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Pseudo Jahn–Teller effect in the decasilanaphthalene molecule: Towards the origin of the buckling in silicene

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ABSTRACT

It has been theoretically predicted that the ground state of free-standing silicene has a periodic buckled structure, whose origin is attributed to the puckering distortion on the individual six-member rings. In this work we present a theoretical analysis of the vibronic instability of the ground state of two hexagonal silicene units (decasilanaphthalene molecule) of D_{2h} planar symmetry to the 3D puckered structure with C_{2h} symmetry. Both, the multilevel superposition vibronic model and possible mixing of excited states of different irreducible representations are studied. We show that contrary to the one six-member ring case, for the decasilanaphthalene molecule, the multilevel PJT does not provide a satisfactory explanation for puckering and a proper description is given by a ground state coupling with two quasi-degenerate excited states. Hence a simple extrapolation of the origin of the puckering distortion in silicene from one to *n*-hexagonal components is not straightforward.

1. Introduction

Silicene, the 2D crystal graphene-like, formed by Si hexagonal lattice, has been recently a field of great scientific interest due to the similar properties to graphene and its potentiality to be integrated into the silicon based industry. Its synthesis has been made possible on substrates through epitaxial deposition mainly on silver [1–5] as well as on zirconium diboride [6] and Ir [7], and free-standing multilayers [8,9]. Recently, it was reported the fabrication of the first silicene field-effect transistor operated at room temperature [10], even it is still limited in its stability and performance, shows a proof of concept. Although single-layer free-standing silicene has not yet been synthesized, its properties have been theoretically studied and predicted a 2D structure, stabilized by an out of plane small distortion forming a buckled structure; and an electron behavior as massless Dirac Fermions and the semi-metal or zero-gap semiconductor characteristic, similar to graphene [11–16]. Theoretical calculations have shown that silicene has a periodic buckled structure whose origin is on each of the six membered rings, which are simulated by hexasilabenzene. Hexasilabenzene, the silicon analog of benzene whose synthesis has presented a great challenge, has only been studied theoretically [17–23]. Planar hexasilabenzene structure instability with D_{6h} symmetry to a puckered D_{3d} structure was originally attributed to the pseudo Jahn–Teller (PJT) effect through the coupling of the planar D_{6h} ground state with just one excited state through a b_{2g} vibrational mode, with the argument that the coupling to other excited states can be neglected due to their larger energy gap [11–15,24]. However, it was recently shown that in order to have consistency with the linear multilevel PJT effect theory, the coupling should be at least with two excited states [25]. It is worth stressing that the relative size of the energy gaps is not an a priori argument to discard the possible couplings; and the instability condition is given by the interplay of the energy gap, the vibronic coupling constant and the primary force constant of the ground state [26,27]. It has been reported that clusters gain stability upon puckering when the number of rings increases from Si_6H_6 to $Si_{70}H_{22}$ and that the puckering distortion of hexasilabenzene is preserved in silicene sheets [28]. This argument is based on studies on energy stability conditions of the puckered structures; and to our knowledge there is not a proper analysis of how the PJT coupling evolves when increasing the number of rings. The question naturally arises whether the same PJT coupling model is maintained on *n*-hexagonal silicene components, and a natural step towards this end is to investigate the PJT vibronic coupling instability of two hexagonal silicene units, $Si_{10}H_8$ (decasilanaphthalene molecule).

In this work we present a theoretical analysis of the instability of decasilanaphthalene molecule of D_{2h} planar symmetry to the 3D puckered structure with C_{2h} symmetry. This is done by study the

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pseudo Jahn–Teller effect through the linear vibronic coupling between the ground and the relevant excited states, which leads to the puckering distortion. Both, the multilevel superposition vibronic model and possible mixing of excited states of different irreducible representations are studied. We show that contrary to the one six-member ring case, for the decasilanaphthalene molecule, the multilevel PJT does not provide a satisfactory explanation for puckering and a proper description is given by a ground state coupling with two quasi-degenerate excited states, therefore showing that the linear extrapolation from one to *n*-hexagonal silicene components is not straightforward. The analysis is based on Density Functional Theory (DFT) and Time Dependent DFT (TDDFT) calculations of the vibronic instability of the ground state of decasilanaphthalene.

2. Computational method

We carried out geometry optimization and frequency calculations of the decasilanaphthalene molecule of D_{2h} planar symmetry and the 3D puckered structure with C_{2h} symmetry using relativistic DFT methods within the scalar zero order regular approximation (ZORA). The exchange and correlation terms were approximated through the GGA B3LYP and meta-GGA TPSSH hybrids functionals, and all electrons TZ2P basis sets were used for the valence orbitals. The power of prediction of these methods have been previously tested for the hexasilabenzene molecule [25]. We followed the method developed by Molina et al. [29] to estimate the Jahn–Teller energy gain (EJT). In order to determine the coupling of the ground state with some excited state, singlet to singlet electronic transitions for the first seventy excited states were evaluated for the D_{2h} $Si_{10}H_8$ cluster using TDDFT with ZORA scalar and all electron TZ2P basis. All DFT and TDDFT calculations were performed as is implemented in Amsterdam Density Functional [30].

3. Results

Fig. 1 presents the optimized structural properties of the $Si_{10}H_8$ molecule in planar D_{2h} (Fig. 1(a)) and puckered C_{2h} (Fig. 1(b)) symmetries. The average bond lengths obtained with the methods B3LYP/TZ2P and TPSSH/TZ2P have very similar values with a maximum difference of 0.007 Å for D_{2h} and 0.019 Å for the distorted C_{2h}. It should be notice that the calculated bond lengths for the planar structure differ at most 0.043 Å compared to Si_6H_6 (2.208 Å) [25], whose value is within the range of decasilanaphthalene. The $Si_{10}H_8$ average puckering angle was of 36.6° for TPSSH/TZ2P and 40.5° for B3LYP/TZ2P; while a puckering angle of 30.9° and 40.0° were obtained for Si_6H_6 with the same methods, respectively. Jose and Datta [28] reported an average puckering angle of 33.7° and 34.3° for Si_6H_6 and $Si_{10}H_8$, respectively, obtained with the methods M05-2X/TZVP and B3PW91/TZVP, which are closer to our TPSSH/TZ2P results. The HOMO–LUMO gaps obtained for planar $Si_{10}H_8$ are 2.0 and 2.35 eV for TPSSH/TZ2P and B3LYP/TZ2P, respectively, against 3.31 and 2.94 eV for Si_6H_6 with the same methods [25].

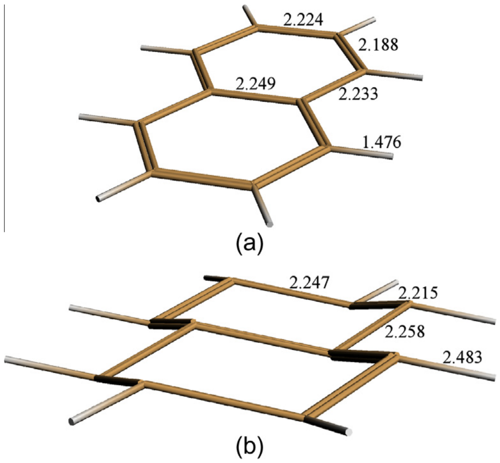

Fig. 1. Schematic diagram of the (a) D_{2h} and (b) C_{2h} symmetric structures of $Si_{10}H_8$ including averaged bond lengths.

Decasilanaphthalene $Si_{10}H_8$ with symmetry D_{2h}, possesses 48 non-degenerated vibrational modes whose representation is given by the decomposition:

$$\Gamma_{vib} = 9a_g + 3b_{1g} + 4b_{2g} + 8b_{3g} + 4a_u + 8b_{1u} + 8b_{2u} + 4b_{3u} \qquad (1)$$

of which, the modes ($9a_g + 3b_{1g} + 4b_{2g} + 8b_{3g}$) are Raman-active, whereas ($8b_{1u} + 8b_{2u} + 4b_{3u}$) are IR-active and just the $4a_u$ are optically silent, all to first order. However, this molecule is unstable [28], presenting five imaginary frequencies with magnitudes: 19.4, 37.4, 50.8, 59.7, 100.5, and 133.1 cm^{-1} and irreducible representations (irreps): $1b_{1g}$, $1a_u$, $1b_{3u}$, $2b_{3u}$, $2a_u$, and $1b_{2g}$ according to the method TPSSH/TZ2P. For the method B3LYP/TZ2P only three imaginary frequencies were found, with magnitudes: 20.2, 99.0, and 137.1 cm^{-1} with irreps $1b_{3u}$, $1a_u$, and $1b_{2g}$. Both results agree with the fact that the maximum imaginary frequency corresponds to the $1b_{2g}$ mode, which is precisely the puckering mode which distorts the planar structure to a puckered C_{2h}. Then, as for hexasilabenzene, the puckering mode is the main candidate to be the pseudo Jahn–Teller (PJT) active vibrational mode. The instability of the D_{2h} decasilanaphthalene non-degenerate ground state can be explained either as the result of a strong coupling between the ground state and one or a few excited states through a multilevel coupling, with the puckering mode similar to hexasilabenzene [25], or due to a strong coupling between two quasi-degenerated excited states with the ground state, through the same puckering mode.

In order to study the vibronic coupling it is necessary to do an adequate estimation of the excited APES (Adiabatic Potential Energy Surface) states. This was performed using TDDFT with the methods previously mentioned (B3LYP/TZ2P and TPSSH/TZ2P), however only the second method worked for all Q values of the distortion coordinate. We calculate the first seventy excited states for singlet to singlet transitions; in Table 1 we present the excitation energies for the corresponding first twenty states. The first

Table 1
Singlet–singlet lowest calculated electronic excitations for the D_{2h} $Si_{10}H_8$ molecule.[a]

Number	E_{ss}	irrep
1	2.007	$1B_{1u}$
2	2.081	$1B_{2u}$
3	2.596	$1B_{3g}$
4	2.814	$1A_u$
5	2.878	$2B_{2u}$
6	2.915	$2B_{1u}$
7	2.931	$1A_g$
8	2.989	$1B_{2g}$
9	3.134	$2A_g$
10	3.140	$2B_{3g}$
11	3.184	$1B_{3u}$
12	3.321	$1B_{1g}$
13	3.404	$3A_g$
14	3.418	$2B_{1g}$
15	3.568	$3B_{3g}$
16	3.628	$2B_{2g}$
17	3.736	$2B_{1g}$
18	3.783	$2A_u$
19	3.806	$3B_{2u}$
20	3.814	$3B_{1u}$

[a] E_{ss} are the transition energies (in eV) singlet–singlet.

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