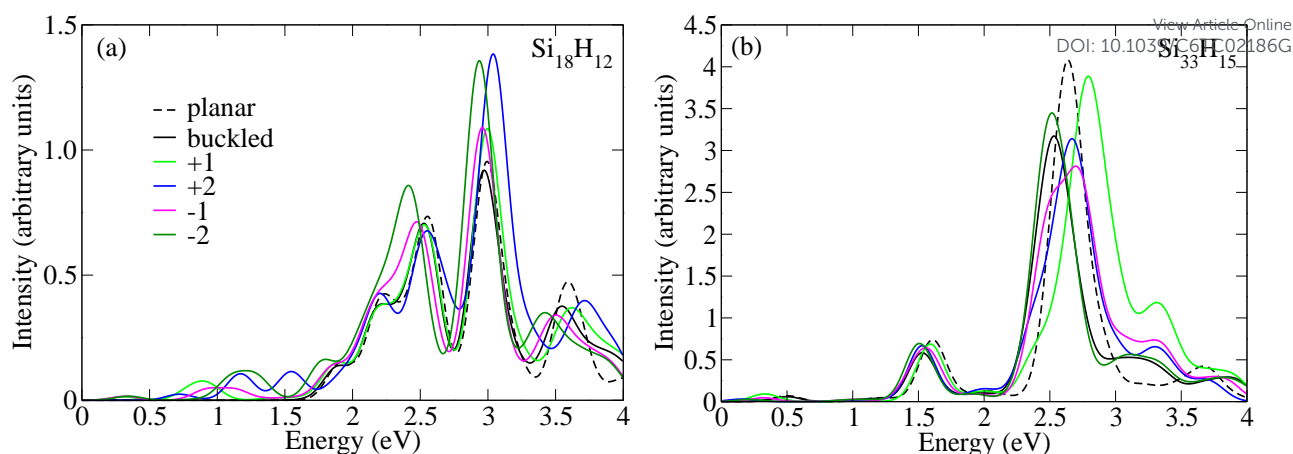


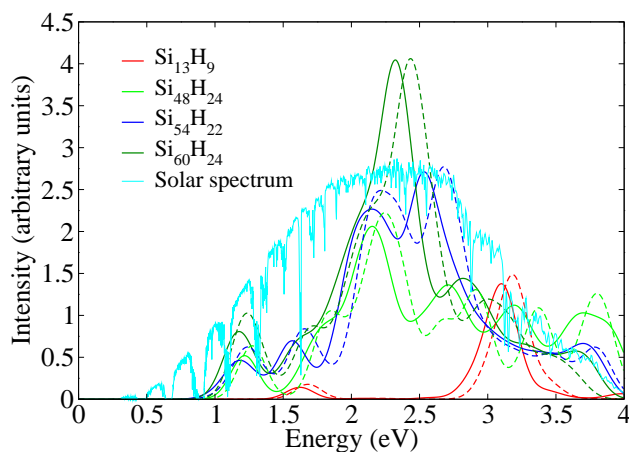
FIG. 2. Absorption spectra of $\text{Si}_{18}\text{H}_{12}$ and $\text{Si}_{33}\text{H}_{15}$, for planar (charge: 0) and buckled geometries (charge: 0, ± 1 and ± 2).

performed for $\text{Si}_{33}\text{H}_{15}$ and reveals a total magnetic moment of $3 \mu_B$, with the edge Si atoms contributing more ($\sim 0.1 \mu_B$) than Si atoms in the center of the cluster ($\sim 0.04 \mu_B$).

We show the absorption spectra of two representative molecules, $\text{Si}_{18}\text{H}_{12}$ and $\text{Si}_{33}\text{H}_{15}$, in Fig. 2. According to Fig. 2(a) the spectra of planar and buckled $\text{Si}_{18}\text{H}_{12}$ reveal only minor differences, except for a small redshift and intensity reduction of the high energy peaks of the buckled molecule. These effects are strongly enhanced for the $\text{Si}_{33}\text{H}_{15}$ molecule, see Fig. 2(b). In contrast to bulk Si, the absorption spectra show rich structures due to the localized nature of the electronic states. The energy differences between the highest occupied and lowest unoccupied molecular orbitals (HOMO-LUMO gap) as well as the energetical positions and

TABLE I. HOMO-LUMO gaps, dominating peaks (plasmonic nature marked boldface), and oscillator strengths.

Molecule	HOMO-LUMO gap (eV)	Dominating peak (eV)	Oscillator strength (a.u.)
Si_{13}H_9	0.42	1.62, 3.10	0.07, 0.20
$\text{Si}_{18}\text{H}_{12}$	1.51	1.89, 2.21 , 2.52 , 2.97 , 3.52	0.07, 0.13, 0.20, 0.36, 0.12
$\text{Si}_{33}\text{H}_{15}$	0.19	0.50, 1.51, 2.52 , 3.21, 3.83	0.05, 0.22, 0.32, 0.01, 0.01
$\text{Si}_{48}\text{H}_{24}$	0.96	1.21, 2.15 , 2.71 , 3.19, 3.70	0.15, 0.09, 0.25, 0.04, 0.01
$\text{Si}_{54}\text{H}_{22}$	0.83	1.16, 1.56 , 2.13 , 2.53, 3.71	0.16, 0.21, 0.13, 0.12, 0.01
$\text{Si}_{60}\text{H}_{24}$	0.89	1.14, 2.30 , 2.82, 3.33, 3.66	0.24, 0.30, 0.03, 0.01, 0.01

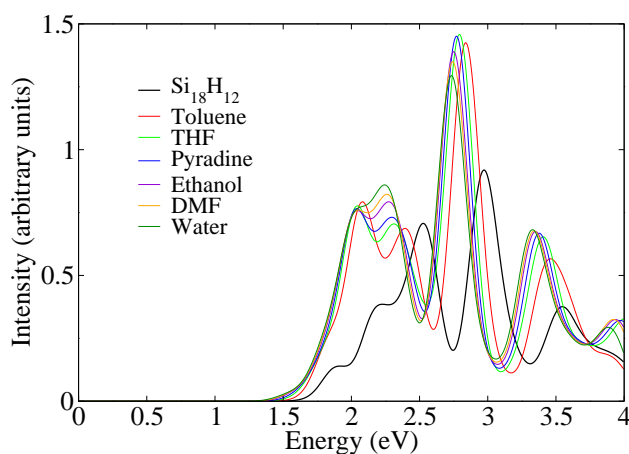


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FIG. 3. Absorption spectra of Si_{13}H_9 , $\text{Si}_{48}\text{H}_{24}$, $\text{Si}_{54}\text{H}_{22}$, and $\text{Si}_{60}\text{H}_{24}$, compared to the solar spectrum [28]. The dashed and full lines represent planar and buckled geometries.

oscillator strengths of the dominating absorption peaks obtained for the buckled molecules are compared in Table I. Similar contributions of various single particle transitions to a specific peak indicate that the absorption is due to a molecular plasmon [20, 21]. In the case of the Si_{13}H_9 molecule, for example, the main absorption peak at 3.10 eV is of plasmonic nature as 25 single particle transitions are required to account for 85% of its weight, whereas 90% of the 1.62 eV absorption peak are due to only 3 transitions. In Table I all absorption peaks of plasmonic nature are marked by boldface numbers.

Concerning the influence of the charge state on the spectrum, Fig. 2 shows for the $\text{Si}_{18}\text{H}_{12}$ molecule that absorption is triggered below 1.5 eV, while the gross shape is maintained. The 1.51 eV HOMO-LUMO gap of the charge neutral state is reduced to 0.04 eV and 0.05 eV, respectively, upon addition and removal of one electron, reflecting high electrical tunability of the optical response. Similar effects are obtained in the case of the $\text{Si}_{33}\text{H}_{15}$ molecule. We note that the 2.52 eV absorption here is much stronger, in agreement with the trend demonstrated in Fig. 3 for the remaining molecules. Besides an increasingly early onset of the absorption with growing size of the molecule (the data from Fig. 2 fit in this trend), more and more spectral weight accumulates between 2 eV and 2.5 eV and also the low energy peak between 1 eV and 1.5 eV gains intensity. The absorption of the molecules thus covers a wide spectral range spanning from the visible to the ultraviolet region of the electromagnetic spectrum. Figure 3 also demonstrates that the absorption spectra match well with the solar spectrum [28], which highlights the potential of silicene molecules in the field of solar energy



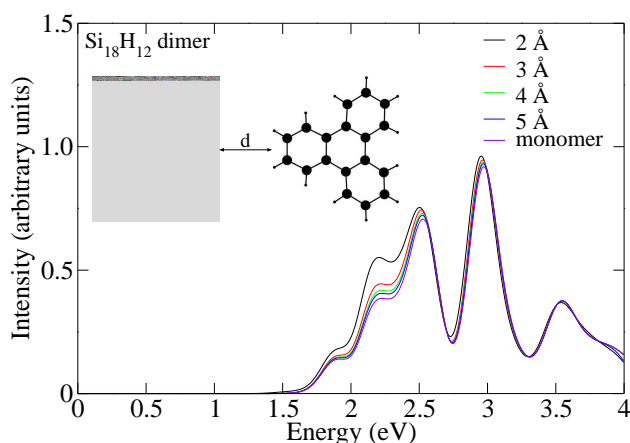
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FIG. 4. Effect of a dielectric medium on the absorption spectrum of $\text{Si}_{18}\text{H}_{12}$.

harvesting.

We next examine the sensitivity of the absorption spectra to the surrounding dielectric environment. Figure 4 shows representative results for the $\text{Si}_{18}\text{H}_{12}$ molecule for six organic solvents with increasing dielectric constant, toluene ($\epsilon = 2.4$), THF ($\epsilon = 7.6$), pyridine ($\epsilon = 12.4$), ethanol ($\epsilon = 24.5$), DMF ($\epsilon = 36.7$), and water ($\epsilon = 78$). We observe systematic changes: The plasmonic excitation originally located at 2.97 eV (black line) is subject to a substantial enhancement, largely independent of the solvent, and a slight red shift. This fact points to a strong interaction between the plasmon and solvent by vibrational coupling, as reported for polyaromatic hydrocarbons solvated in pyridine [20]. Since interaction of molecules can result in plasmon hybridization [21, 29], we study as an example a $\text{Si}_{18}\text{H}_{12}$ dimer in that two molecules are connected via corners, see Fig. 5. For intermolecular distances from 2 Å to 5 Å the absorption spectrum shows almost no change except for the 2.21 eV peak, which is substantially enhanced when the two molecules come close to each other. As the peak is of plasmonic nature, see above, this observation reflects plasmon hybridization.

In conclusion, we have employed time dependent density functional theory to evaluate the optical properties of silicene molecules, especially size effects. We have also described the influence of the buckling, charge state, and dielectric environment. The absorption spans a wide spectral range from the visible to the ultraviolet region, which indicates potential of silicene molecules in solar energy harvesting. In particular, the observed tunability of the optical properties as a function of the molecular size makes them to exciting targets



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FIG. 5. Absorption spectrum of a $\text{Si}_{18}\text{H}_{12}$ dimer with increasing intermolecular distance d .

for synthesis. In addition, silicene molecules open venues to photonic devices exploiting molecular plasmons.

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