Novel structures and energy spectra of hydroxylated $(SiO_2)_8$-based clusters: Searching for the magic $(SiO_2)_8O_2H_3^-$ cluster

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The prominent $(SiO_2)_8O_2H_3^-$ mass peak resulting from the laser ablation of hydroxylated silica, attributed to magic cluster formation, is investigated employing global optimization with a dedicated interatomic potential and density functional calculations. The low-energy spectra of cluster isomers are calculated for the closed shell clusters: $(SiO_2)_8OH^-$ and $(SiO_2)_8O_2H_3^-$ giving the likely global minima in each case. Based upon our calculated cluster structures and energetics, and further on the known experimental details, it is proposed that the abundant formation of $(SiO_2)_8O_2H_3^-$ clusters is largely dependent on the high stability of the $(SiO_2)_8OH^-$ ground state cluster. Both the $(SiO_2)_8O_2H_3^-$ and $(SiO_2)_8OH^-$ ground state clusters are found to exhibit cagelike structures with the latter containing a particularly unusual tetrahedrally four-coordinated oxygen center not observed before in either bulk silica or silica clusters. The bare ground state $(SiO_2)_8O^{2-}$ cluster ion core is also found to have four tetrahedrally symmetric $Si=O$ terminations making it a possible candidate, when combined with suitable cations, for extended cluster-based structures/materials. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1861889]

I. INTRODUCTION

The discovery of "magic" clusters displaying unusually high abundances in cluster beam experiments has lead to numerous theoretical investigations aimed at explaining such observations in terms of energetic and atomic/electronic structure grounds. Such studies have been largely successful in providing explanations for many metallic, rare-gas, and ionic cluster systems.[1–3] Recently, it has been increasingly realized that, for a particular known cluster size, the potential energy surface (PES) of cluster isomers, and their accessibility subject to the experimental conditions, can strongly influence the favored cluster structure.[4,5] Such considerations are particularly difficult to assess for clusters for which the PES exhibits many minima of similar energy with varying degrees of thermal accessibility.[6] From our, and other, investigations into pure[7–12] and hydroxylated[13–17] silica nanoclusters, it would appear from the evident rich structural diversity of low energy forms that SiO_2-based nanostructures possess PES of this type. Indeed, although it is appealing to assign observed prominent peaks in cluster beam mass spectra to a collection of magic clusters all possessing one specific particularly stable structure, it is quite possible that such peaks can correspond to a range of structurally distinct but similarly stable clusters of the same composition and/or to clusters favored, not particularly by stability but rather by facile formation routes. In this study, knowing the chemical composition of the supposed magic SiO_8-based cluster observed from laser ablating hydroxylated silica,[17] i.e., $(SiO_2)_8O_2H_3^-$, and further some experimental hints at the cluster formation mechanism,[17,18] we have scanned the PES for low-energy isomers of the likely experimentally relevant closed-shell clusters: $(SiO_2)_8OH^-$ and $(SiO_2)_8O_2H_3^-$. In order to ensure a comprehensive search as possible in each case, we use a powerful combination of global optimization, employing our interatomic potential specifically parametrized for nanoscale SiO_2, together with density functional (DF) calculations to accurately confirm the structures and relative energies of the clusters. The resulting low energy spectrum of isomers from this procedure, for each cluster type, is examined for indications of particularly stable clusters with large energy gaps from other isomers and/or indications of highly symmetric structures often associated with "magicness." From such considerations, we propose that although there is a specific cluster structure that can be assigned to the observed magic $(SiO_2)_8O_2H_3^-$ cluster mass peak, this isomer is only moderately energetically favored over other $(SiO_2)_8O_2H_3^-$ cluster isomers. The reason for its high abundance, we argue, is that the magic $(SiO_2)_8O_2H_3^-$ cluster is dependent on the relative high energetic stability of the $(SiO_2)_8OH^-$ ground state cluster structure with respect to its isomers; the former resulting from addition of H_2O to the latter. Both precursor and resulting magic $(SiO_2)_8$-based clusters are found to exhibit a similar cagelike structure, with the former containing an unusual symmetric four-coordinated oxygen center within a stable tetrahedrally terminated $(SiO_2)_8O^{2-}$ core. Interestingly, the precursor ground

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state $(SiO_2)_8OH^-$ cluster, although in a sense being the real magic cluster, appears not to be simply structurally linked to our previously established stoichiometric $(SiO_2)_8$ magic ground state cluster,[8] e.g., via addition of a hydroxyl ion. However, it is noted that both $(SiO_2)_8O_2H_3^-$ and $(SiO_2)_8OH^-$ ground state clusters bear strong structural similarities to our previously discovered low-energy Si_7O_{14} cluster.[8,19] The study highlights the influence of cluster formation conditions, which seem to play an important role in producing the predicted observed $(SiO_2)_8O_2H_3^-$ magic cluster structure.

II. COMPUTATIONAL METHODOLOGY

Building upon our previous global optimization studies of stoichiometric silica nanoclusters,[8,19] we employ our own specifically parametrized SiO_2 interatomic potential set.[19] The potential has been found to accurately predict the energies and structures of silica nanoclusters enabling us to predict likely ground state candidates for $(SiO_2)_N$ $N=6-12$.[8] The interatomic potential set consists of three potentials (Si-Si, O-O, and Si-O), each of Buckingham form, combined with electrostatic interactions. In this study we use the potential set to explore the isomers of the nonstoichiometric clusters: SiO_2O^{2-} and $SiO_2O_2^{4-}$. The SiO_2 interatomic potentials are combined with the basin hopping (BH) global optimization algorithm[20] to search for low-lying minima on the respective nanocluster PES. The BH algorithm uses a combination of Metropolis Monte Carlo sampling and local optimization to sample the phase space of cluster configurations. We base our implementation of the BH algorithm on the GMIN program[21] extended in order to treat systems with multiple elements (i.e., Si and O). An additional hard-core potential was also introduced to all potentials to prevent atoms from falling on top of each other, during a BH run, due to the unphysical infinite attractive well, inherent to the Buckingham potential form for very short distances. Although the BH algorithm is one of the least hindered global optimization methods with respect to the specific topology of the PES,[22] due to the inherent finite sampling time, the form of the PES largely dictates the extent of the sampling achieved.[6] In order to overcome such problems a selection of different starting structures can be made to help ensure an even and extensive phase space sampling.[20] For each of our BH runs a number of randomly generated cluster structures, of the respective size and stoichiometry, were used as starting structures. Also, we took selected low-energy cluster structures from completed BH runs as starting points for subsequent runs, using relatively lower temperatures, to specifically sample low energy regions of phase space. The length of a typical run was 10^6 steps and for each run the 100 lowest energy structures encountered were retained.

It is assumed that the SiO_2O^{2-} and $SiO_2O_2^{4-}$ clusters resulting from the BH procedure form the core of the respective cluster anions $(SiO_2)_8OH^-$ and $(SiO_2)_8O_2H_3^-$ and that the addition of the hydrogen atoms to such cluster cores does not significantly perturb the energetic ordering of the respective isomers nor the structure of the cluster core. The latter assumption is based upon the grounds that hydrogen is a monovalent atom, which is known to form dangling hy-

droxyl groups on silica surfaces rather than embedding itself within the material. Due to the high number of terminating oxygen atoms in all of the cluster core isomers, hydrogen atoms were thus added to form terminal OH groups on each cluster core in all possible symmetrically independent configurations. Only in the case of the cagelike ground state clusters did we attempt to place a separate OH^- within the center of the cluster structure resulting, however, in very high-energy isomers, which are not reported. The former assumption, that the energetic ordering of the hydrogen-terminated cluster isomers is not significantly different from their BH-derived cluster cores, is tested by comparing the energetic ordering of the cluster cores, as given by the interatomic potential, with that of the hydrogen-terminated clusters as given by DF energy minimization calculations (see Figs. 1 and 2) showing reasonable agreement. The ten lowest energy cluster cores from each class were terminated with hydrogen to form OH groups in all possible symmetrically independent positions, and were then energy minimized using DF optimizations employing the B3LYP hybrid exchange-correlation functional[23] together with a 6-31 $+G^{**}$ basis set, employing no symmetry constraints. In all terminating positions the added hydrogen atoms were also checked to be in the energetically most favorable orientations with respect to possible local hydrogen bonding alternatives. All DF calculations were performed using the GAMESS-UK (Ref. 24) code.

III. RESULTS AND DISCUSSION

In Fig. 1 all $(SiO_2)_8O_2H_3^-$ cluster structures found within 1 eV of the lowest energy cluster as by our procedure are shown. The x-axis ordering of the clusters (N) follows the energetic ordering (lowest energy first) of the $(SiO_2)_8O_2^{4-}$ cluster cores as found by the BH procedure. The y-axis energy scale indicates the energies resulting from terminating these cores with three hydrogen atoms in all possible non-symmetric positions, and energy minimizing the resulting $(SiO_2)_8O_2H_3^-$ clusters employing DF calculations. We find that the five lowest energy cluster cores from the BH procedure do indeed correspond to the bottom five DF-optimized hydrogen-terminated clusters albeit with a small error in the energetic ordering. Five other energetically higher lying cluster cores other than the five used in Fig. 1 were all found to correspond accordingly to H-terminated clusters outside of the 1 eV displayed range and are not reported. It is clearly seen that the energy spectrum of $(SiO_2)_8O_2H_3^-$ cluster isomers is very dense with 20 clusters occupying the 1 eV energy range, six isomers within 0.2 eV (6.9 meV/atom) of the ground state, and the second lowest energy cluster being only 0.121 eV (4.2 meV/atom) above the ground state. Such an energy difference would seem to make it unlikely that any particular isomer would be very strongly preferred after cooling from the highly energetic laser ablation procedure used in experiment.[17,18] It can be seen that by only varying the position of the three hydrogen centers on the same $(SiO_2)_8O_2^{4-}$ cluster core one can typically produce a range of cluster energies spanning ≥ 0.15 eV. Within the bottom four energetically favored clusters, however, three different clus-
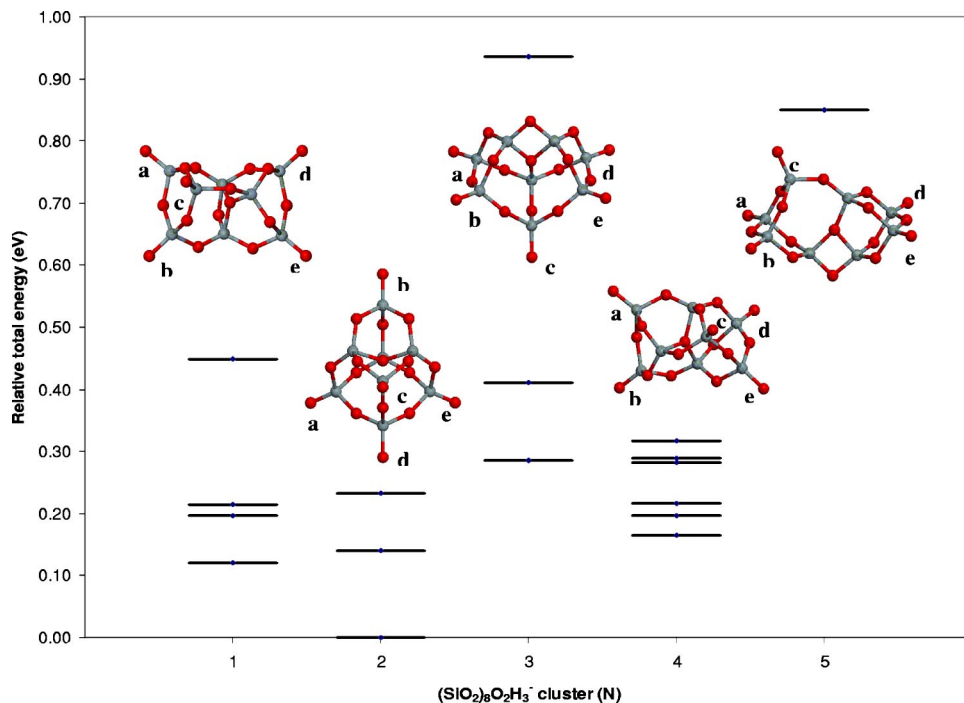
FIG. 1. The 20 lowest energy (SiO$_8$)$_2$O$_2$H$_3^-$ clusters as found by our BH/DFT procedure. The x-axis label (N) denotes the energetic order (lowest to highest) of the anionic (SiO$_8$)$_2$O$_2^{4-}$ cluster cores as found via the BH methodology. The energy level corresponding to the various (SiO$_8$)$_2$O$_2$H$_8^-$ isomers resulting from terminating each cluster core (N) with three hydrogen centers in three of the possible labeled positions (i.e., $a,b,c,\ldots$) can be found by reference to Table I.

ter core types are represented showing that the spectrum is dense with respect to silicon and oxygen atomic ordering and not simply just due to different hydrogen termination possibilities. The lowest energy cluster isomer is also not particularly special with respect to its electronic spectrum, with its gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) being equal or surpassed in magnitude by seven other of the 20

lowest energy clusters (see Table I). Of all the cluster (SiO$_2$)$_8$O$_2^{4-}$ cores and derived (SiO$_2$)$_8$O$_2$H$_3^-$ clusters, only the lowest energy cluster core (and one of its hydrogen-terminated derived clusters) shows a highly symmetric structure (C_{3v}) with all nine other calculated cluster cores and their respective hydrogen-terminated isomers having point symmetries of C_s or lower. These C_{3v} symmetric clusters also interestingly display a three-coordinated oxygen center;
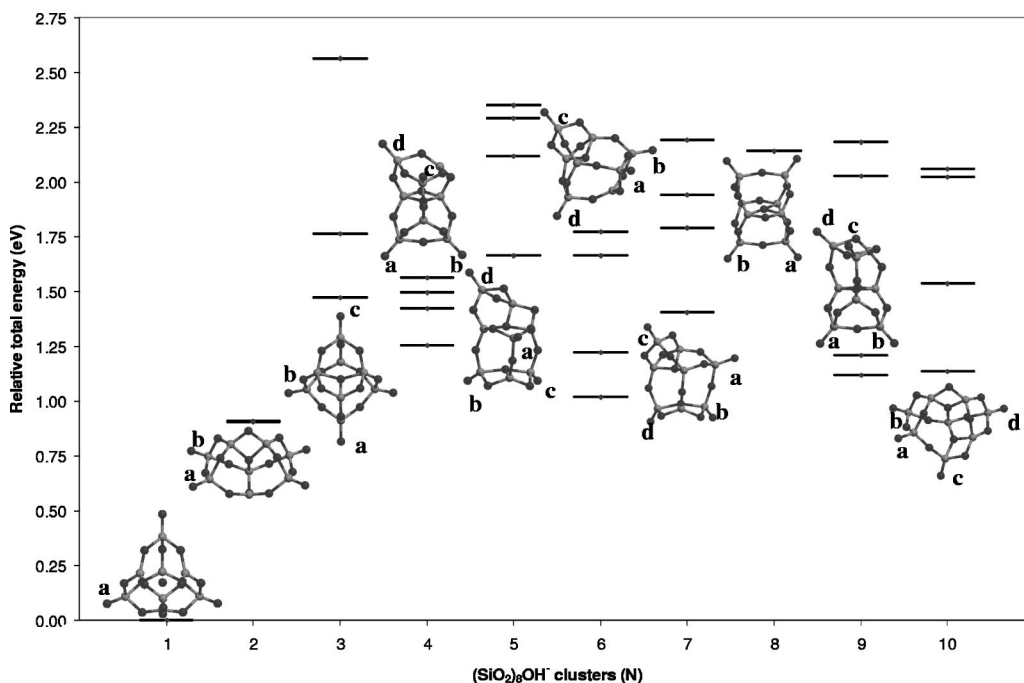

FIG. 2. The lowest energy (SiO$_8$)$_2$OH$^-$ clusters as found by our BH/DFT procedure (y-axis) corresponding to the ten lowest energy cluster cores. The x-axis label (N) denotes the energetic order (lowest to highest) of the anionic (SiO$_8$)$_2$O$_2^{2-}$ cluster cores as found via the BH methodology. The labels a, b, $c\ldots$ for each cluster core shown denote H-termination positions. The ordering of the energy levels for each cluster follow alphabetical ordering with the lowest energy isomer level being the lowest in each displayed spectrum (i.e., a=lowest energy, b=second lowest energy, c=$\ldots$). For clusters 2 and 8 the two respective isomers (a and b) are so close in energy as to make the energy levels indistinguishable in the figure.

TABLE I. Relative energies and HOMO-LUMO gaps of the 20 lowest energy $(SiO_2)_8O_2H_3^-$ cluster isomers. See Fig. 1 for structures corresponding to the notation in column one, i.e., N-(a,b,c), where N is the cluster-core number (x axis) and (a,b,c) is the specific hydrogen-termination combination.

$(SiO_2)_8O_2H_3^-$ cluster isomer: N-(hydrogen positions)	Relative total energy (eV)	HOMO-LUMO gap (eV)
2-(a,c,d)	0.000	4.89
1-(a,c,e)	0.121	4.94
4-(a,c,e)	0.141	4.89
2-(a,c,e)	0.165	4.93
4-(a,d,e)	0.196	4.79
4-(b,c,e)	0.197	4.93
1-(a,c,d)	0.215	4.72
1-(a,b,d)	0.216	4.98
2-(b,c,d)	0.232	4.71
4-(b,c,d)	0.283	4.99
4-(a,c,d)	0.285	4.86
3-(b,c,e)	0.289	4.89
4-(b,d,e)	0.316	4.85
3-(a,c,e)	0.411	4.74
1-(a,b,c)	0.449	4.31
5-(a,c,d)	0.719	4.79
5-(a,c,e)	0.725	4.73
3-(a,c,d)	0.755	4.53
5-(a,b,d)	0.849	4.62
3-(a,b,c)	0.935	3.96

a motif which has been noted before in our investigation into the low-energy isomers of stoichiometic $(SiO_2)_N$ $N=6-12$ clusters.[8,19]

The spectrum of energetically low-lying $(SiO_2)_8OH^-$ cluster isomers (see Fig. 2), in contrast to that of $(SiO_2)_8O_2H_3^-$, has a single strongly preferred isomer with a highly symmetric (T_d) $(SiO_2)_8O^{2-}$ cluster core. As with the $(SiO_2)_8O_2H_3^-$ cluster isomers the ground state $(SiO_2)_8OH^-$ cluster core has a higher symmetry than all other nine SiO_2O^{2-} cluster cores and respective hydrogen-terminated clusters. The energetic ordering of the cluster cores as found by the FB/BH procedure (x axis, Fig. 2) is again found to correlate quite well with the energetic ordering of the $(SiO_2)_8OH^-$ clusters as determined by DF calculations. Specifically, the lowest energy symmetric ground state is identified accurately by both methods. This consistency between both approaches is particularly pleasing when considering the structure of the $(SiO_2)_8O^{2-}$ cluster. The ground state $(SiO_2)_8O^{2-}$ cluster core possesses four tetrahedrally symmetric Si=O terminations. Due to this high symmetry there is only one independent position to terminate it with hydrogen, resulting in a distinct lowest energy $(SiO_2)_8OH^-$ cluster separated from all other cluster isomers by ≈ 0.9 eV. The cluster core also displays a centrally placed tetrahedrally coordinated oxygen center. Similar oxygen centers are known to exist in some bulk oxides (e.g., ZnO and ZrO₂) where they play the role more of noncovalently bonded ions rather than as part of a continuously bonded semicovalent network as is usual in SiO₂. The addition of a single proton to a dangling Si=O termination, to form the $(SiO_2)_8OH^-$ anion, results

only in a slight perturbation of the tetrahedrally coordinated oxygen center towards the hydroxylated silicon (~ 0.1 Å) atom. The central oxygen species appears to play a role similar to that of a complex ion with the remainder of the cluster acting as a quadridentate ligand. The closest silicon atoms of the cage to the oxygen center are considerably larger ($\sim 1.9-2.0$ Å) than that found in typical Si–O–Si bridging oxygen species ($\sim 1.65-1.7$ Å). The charge the central oxygen, as simply judged by Mulliken charge partitioning, is 0.6e more negative than the other oxygen atoms in the cluster also indicating its special status. Such a tetrahedrally terminated ionic cluster core ligand, when combined with suitable cations, other than simply protons, may be useful in the design of interesting cluster-based materials/structures.

Considered as energy per atom, the ground state gap in the $(SiO_2)_8OH^-$ spectrum (35 meV/atom) is over eight times larger than the corresponding largest gap in the $(SiO_2)_8O_2H_3^-$ spectrum (4.2 meV/atom). This relatively large energy gap would suggest that, if the proposed symmetric ground state $(SiO_2)_8OH^-$ cluster structure were accessible under the experimental conditions in Ref. 17, its persistence would be thermodynamically favored. In this way we consider that the occurrence of the magic $(SiO_2)_8O_2H_3^-$ cluster is actually mainly due to the proposed likely high abundance of the specific $(SiO_2)_8OH^-$ ground state structure we have identified. The transition between the strongly energetically favored $(SiO_2)_8OH^-$ structure and ground state $(SiO_2)_8O_2H_3^-$ structure could occur, we speculate, by the reaction of the former with water, either eventually produced in the cooling plasma resulting from the laser ablation of the hydroxylated silica or simply as present in trace amounts. The reaction of single H₂O molecule with clusters has been previously observed in mass spectra for other cluster systems. In particular, in the production of cluster from the laser ablation of bulk aluminum gives rise to both Al_n^+ and $Al_n^+H_2O$ series of clusters; the latter series is produced by the reaction of the former with trace amounts of water.[25] It is interesting to note that this reaction also gives rise to a magic cluster in the $Al_n^+H_2O$ series ($Al_{13}^+ + H_2O \rightarrow Al_{13}^+H_2O$). In addition to the known thermodynamic favorability of silica hydroxylation reactions, simply by comparing the structures of the two ground states (see Fig. 4), it can be seen that such a reaction would not require significant structural change to the $(SiO_2)_8OH^-$ ground state. This, we argue, would make it more likely that the ground state $(SiO_2)_8O_2H_3^-$ structure is produced rather than other energetically low-lying isomers. Finally, the transition from a preferred population of $(SiO_2)_8OH^-$ clusters to that of $(SiO_2)_8O_2H_3^-$ clusters is strongly corroborated by the experimental results which point to a steady production of sequence of $(SiO_2)_8OH^-$ clusters with a increasingly fast transformation of a part of this cluster sequence to $(SiO_2)_8O_2H_3^-$ clusters.[17,18] In the laser ablation experiment the cluster formation conditions are changing with time (e.g., concentration of different species in plasma with time/number of laser pulses). We suggest that the observed high abundance of magic $(SiO_2)_8O_2H_3^-$ clusters only occurs when the conditions are such that they are suitable to allow for the thermodynamically preferred production of the magic $(SiO_2)_8OH^-$ cluster, which quickly become
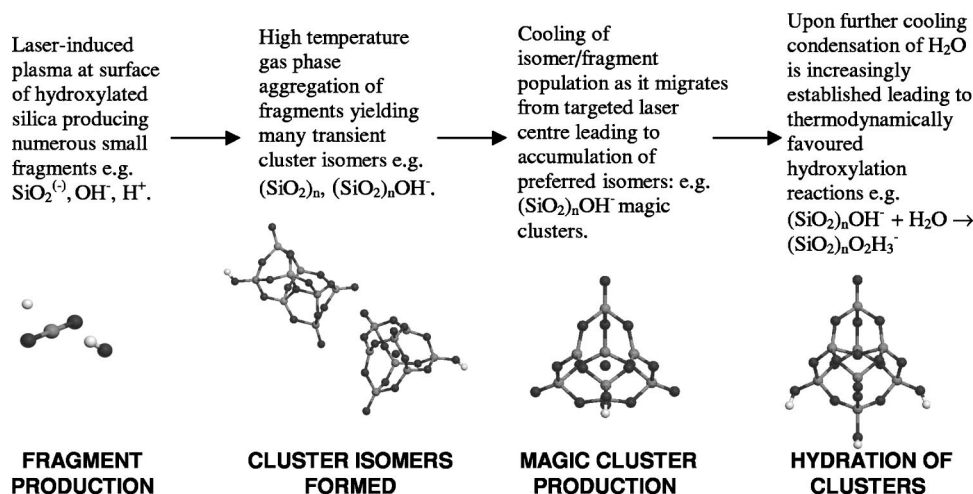
Laser-induced plasma at surface of hydroxylated silica producing numerous small fragments e.g. $SiO_2^{(-)}$, OH^-, H^+.

High temperature gas phase aggregation of fragments yielding many transient cluster isomers e.g. $(SiO_2)_n$, $(SiO_2)_nOH^-$.

Cooling of isomer/fragment population as it migrates from targeted laser centre leading to accumulation of preferred isomers: e.g. $(SiO_2)_nOH^-$ magic clusters.

Upon further cooling condensation of H_2O is increasingly established leading to thermodynamically favoured hydroxylation reactions e.g. $(SiO_2)_nOH^- + H_2O \rightarrow (SiO_2)_nO_2H_3^-$

FIG. 3. Schematic diagram to illustrate our proposed likely magic $(SiO_8)_2O_2H_3^-$ cluster formation mechanism.

FRAGMENT PRODUCTION **CLUSTER ISOMERS FORMED** **MAGIC CLUSTER PRODUCTION** **HYDRATION OF CLUSTERS**

very abundant. This magic cluster population, however, we suggest, although stable against transforming into other higher energy cluster isomers would, like most silica species, in the presence of H_2O rapidly react to give rise to the observed magic $(SiO_2)_8O_2H_3^-$ cluster peak. In order for this supposed magic cluster formation process to occur we would assume that the presence of significant quantities of water would only be favorable at conditions prevailing after the production of magic $(SiO_2)_8OH^-$ clusters. This could simply be due to a cooling of the laser-induced plasma as it leaves the silica surface with first silica cluster isomers (possibly containing OH^-/H^+) forming and then later water forming from the condensation of OH^- and H^+ ions. Only at this later stage would we suppose that the magic $(SiO_2)_8O_2H_3^-$ clusters would be formed via hydration reaction. A schematic illustration of this hypothesis is shown in Fig. 3.

In a previous investigation we have theoretically identified a particularly stable stoichiometric $(SiO_2)_8$ magic cluster structure,[8] the occurrence of which we hope will be verified by experiment. This ground state cluster, like the ground state $(SiO_2)_8O^{2-}$ cluster core, also has a relatively large gap in its energy spectrum between it and its energetic next near-

est neighbor isomer and also displays four symmetric terminating $Si=O$ groups. The two clusters, however, are otherwise quite different structurally with the $(SiO_2)_8OH^-$ ground state cluster having a cagelike morphology whereas the stoichiometric $(SiO_2)_8$ cluster takes an open, near-planar form. Although it is tempting to link these two magic clusters, the differences in structure make it unlikely that the formation route of the $(SiO_2)_8OH^-$ magic cluster proceeds via its stoichiometric counterpart. Conversely, we note that we have previously found a very low-energy Si_7O_{14} cluster (energetically ~8 meV/atom above the ground state Si_7O_{14} cluster calculated at a 6-31G(d,p)/B3LYP level of theory[8,19]) which displays many of the structural motifs of both the $(SiO_2)_8OH^-$ and $(SiO_2)_8O_2H_3^-$ cluster cores. This low-energy Si_7O_{14} has C_{3v} symmetry and a symmetric three-coordinated oxygen center [like the $(SiO_2)_8O_2H_3^-$ ground state cluster core] and has four near-tetrahedrally arranged $Si=O$ terminations [much like both the $(SiO_2)_8OH^-$ and $(SiO_2)_8O_2H_3^-$ ground state cluster cores]. This Si_7O_{14} cluster is shown in Fig. 4, where the obvious structural similarities between it and the hydrogen-terminated Si_8O_{16}-based clusters can be seen. Based on the comparable structures and the low energy
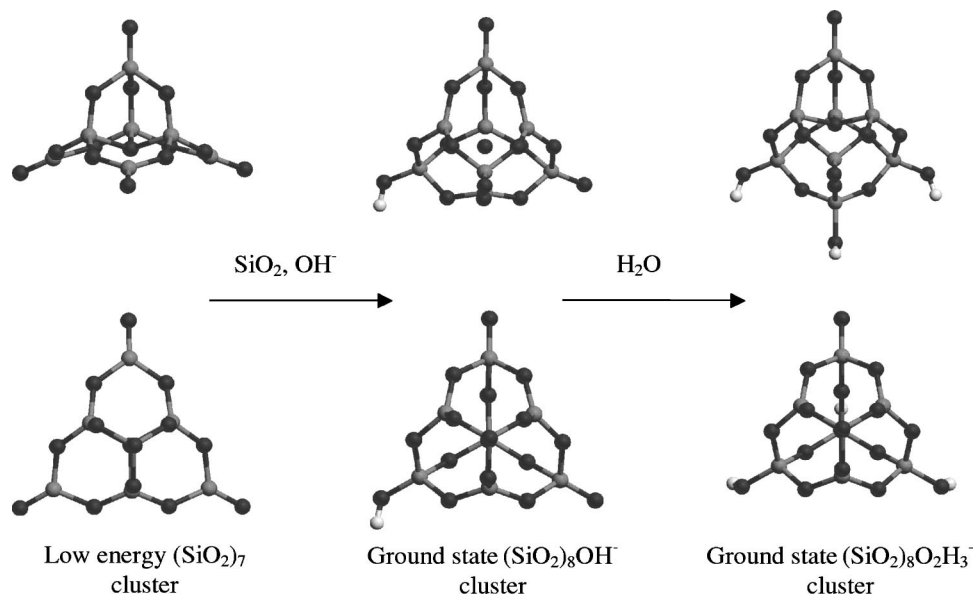

SiO_2, OH^- H_2O

Low energy $(SiO_2)_7$ cluster   Ground state $(SiO_2)_8OH^-$ cluster   Ground state $(SiO_2)_8O_2H_3^-$ cluster

FIG. 4. Structural relationships between a low-energy $(SiO)_7$ cluster (left), the ground state $(SiO_8)_2OH^-$ cluster (middle), and the ground state $(SiO_8)_2O_2H_3^-$ cluster (right). The top group of three clusters and the bottom group of three clusters are viewed from similar angles, respectively, for ease of comparison.

of the Si_7O_{14} cluster it is possible that, via addition of SiO_2 and OH^-, it may also play a role in the formation of the $(SiO_2)_8OH^-$ magic cluster.

IV. CONCLUSIONS

Via carefully exploring the PES of $(SiO_2)_8OH^-$ and $(SiO_2)_8O_2H_3^-$ clusters, the low-energy isomer spectra of both are calculated employing accurate DF calculations. Using both these spectra and the corresponding DF energy-minimized structures, we attempt to rationalize the structure and the observed unusually high abundance of $(SiO_2)_8O_2H_3^-$ magic clusters resulting from the laser ablation of hydroxylated silica. We find that there seems to be no strong energetic preference for any particular $(SiO_2)_8O_2H_3^-$ isomer but that the ground state $(SiO_2)_8O_2H_3^-$ cluster is structurally very similar to a specific ground state $(SiO_2)_8OH^-$ cluster which itself seems to be strongly preferred over other isomers. On this basis, and the known occurrences of both $(SiO_2)_8O_2H_3^-$ and $(SiO_2)_8OH^-$ cluster populations in experiment, we suggest that the observed abundance of the magic $(SiO_2)_8O_2H_3^-$ cluster is dependent on the presence of the energetically preferred ground state $(SiO_2)_8OH^-$ cluster. The structure of both $(SiO_2)_8$-based ground state clusters appears not to be linked to the previously established stoichiometric $(SiO_2)_8$ ground state[8] but is, however, structurally similar to a low-energy $(SiO_2)_7$ also found in previous studies.[8,19] The ground state $(SiO_2)_8OH^-$ cluster is found to have a very symmetric cage-like core structure with a tetrahedrally coordinated oxygen center. This $(SiO_2)_8O^{2-}$ cluster core is also found to possess four tetrahedrally symmetric Si=O terminations making it a possible candidate for cluster-based ionic materials.

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