

Comment on “Fully Coordinated Silica Nanoclusters: $(\text{SiO}_2)_N$ Molecular Rings”

In a recent Letter, Bromley *et al.* [1] reported that the fully coordinated ring structures of $(\text{SiO}_2)_N$ ($N = 4-14$) clusters are more stable than the chains for $N > 11$. While one may find it logical that a silica cluster with fully coordinated Si atoms should be energetically more stable than the others, it should be noted that the curvature of the ring and hence the strain in the bonds could play an adverse role. This is indeed what happens. First, we study $(\text{SiO}_2)_{12}$. Our calculations are carried out using the same procedure used in Ref. [1], namely, density functional theory with the B3LYP form for the generalized gradient approximation 6-31G* basis set for Si and 6-311 + G(*d, p*) for O atoms as implemented in the GAUSSIAN 98 code [2]. The structure in Fig. 1(a) is derived by the linking of one $(\text{SiO}_2)_2$ chain with a $(\text{SiO}_2)_{10}$ ring, which lies 0.41 eV lower in energy than that of the $(\text{SiO}_2)_{12}$ ring. If two $(\text{SiO}_2)_2$ chains are linked symmetrically with two $(\text{SiO}_2)_4$ chains [Fig. 1(b)], the energy is 1.35 eV lower. In Fig. 1(c) four $(\text{SiO}_2)_2$ chains are linked symmetrically with a ring composed of four SiO_2 units. In this C_{2v} structure there are eight 4-coordinated Si atoms and four 3-coordinated Si atoms, and the energy of this structure is 2.51 eV lower than that of the simple ring structure. The IR spectrum for this structure is given in Fig. 1(d). Three modes, labeled as A, B, and C, have frequencies of 898, 910, and 936 cm^{-1} , which are also close to the experimental IR data of 888, 908, and 932 cm^{-1} observed for dehydrated silica surfaces. Note the frequencies calculated for the ring structure [1] are 886, 902, and 933 cm^{-1} . Since these frequencies are not sensitive to the above structures, it is difficult to assign the experimental frequencies to one form or the other.

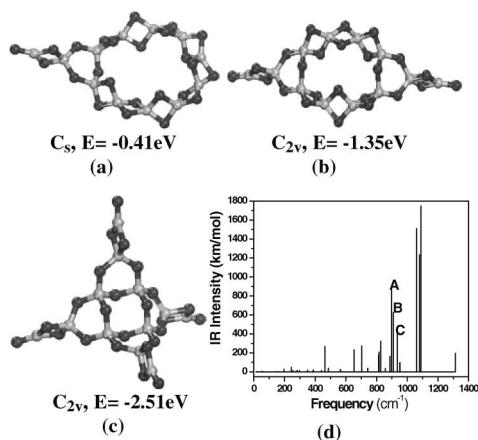


FIG. 1. Symmetry and energy relative to the ring structure for the isomers of the $(\text{SiO}_2)_{12}$ cluster (a)–(c). The IR spectrum of the isomer (c) is shown in (d). O atoms are presented in the dark color, and Si atoms in the light color.

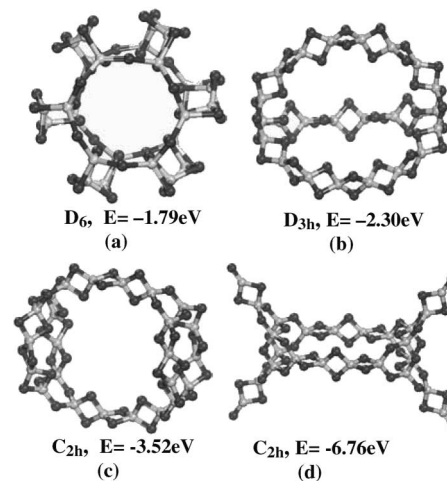


FIG. 2. Symmetry and energy relative to the ring structure for the isomers of the $(\text{SiO}_2)_{24}$ cluster.

Next we study $(\text{SiO}_2)_{24}$. Because of the large number of atoms, we use the composite basis set 3-21G for Si and 6-31G* for O, which have been extensively tested and determined to be an economic basis set for silicon oxide systems [3]. We have found four isomers (Fig. 2) with lower energies than the ring structure suggested in Ref. [1]. The first one [Fig. 2(a)] is composed of six interlinking $(\text{SiO}_2)_4$ chains resulting in a D_6 symmetry tubelike structure. Its energy is 1.79 eV lower than the ring structure. The second one, derived from three interlinking $(\text{SiO}_2)_8$ chains [Fig. 2(b)], has D_{3h} symmetry and lies 2.30 eV lower in energy. If six $(\text{SiO}_2)_4$ chains are arranged in such a way that four $(\text{SiO}_2)_4$ chains form two rings linked by two $(\text{SiO}_2)_4$ chains, as shown in Fig. 2(c), the resulting structure has C_{2h} symmetry. It lies 3.52 eV lower in energy as compared to the simple ring structure. Different from the first three fully coordinated structures, the fourth one [Fig. 2(d)] is not fully coordinated, where 20 Si atoms are fourfold coordinated, and four Si atoms are threefold coordinated with an average O-Si-O bonding angle of 110.4° . It lies 6.76 eV lower than that of the ring structure. In summary we show that the coordination of atoms and the strain of bonds are two competing factors for the stability of clusters.

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