On the Origin of the Pseudo Jahn–Teller Puckering Instability in Silicene

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Silicene, the graphene-like 2D crystal formed by Si hexagonal lattice, has attracted great interest, both theoretical and experimental. This interest has been motivated by its predicted physical and chemical properties, which are very similar to those of graphene and also on its greater potential, compared to graphene, to be integrated into the silicon based electronic industry. Its synthesis has been made possible through epitaxial deposition mainly on silver substrates, as well as on zirconium diboride and Ir surfaces and as free-standing multilayers. Recently, it was reported the fabrication of the first silicene field-effect transistor operated at room temperature [1], although still limited on 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 a periodic out of plane small distortion forming a buckled structure. The origin of this distortion, attributed to a pseudo Jahn-Teller instability, has been assumed that resides on each of the six membered rings, which are simulated by hexasilabenzene (Si_6H_6). It has been reported that clusters gain stability upon puckering when the number of rings increases and the puckering distortion of hexasilabenzene is preserved in silicene sheets. Planar hexasilabenzene structure instability with D_{6h} symmetry to a puckered D_{3d} structure was originally attributed to the pseudo JahnTeller (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 [2-4]. 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 [5].

References

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[7] We are thankful with the computer facilities of the Dirección General de Cómputo y de Tecnologías de la Información (DGTIC- UNAM) and with the GENERAL COORDINATION OF INFORMATION AND COMMUNICATIONS TECHNOLOGIES (CGSTIC) at CINVESTAV for providing HPC resources on the Hybrid Cluster Supercomputer ''Xiuhcoatl''.

In this work we present a complete study of the PJT effect based on DFT and Time Dependent DFT (TDDFT) calculations, as implemented in the ADF program, of the ground and excited states responsible for the buckled structure in silicene. This is done by analyzing the puckering instability of the ground state of hexasilabenzene (Si_6H_6) (Fig. 1), the basic silicon hexagonal ring unit defining silicene and two hexagonal silicene units, decasilanaphthalene molecule ($Si_{10}H_8$) (Fig. 2). We show that for Si_6H_6 the instability can be explained by multilevel PJT, whereas for $Si_{10}H_8$, puckering distortion is given by a coupling between the ground state and two quasi-degenerate excited states. In particular, it is shown that the usually assumed vibronic coupling of the ground state with only one excited state to explain the planar instability of hexasilabenzene is inconsistent with the linear multilevel PJT effect theory, and that in order to have consistency, it is necessary that the coupling should be through at least with two excited states. It is also shown 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 instead by a ground state coupling with two quasi-degenerated excited states i.e. a 3-state coupling of the kind $(1A_g + 2A_g + B_{2g}) \otimes b_{2g}$, where the first state corresponds to the ground state, and the following two to the excited states [6]. In this case, the PJT effect is a manifestation of the non-crossing rule between states with different irreducible representations in the more symmetric configuration.

In conclusion, through DFT and TDDFT calculations of the electronic states of one and two units of silicene, represented by the hexasilabenzene and decasilanaphthalene molecules , we show that a simple extrapolation of a PJT coupling from one to n-hexagonal silicene components is not straightforward. A more detailed analysis, based in a complete PJT study, which models simultaneously ground and excited states involved in the puckering distortion, is necessary for a proper understanding of the origin of the buckled structure of silicene [7].
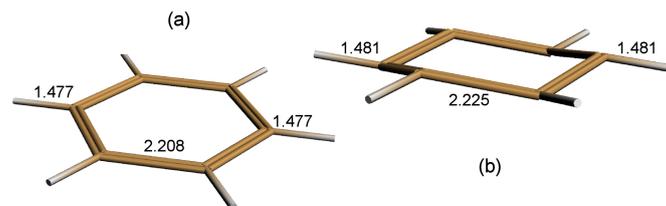

Figure 1: Diagram of the (a) D_{6h} and (b) D_{3d} symmetry structures of Si_6H_6.

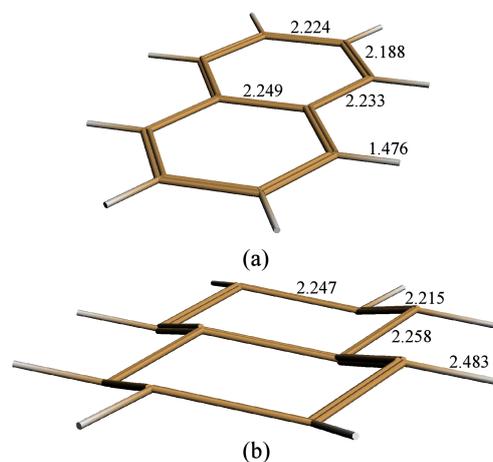Figure 2: Diagram of the (a) D_{2h} and (b) C_{2h} symmetry structures of $Si_{10}H_8$.