Fully Coordinated Silica Nanoclusters: $(SiO_2)_N$ Molecular Rings

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A new form of finite silica with edge-sharing SiO_2 units connected in a ring is proposed. High-level density-functional calculations for $(SiO_2)_N$, $N = 4$–14, show the rings to be energetically more stable than the corresponding $(SiO_2)_N$ linear chains for $N > 11$. The rings display frequency modes in remarkable agreement with infrared bands measured on dehydrated silica surfaces indicating their potential as models of strained extended silica systems. Silica rings, if synthesized, may also be useful precursors for new bulk-silica polymorphs with tubular or porous morphologies.

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Pure silica is enormously versatile, exhibiting a large and diverse spectrum of natural polymorphs. Silica is also often deliberately engineered to have specific properties such as porous or thin film topologies and/or particular optical/electronic characteristics resulting in materials having applications ranging from microelectronics to catalysis. The structural basis for the vast majority of silicas is a three-dimensional network of silicon-centered corner-sharing SiO_4 tetrahedra. In contrast, silica tetrahedra can also participate in edge sharing, giving rise to rings containing two silicon atoms and two oxygen atoms. We propose a new two-ring-based fully coordinated, $(SiO_2)_N$, structure type, in the form of a molecular ring; see Fig. 1.

Recent studies have provided a wealth of evidence confirming that two-rings exist at the surfaces of amorphous and crystalline silica [1–7]. Two-rings at silica surfaces form, at temperatures above 900 K, from the condensation of vicinal hydroxyl groups but are strained species, which are readily reversibly hydrolyzed [1,2]. At higher temperatures (1400–1700 K), in the absence of water, thermodynamic rearrangement of the pure silica structure favors the formation of two-rings at the surface [3–7]. The elevated temperatures of this process cause the surface to be more flexible and potentially allows for more stable two-rings to form within a relaxed environment. The formation of two-rings via this process is probably energetically favored over forming reactive nonbridging oxygen (NBO) defect sites, and also entropically, due to the restrictive two-dimensional surface layer, making large surface rings unlikely. As with the thermally driven formation of two-rings on the two-dimensional surface of silica, high temperatures can also be used to synthesize one-dimensional silica structures with edge-sharing units. Combining more than one SiO_2 unit as to only having edge sharing gives rise to chains of two-rings; see Fig. 1. For $N = 1$–6, $(SiO_2)_N$ chains are predicted to be the most thermodynamically stable form of silica, being energetically favored over all other such stoichiometric silica clusters [8,9]. For larger N, two-ring chains of arbitrary length may be formed in the high temperature synthesis of fibrous silica-w [10]. These structures show that the energetic disadvantage of strain within two-rings can be outweighed by the energy of their formation and suggests that edge sharing in silica may be thermodynamically favored in environments of reduced dimensions.

To investigate the effects of environmental strain on the energetic stability of multi-two-ring silica systems in low dimensions, we performed high-level density functional (DF) calculations on $(SiO_2)_N$ edge-sharing chains and rings. Chains are formed by edge-sharing two-rings terminated at either end by an NBO group. Our proposed molecular rings can be thought of as structures resulting from joining the NBO end groups of a chain. Unlike the chains, the rings have the novel property of being a fully coordinated cluster: each oxygen to two silicon atoms and each silicon to four oxygen atoms. Whereas the strain in a linear chain is not expected to vary significantly with N, the interconnectivity of the rings allows us to systematically vary the structural strain by changing the number of SiO_2 units.

For all DF calculations the Becke-type three-parameter hybrid exchange-correlation functional, B3LYP [11], was employed. DF calculations have

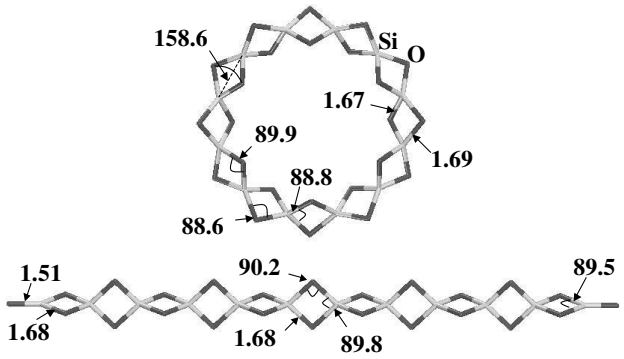

FIG. 1. Structures of the $N = 12$ $(SiO_2)_N$ molecular ring and chain. Bond lengths are in Å, angles in degrees.

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accurately reproduced the properties of silica clusters obtained from both experimental studies and other high-level calculations [8,9]. Cluster geometries were optimized at the AM1 semiempirical level and then further at the B3LYP/6-31G* level, imposing no symmetry constraints. For the final optimizations the basis set included both polarization and diffuse functions, 6-311 + G(*d, p*), to accurately account for oxygen polarization effects and strained bonds. Binding energies (BE) were calculated from the difference between the total energy of a cluster, $E_{N\text{-clus}}$, and the energy of the corresponding isolated triplet-state O and Si atoms at the B3LYP/6-311 + G(*d, p*) level. Gaussian 98 [12] was used throughout.

The $(SiO_2)_N$ chains were all found to consist of planar two-rings, each having a 90° orientation relative to its neighbor (all with a similar geometry regardless of N); see Fig. 1. This alternating structure enables the silicon atoms to be as close as possible to the energetically favored SiO_4 tetrahedral coordination. At the ends of the chains the terminating NBOs cause small distortions to the peripheral two-rings, with a decreasing effect towards the center of the chain. For the $(SiO_2)_N$ rings structural distortion is caused by the enhanced internal strain needed to form a fully coordinated system. We define this "cyclic strain," E_{cyc}, to be distinguished from the intrinsic strain possessed by the constituent two-rings, as the difference between the energy, E_1, consumed or released in deforming a chain to form a molecular ring ($E_1 = E_{N\text{-ring}} - E_{N\text{-chain}}$), and the energy, E_2, released in forming a chain from two smaller similarly sized subchains (e.g., for even N, $E_2 = E_{N\text{-chain}} - 2E_{N/2\text{-chain}}$). The assumption in this Born-Haber cycle estimate is that the energy released in forming a localized two-ring when combining two small chains, E_2, is similar to that in the corresponding process in joining a suitably bent N-chain. This is supported by examining the cyclic strain, which is mainly due, not to the individual two-rings, which stay relatively intact, but in the bending of the links between them. This results in the outer (farthest from the molecular ring center) oxygen atoms being spaced farther from each other relative to the chain oxygens, and the inner (nearest to the molecular ring center) oxygens being relatively closer together; see Table I. The cyclic strain in molecular rings also leads to some folding of the two-rings along their Si-Si axes with the pairs of oxygen atoms moving away from the molecular ring center. The folded two-rings open as the molecular ring size increases, being approximately 20° from planarity for the 14-ring. The cyclic strain of the molecular rings also manifests itself in a mismatch between the inner and outer Si-O-Si internal two-ring angles and Si-O bond lengths. The inner Si-O-Si internal two-ring angles are slightly larger than the outer internal two-ring Si-O-Si angles and the inner Si-O bond lengths are slightly smaller than their outer counterparts. The inner and outer Si-O lengths and Si-O-Si angles of the two-rings quickly converge to constant equal values, like the chains, as N increases. The rings naturally divide into an N-even set, and an N-odd set. The N-even rings consist of linked structurally equivalent two-rings with a regular alternating orientation pattern and high rotational symmetry ($D_{N/2}d$), about an axis through the ring's radial center, perpendicular to the ring plane. The N-odd set, however, has only C_2 symmetry about an axis within the ring plane through the radial center, with half of the two-rings being structurally nonequivalent. This division is due to the ability of the rings to mimic the favored alternating structure found in the chains. For N even this is achieved with the opposite orientations of the two-rings at the ends of a chain. For N odd there is no such match and the ring attempts to distribute this extra cyclic strain throughout the ring. The separation of the two sets of rings due to this mismatch strain can be seen in the E_{cyc} values in Table II, the BEs in Fig. 2, and in the energy gap in Fig. 3, where an oscillation between the lower N-even and higher N-odd ring energy scales is observed.

Spectroscopically, molecular rings possess IR bands characteristic of their connectedness distinct from those of the chains. Calculated 12-chain harmonic frequencies give prominent modes (866, 915, 838 cm^{-1}), and for the 12-ring, three main modes (902, 886, 933 cm^{-1}). The

TABLE I. N-even $(SiO_2)_N$ ring geometric parameters. Two-ring parameters of the 14-chain are given for comparison. Distances are in Å and (interior) two-ring angles in degrees. "Outer" and "Inner" refer to the distance from the molecular ring center.

	Si-O Outer	Si-O Inner	O-O Outer	O-O Inner	Si-Si	$\angle_{\text{Si-O-Si}}$ Outer	$\angle_{\text{Si-O-Si}}$ Inner	$\angle_{\text{O-Si-O}}$	$\angle_{\text{O-Si-Si-O}}$ Fold
4-R	1.78	1.70	3.56	3.03	2.35	82.4	87.5	82.2	126.0
6-R	1.73	1.67	3.39	2.80	2.35	85.6	89.0	86.2	141.6
8-R	1.70	1.67	3.26	2.78	2.35	87.0	89.2	87.8	149.6
10-R	1.69	1.67	3.18	2.79	2.35	87.9	89.6	88.4	154.9
12-R	1.69	1.67	3.13	2.80	2.36	88.6	89.9	88.7	158.6
14-R	1.69	1.67	3.10	2.81	2.36	89.0	90.1	88.9	161.3
14-C	1.67	1.67	2.90	2.90	2.38	90.5	90.5	89.4	180.0

TABLE II. Molecular ring energetics (eV/SiO_2). $\Delta BE = BE_{N\text{-chain}} - BE_{N\text{-ring}}$, E_{cyc} = cyclic strain energy, E_{cyc}/BE = ratio of cyclic strain to binding energy, and $E_{Q\to R}$ = formation energy difference between α-quartz and an N-ring.

	4-R	6-R	8-R	10-R	11-R	12-R	13-R	14-R
ΔBE	2.310	0.712	0.229	0.056	0.059	−0.024	−0.015	−0.066
E_{cyc}	3.453	1.474	0.801	0.514	0.473	0.354	0.334	0.260
E_{cyc}/BE	0.274	0.101	0.053	0.033	0.030	0.023	0.021	0.016
$E_{Q\to R}$	4.073	2.094	1.421	1.134	1.093	0.974	0.953	0.880

12-ring modes are in remarkable agreement with experimental IR measurements on dehydrated silica surfaces (908, 888, 932 cm^{-1}) [1,13,14], indicating their potential use as models for strained silica surfaces much like modeling silica defects with terminated silica clusters [15]. This surfacelike signature of the rings contrasts with the chains, which also display NBO modes at 1321 cm^{-1}.

For $(SiO_2)_3$ rings we found that E_{cyc} was too great and that the cluster would spontaneously break into the corresponding chain. For $N > 3$ molecular rings could always be stabilized, due to the greater stabilization from the bonding of two terminal NBO groups relative to the cyclic strain induced in the ring. Moving through $N =$ 4–14, we observe a monotonic increase in energetic stability of the molecular rings and chains (see Fig. 2), with a corresponding decrease in the cyclic strain in the rings (see Table II). For $N = 4$ the rings are much higher in energy than the chains, with E_{cyc} being over a quarter of the BE per SiO_2 unit. With increasing N, however, the stabilization rate is greater for the rings than for the chains, and, eventually for $N = 12$ the energetic stability of the rings exceeds that of the chains by 0.024 eV/SiO_2, with E_{cyc} being only 1.6% of the BE per SiO_2 unit. For additional increases in N, E_{cyc} continues to drop, along with the BE of the rings dropping further below that of the corresponding chains.

By definition, E_{cyc} does not include the intrinsic internal strain of the constituent individual two-rings. The strain energy of a relaxed two-ring has been estimated by numerous high-level calculations in the literature, all giving similar values. Cluster DF calculations using hydrogen-terminated two-rings yield relatively high estimates (0.72 eV/SiO_2 [16]) but neglect the stabilizing effect of an extended silica bonding environment [17]. Periodic DF calculations on two-rings in a relaxed amorphous silica surface give a value of 0.69 eV/SiO_2 [6], while similar calculations comparing the energy of silica-w to that of α-quartz, yield 0.62 eV/SiO_2 [18]. Using the latter value, and adding it to the cyclic strain in our molecular rings, gives an estimate of the formation energy of our rings with respect to α-quartz per SiO_2 unit, $E_{Q\to R}$; see Table II. E_{cyc} for the smaller molecular rings is found to be much larger than the intrinsic strain of a two-ring giving relatively large $E_{Q\to R}$ values (for $N <$ 8 $E_{Q\to R} > 1.5$ eV/SiO_2). For $N > 11$ E_{cyc} falls to

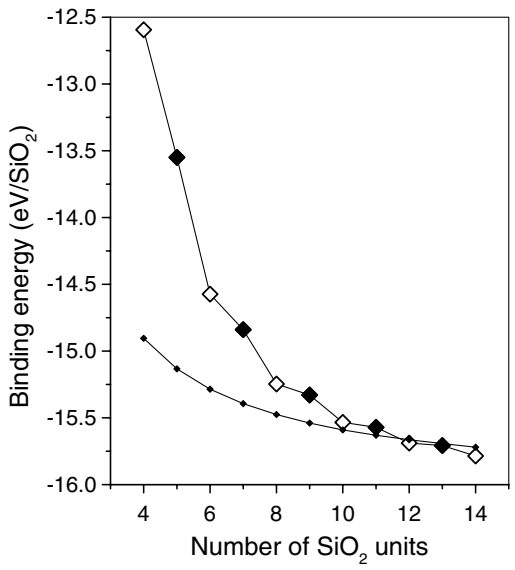

FIG. 2. Variation of the binding energy of the $(SiO_2)_N$ molecular rings and chains with N.

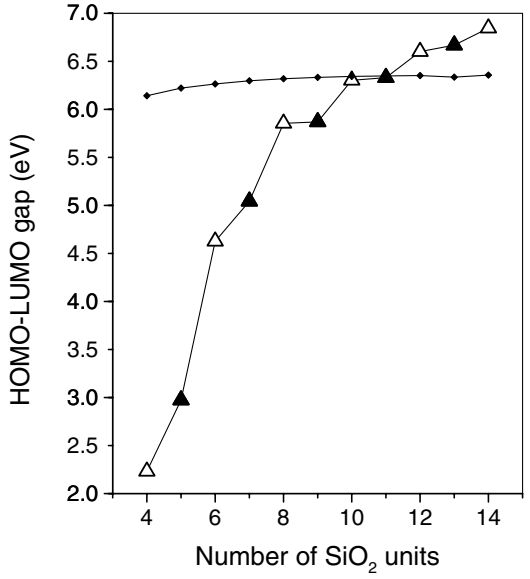

FIG. 3. Variation of the HOMO-LUMO gap of the $(SiO_2)_N$ rings and chains with N.

approximately half the intrinsic two-ring strain yielding, for the 12-ring, $E_{Q\to R} = 0.97$ eV/SiO_2.

Although important in assessing the likely formation of a system and the energy released once broken, the strain tells little about the stability of a ring, as once formed it is the energy required to break the connected $(SiO_2)_N$ structure (e.g., by external force, or reaction), which is more important. In addition to the energetic stability of $N > 11$ rings, having lower total energies and BEs over the $N > 11$ chains, due to the similarity of each bonded SiO_2 unit throughout a ring or chain, the lower BE (eV/SiO_2) also indicates a corresponding excess structural stability. The reactive stability of an SiO_2 cluster can also be assessed by the size of the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). For increasing $(SiO_2)_N$ chain lengths this gap remains almost constant. For the rings, the HOMO-LUMO gap is initially smaller than that of the chains but increases rapidly with increasing N, exceeding that of the chains by 0.25 eV for $N = 12$; see Fig. 3. We find that the frontier orbitals on the rings and chains have different characters: the chains have both HOMO and LUMO highly localized on the NBO end groups, while the rings have both orbitals distributed regularly over all atomic centers. The chain ends also have a dipolar character, making these regions likely reactive centers. The spatial extent of the electron-accepting LUMO of the rings is radially asymmetric with significant magnitude only around the outer periphery of the ring, but an almost total absence towards the center of the ring. Our calculations also show that the outer environment of the rings has a mostly positive electrostatic potential, whereas towards the center of the rings the potential is negative, indicating, along with the LUMO, that the ring interiors would be less reactive than the exteriors.

Recent DF/B3LYP calculations of the reaction of isolated hydrogen-terminated two-rings with water give a barrier of 0.71 eV increasing to 1.11 eV when including a more realistic extended environment [17]. Other studies found it necessary to include two-rings in extended surface models of annealed silica to reproduce its known hydrolysis stability [5]. In our silica rings each two-ring is, as on an extended surface, fully coordinated in a constrained environment, helping to increase its hydrolysis barrier over isolated two-rings, or terminated two-ring clusters. Experimentally, extended two-ring containing fibers of silica-w are structurally stable but susceptible to hydrolysis, although with only isolated bonds being attacked leaving intact two-ring $(SiO_2)_N$ chains estimated to have $12.5 < N < 100$ units [10]. To form more stable multi-two-ring materials we envisage, instead of long flexible chains, fully connected small clusters, such as our molecular rings, as material building blocks. If our proposed silica molecular rings could be successfully synthesized, then via their mutual interaction, the possibility arises for new extended silica polymorphs, which may show bulk features reminiscent of its building blocks such as tubular or porous morphologies. The interiors of such tubes or pores, due to the properties of the rings, are also likely to be relatively stable to hydrolysis, and the size of such pores even tailored by the size of the molecular ring employed. Although such ideas are highly speculative, we feel that if the synthetic challenge, inherent in these studies, could be mastered successfully, fully coordinated finite silica clusters and polymorphs based upon their combination, as proposed here, could provide a new route to the synthesis of novel materials and the further fundamental understanding of silica.

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