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Structure, energies, and vibrational properties of silica rings in SiO₂ glass

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We have carried out *ab initio* molecular orbital calculations on four isomers of Si₉O₂₅H₁₄ modeling the local structure of SiO₂ glass at the Hartree-Fock level. These clusters consist of two-, three-, four-, five-, and/or six-membered silica rings. The strain energies of the two-, three-, and four-membered rings are estimated by comparing the total energies of the relevant isomers. The strain energy of the four-membered ring is estimated to be 0.02 eV, indicating that the configuration of the four-membered ring is almost fully relaxed. The strain energies of the two- and three-membered rings are calculated to be 1.85 and 0.26 eV, respectively, and these values are in good agreement with the previous results calculated for the continuous SiO₂ network models based on a generalized-gradient approximation to density-functional theory [D. R. Hamann, Phys. Rev. B **55**, 14 784 (1997)]. It has been shown that there exist bonding wave functions that are localized in these small membered rings. We then have performed frequency calculations for the clusters, and the vibrational modes associated with these silica rings are discussed.

I. INTRODUCTION

There is a general agreement that the structure of vitreous silica consists of a disordered network of corner-sharing SiO₄ tetrahedra.^{1,2} However, two distinctive lines seen at 495 (*D*₁) and 606 (*D*₂) cm⁻¹ in the Raman spectra of vitreous silica cannot be predicted by a simple random network of corner-sharing SiO₄ tetrahedra because of their unusually sharp features.³ Although numerous structural models have been proposed for their origin,⁴ recent first-principles approaches such as molecular-dynamics simulations⁵ and quantum chemical calculations⁶ conclusively demonstrated that, as has been proposed originally by Galeener and co-workers,^{7,8} the *D*₁ and *D*₂ lines should be assigned to in-phase breathing motions of oxygen atoms in puckered four- and planar three-membered ring structures, respectively. This is certainly a clear evidence for regular structures of intertetrahedral linkage, namely, the intermediate-range order¹ in SiO₂ glass.

It is worth mentioning that such small-membered ordered rings cannot usually be found in any of silica crystalline polymorphs, indicating that these rings can be regarded as inherent structures in SiO₂ glass. It is probable that the configurations of the small rings peculiar to a glassy system originate from the potential surfaces localized on the intermediate-range scale (~10–20 Å) in its liquid state. If a liquid is cooled rapidly enough so that detectable nucleation and crystal growth cannot occur at the melting point *T*_m, the atomic configurations characterized by the localized potential surface will be retained depending on the cooling rate. That is, as for SiO₂ glass, the populations of three- and four-membered rings are expected to increase with increasing cooling rate. This expectation is indeed in agreement with the experimental results showing that the intensities of *D*₁ and *D*₂ lines increase with increasing cooling rate or fictive temperature⁹ (see Fig. 1). Recent molecular-dynamics simulations also have demonstrated similar cooling-rate effects on the size distribution of rings in amorphous silica.¹⁰ It can hence safely be said that the stability of the intermediate-

range order in a glass is a measure of the stability of the glass itself and that the locally stable sites in the glass structure will behave as a “built-in resistance to structural change”¹¹ to show little reorganization of the atomic configurations on cooling from *T*_m to glass transition temperature *T*_g. Furthermore, it is interesting to note that the vibrations associated with the intermediate-range ordering regions are suggested to explain the anomalous low-frequency (10–100 cm⁻¹) dynamics of glasses,^{12,13} i.e., the so-called “boson peak.”

Thus, our knowledge of the energetics of small silica rings will shed light on the stability, structure, and dynamics of SiO₂ glass. The strain energies in small-membered silica rings were previously estimated from the Hartree-Fock (HF) cluster calculations on the basis of the Born-Haber cycles.^{14–17} As for the three-membered ring, for example, the strain energy was obtained from the reaction

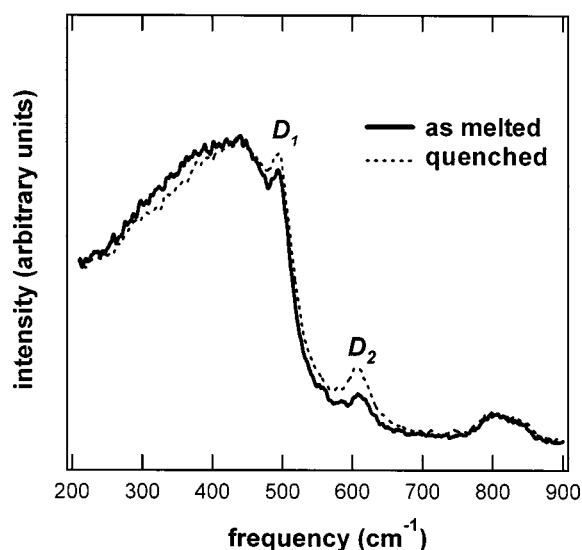


FIG. 1. Unpolarized Raman spectra of as-melted and quenched vitreous silica. The quenched sample was obtained by rapid removal of the sample from the furnace into water. Raman spectra were measured using 514.5 nm line of Ar⁺ laser as an exciting beam.

$H_6Si_3O_3 + 3SiH_2(OH)_2 = 3(SiH_2OH)_2O$, in which three Si-O bonds in the ring are converted to similar bridging bonds in the open cluster. Hamann¹⁸ has, however, proposed that these HF calculations do not reflect possible effect of the condensed environments in which the strained rings of interest actually reside. Furthermore, the author¹⁸ pointed out that the obtained strain energies are less than straightforward since they will include errors produced by the substitution of H_2SiO_2 tetrahedra for SiO_4 tetrahedra and by a transferability assumption of a hydration energy. Hamann,¹⁸ therefore, used continuous SiO_2 network models and carried out density-functional theory calculations based on the generalized-gradient approximation (GGA) to evaluate the strain energies of the two- and three-membered rings in his models; the strain energies were obtained by a straightforward subtraction of the energy of α quartz from the energies of the strained-ring solids. The results of his calculations gave significantly lower strain energies than the previous estimates from the cluster calculations; for example, he obtained a strain energy of 0.25 eV for three-membered rings, compared to the most reliable value [0.81 eV (Ref. 14)] obtained from the HF cluster calculations.

However, it would be difficult to conclude which methods, HF or GGA approximations, yield more reliable strain energy because no direct experimental comparisons are possible at present. It will hence be useful to estimate the strain energies by an alternative approach. In this paper, we evaluate the energies of strained silica rings from HF cluster calculations without using the idea of Born-Haber cycles. We employ here relatively large clusters consisting of two-, three-, four-, five-, and/or six-membered silica rings, and a strain energy of interest is estimated straightforwardly from the difference in total energy between the relevant clusters. We also investigate the vibrational properties of the model clusters and compare the calculated results with the observed vibrational spectra.

II. MODELS AND CALCULATIONAL PROCEDURES

In a previous paper,⁶ we reported the results of *ab initio* molecular-orbital (MO) calculations of a silica cluster consisting of 9 $Si(O_{1/2})_4$ tetrahedra in which the three- and four-membered rings were so connected by bridging oxygens as to form an additional six-membered ring; the dangling bonds of “surface” oxygen atoms of the cluster were terminated by hydrogen atoms, resulting in the $Si_9O_{25}H_{14}$ composition. It has been shown that the predicted geometries are in good agreement with the observed ones and that the cluster yields the well localized breathing modes of the four- and three-membered rings, which are quite consistent with the observed frequencies and isotopic shifts of the D_1 and D_2 Raman lines, respectively. In the present paper, we further employ three additional isomers of $Si_9O_{25}H_{14}$ to estimate the strain energies of silica rings. In what follows, the cluster consisting of l -, m -, and n -membered rings is referred to as model l - m - n ; the clusters used in this study are models 4-4-5, 3-5-5, and 2-4-5 as well as model 3-4-6 reported previously⁶ (see Fig. 2). The geometries of these clusters were fully optimized at the HF/6-31G(*d*) level.¹⁹ We have also evaluated their harmonic vibrational frequencies at the same level of theory. No imaginary frequencies were obtained for all the

clusters employed, indicating that thus obtained optimized geometries correspond, respectively, to the different minimum energy structures. All *ab initio* MO calculations in this work were carried out using the GAUSSIAN 94 computer program²⁰ on the CRAY T94/4128 supercomputer.

III. RESULTS

A. Structural parameters

Figure 2 shows the optimized geometry of the model clusters calculated at the HF/6-31G(*d*) level, and Table I shows the optimized structural parameters. One sees that the average structural parameters are insensitive to the type of the clusters employed. The exceptions are the Si—Si bond distance and the Si—O—Si bond angle calculated for model 2-4-5, which are appreciably shorter and smaller, respectively, than those calculated for the other clusters. This discrepancy results from the edge-sharing unit in model 2-4-5; the optimized Si—Si bond distance and Si—O—Si bond angles for the edge-sharing unit were calculated to be 2.367 Å and 91°, respectively.

It should be noted that all the structural parameters calculated for the present model clusters, except the Si—Si bond distance and Si—O—Si bond angle in model 2-4-5, are in good agreement with the experimental values observed for SiO_2 glass.²¹⁻²³ This indicates that not only model 3-4-6, whose structural parameters were reported in a previous paper,⁶ but also the other models newly employed here reasonably represent the structure of actual SiO_2 glass on the intermediate-range scale.

We further notice from Fig. 2 that the geometries of the three- and four-membered rings are basically the same irrespective of the type of the clusters containing these rings, indicating that the three- and four-membered rings have their own favorable intertetrahedral linkages. That is, the three- and four-membered rings embedded in the present model clusters are all characterized by nearly planar and puckered configurations, respectively. This result suggests that such planar and puckered structures are highly stable even if they are connected by Si—O—Si bond with the other types of silica rings and that most of the three- and four-membered rings in actual SiO_2 glass will have such regular configurations. On the other hand, the geometries of the larger five- and six-membered rings are considerably distorted, resulting in the irregular configurations depending on the clusters. Thus we consider that the potential energy function of these larger rings will be rather flat compared with that of the smaller three- and four-membered rings, allowing a great variety of configurations. In other words, these larger rings will permit full relaxation owing to a number of internal degrees of freedom, and the strain energy of these larger rings will be almost completely relaxed by changing their configurations.

The two-membered ring in model 2-4-5, or the edge-sharing unit, is also characterized by a planar regular structure. As mentioned above, however, the edge sharing tetrahedra are significantly strained, showing a considerable distortion of the O-Si-O (89°) and Si-O-Si (91°) bond angles. Thus we consider that this regular configuration of the two-membered ring results from the structural constraint to keep such an edge-sharing geometry.

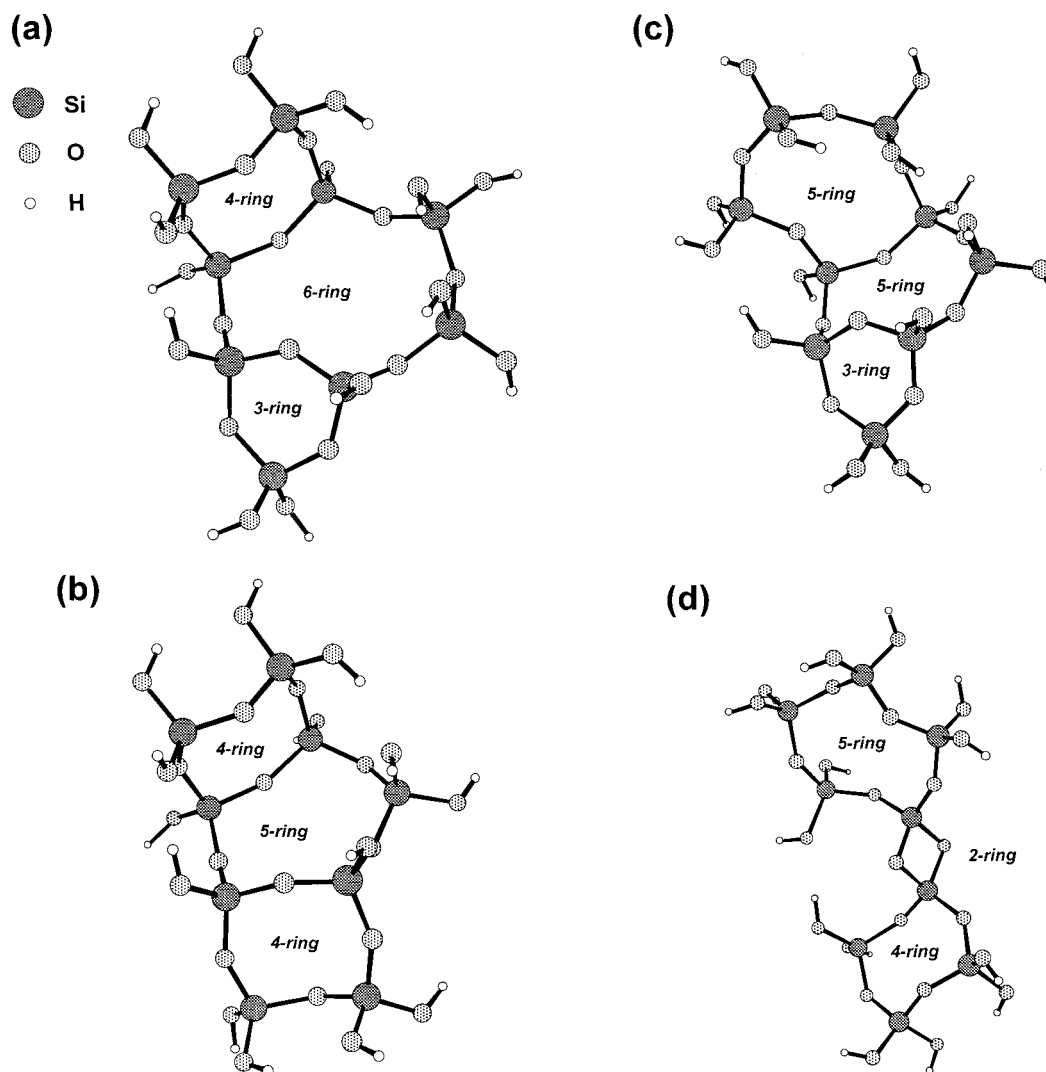


FIG. 2. Optimized geometries of the model clusters calculated at the HF/6-31G(d) level. All the clusters have the same stoichiometry of $\text{Si}_9\text{O}_{25}\text{H}_{14}$: (a) Model 3-4-6, (b) model 4-4-5, (c) model 3-5-5, and (d) model 2-4-5.

B. Strain energies of two-, three, and four-membered rings

We next turn our attention to the strain energies ΔE of the silica rings. As pointed out in the previous subsection, the five- and six-membered rings in the present model clusters will have relatively unconstrained geometries. In this study,

we hence assume that these rings do not have appreciable strain energies, namely, ΔE_5 and $\Delta E_6 = 0$. We further assume that strain energies of the two- (ΔE_2), three- (ΔE_3), and four-membered rings (ΔE_4) are independent of the type of the cluster since the geometries of the respective rings do

TABLE I. Optimized structural parameters (averaged values) of the model clusters calculated at the HF/6-31G(d) level. The corresponding observed values for SiO_2 glass are also shown.

| | Bond distances (\AA) | | | Bond angles (degree) | |
|-------------|--|--|--------------------|----------------------|--------------------|
| | Si—O | O—O | Si—Si | Si—O—Si | O—Si—O |
| calc. | | | | | |
| Model 2-4-5 | 1.624 | 2.657 | 2.999 | 133.9 | 109.4 |
| Model 3-4-6 | 1.622 | 2.653 | 3.059 | 142.3 | 109.5 |
| Model 3-5-5 | 1.622 | 2.648 | 3.057 | 142.1 | 109.5 |
| Model 4-4-5 | 1.621 | 2.647 | 3.097 | 146.8 | 109.5 |
| Obs. | 1.608, ^a 1.624 ^b | 2.626, ^a 2.652 ^b | 3.077 ^a | 143 ^c | 109.5 ^b |

^aReference 21.

^bReference 22.

^cReference 23.

TABLE II. Total energies of the model clusters calculated at the HF/6-31G(d) level.

| | Energy (eV) |
|-------------|-------------|
| Model 2-4-5 | -121 960.13 |
| Model 3-4-6 | -121 961.72 |
| Model 3-5-5 | -121 961.74 |
| Model 4-4-5 | -121 961.96 |

not show any cluster dependence as well.

On the basis of the above assumptions, we can estimate the values of ΔE_n ($n=2, 3$, and 4) by calculating the total-energy difference between the relevant clusters. The total energies of the model clusters are shown in Table II. To begin with, we calculate the values of ΔE_4 . The total-energy difference between models 3-4-6 and 3-5-5 will represent the strain energy difference between $\Delta E_3 + \Delta E_4$ and ΔE_3 , namely, ΔE_4 . This difference is calculated to be 0.02 eV indicating that the strain energy for the four-membered ring is almost zero. We can further calculate the value of $\Delta E_3 - \Delta E_4$ by subtracting the total energy of model 3-4-6 and that of model 4-4-5, which is calculated to be 0.24 eV. Since we have got the value of ΔE_4 (0.02 eV), ΔE_3 is estimated to be 0.26 eV. Finally, we subtract the total energy of model 2-4-5 between that of model 4-4-5, which represents $\Delta E_2 - \Delta E_4$ (1.83 eV) and then the value of ΔE_2 results in 1.85 eV. Consequently, the values of ΔE_2 , ΔE_3 , and ΔE_4 are estimated to be 1.85, 0.26, and 0.02 eV, respectively.

IV. DISCUSSION

A. Comparison with the previous strain energies

1. Four-membered rings

To our knowledge, the strain energies of puckered four-membered rings have not been estimated from GGA and HF calculations. Galeener⁷ previously estimated the strain energy of a planar four-membered ring on the basis of the angular dependence of the energy of a Si—O—Si bridging unit derived from H₆Si₂O₇ HF calculations;²⁴ the value of ΔE_4 for the planar four-membered ring was estimated to be 0.16 eV. Assuming the ideal tetrahedral SiO₄ units, Galeener⁷ found that each Si—O—Si bond angle θ of the planar four-membered ring is calculated to be 160.5°, which is greater than the minimum (152°) in the Si—O—Si bond-bending potential function.²⁴ Galeener⁷ then predicted that the planar four-membered ring will tend to become puckered, since this puckering always results in a lowering of the angle θ and hence reduces ring energy. Such Galeener's prediction is indeed consistent with our calculations. That is, all the four-membered rings in the present model clusters have puckered configurations, and the strain energy of the puckered ring is 0.02 eV, which is much smaller than the value estimated from the planar four-membered rings. It is hence probable that the four-membered rings in actual SiO₂ glass attempt to reduce its strain energy by relaxing the ring geometry, resulting in a puckered configuration having almost no strain energy.

TABLE III. Strain energies and geometries of three-membered rings.

| | ΔE_3 (eV) | Si—O (Å) | Si—O—Si (°) | O—Si—O (°) |
|------------------|-------------------|--------------------|--------------------|--------------------|
| This work | 0.26 | 1.627 ^a | 132.9 ^a | 106.5 ^a |
| GGA ^b | 0.25 | 1.640 | 131.0 | 109.0 |
| HF ^c | 0.81 | 1.646 | 136.7 | 103.3 |

^aAverage values calculated for the three-membered rings in models 3-4-6 and 3-5-5.

^bReference 18.

^cReference 14.

2. Three-membered rings

Table III shows the strain energy and average ring bonding geometries obtained for the present three-membered rings along with those reported previously. As for the HF strain energy based on a Born-Haber cycle, we only show the most reliable value,¹⁴ which was pointed out by Hamann,¹⁸ among the previous HF studies.

Hamann¹⁸ previously pointed out that the GGA strain energy is more than three times smaller than the HF strain energy. However, we do not see such a discrepancy between the present HF (0.26 eV) and GGA (0.25 eV) strain energies; rather there is a good agreement between the two methods. This result indicates that if we do not use the Born-Haber cycle and transferability assumptions of a hydration energy, which are probably the main drawback of the previous HF calculations, we can get the HF strain energy of the three-membered ring that is comparable to the GGA strain energy.

It is also interesting to note that the Si—O—Si and O—Si—O bond angles calculated for the present three-membered rings agree well with those obtained from the GGA calculations (see Table III). Such good correspondence between the present cluster calculations and the GGA allows us to suggest that long-range Coulombic forces that will exist in actual silica glass do not play an important role in determining the geometry and strain energy of three-membered rings. In other words, the bonding wave functions around the three-membered rings are expected to be localized, and their structures and energies are hardly affected by the surrounding environments. Indeed, we have found that in the valence states there exists a molecular orbital that is highly localized in a three-membered ring [see Fig. 3(b)]. We also have found a valence orbital localized in a four-membered ring [see Fig. 3(a)]. These localized orbitals result from an overlap of the O 2*p* orbitals, resulting in π -like bonding. Thus we consider that the stability of the π -like bonds will play a vital role in determining the regular geometries of the three- and four-membered rings in SiO₂ glass.

3. Two-membered rings

Table IV compares the strain energies and average ring bonding geometries of two-membered rings obtained from different methods. We see from Table IV that the present strain energy of the two-membered ring is much larger than that of the three-membered ring shown in Table III. Such a large strain energy of the two-membered rings most likely results from a significant distortion of the SiO₄ tetrahedral units in the edge-sharing structure.

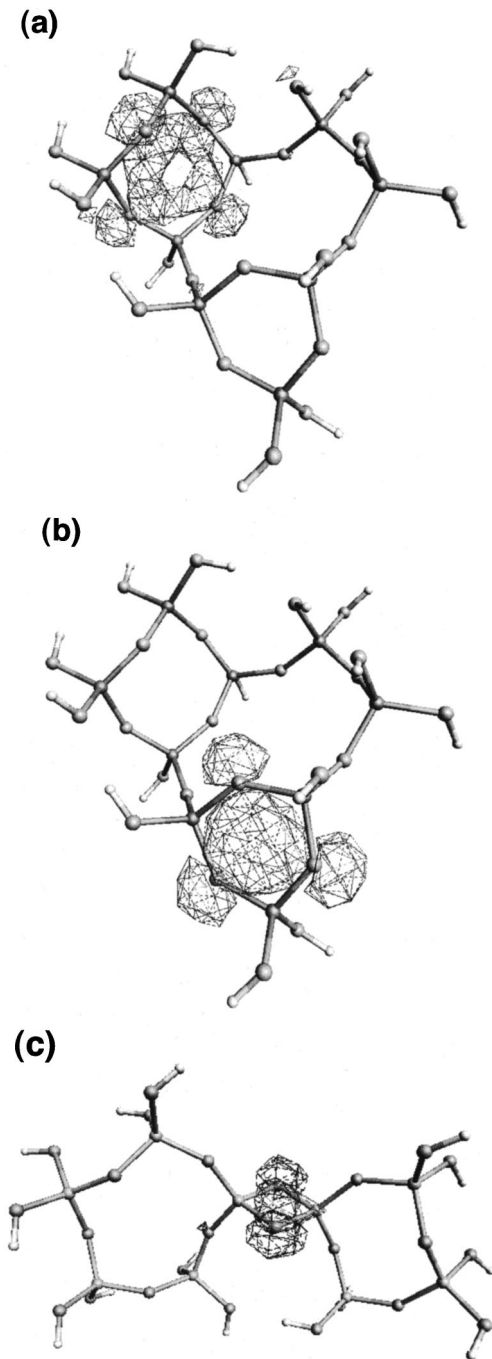


FIG. 3. Examples of the valence molecular orbitals localized in (a) four-, (b) three-, and (c) two-membered silica rings.

We also notice from Table IV that the present strain energy is slightly higher than the GGA value by ~ 0.6 eV. This discrepancy may be ascribed to the strain energies of the four- and/or five-membered rings in model 2-4-5. In the present calculations, we assumed that all the clusters employed in this study have the same strain energy for the respective n -membered silica rings. However, the SiO_4 tetrahedra in the two-membered ring in model 2-4-5 are considerably deformed, and the adjacent four- and five-membered rings also share the deformed SiO_4 units. It is hence probable that such four- and five-membered rings in model 2-4-5 are geometrically constrained as compared with those in the other clusters, resulting in the larger values of

TABLE IV. Strain energies and geometries of two-membered rings.

| | ΔE_2 (eV) | Si—O (Å) | Si—O—Si ($^\circ$) | O—Si—O ($^\circ$) |
|------------------|-------------------|--------------------|----------------------|---------------------|
| This work | 1.85 | 1.657 ^a | 91.2 ^a | 88.8 ^a |
| GGA ^b | 1.23 | 1.678 | 90.3 | 89.7 |
| HF ^c | 1.83 | 1.660 | 91.3 | 88.7 |

^aAverage values calculated for the two-membered rings in model 2-4-5.

^bReference 18.

^cReference 15.

ΔE_4 and ΔE_5 than the other ones. Consequently, a simple subtraction of the total energy of model 2-4-5 from that of model 4-4-5 will represent the strain energy not only of the two-membered ring but also of the “strained” four- and five-membered rings in model 2-4-5.

In spite of the discrepancy between the present and GGA values, it can be said that relative energy differences among the strain energies shown in Table IV are not so large as compared with the case of the three-membered rings shown in Table III. Even the previous HF calculation based on a Born-Haber cycle¹⁵ can predict the strain energy that is comparable to the present value as well as the GGA approximations.²⁵ Thus we consider that the bonding wave functions around the two-membered rings are much more localized than those around the three-membered rings; as shown in Fig. 3(c), such a highly localized molecular orbital can be found in model 2-4-5. This indicates that the solid-state environment has only a minor effect on the strain energy of the two-membered rings similar to the case of the three-membered rings.

B. Vibrational properties of rings

We have previously shown that clusters of atoms modeling the local structure of silica glass, for example, model 3-4-6 in this study, yield the well localized breathing modes of the four- and three-membered rings, which are quite consistent with all known vibrational properties of the D_1 and D_2 defect lines, respectively, in the Raman spectrum of vitreous SiO_2 .⁶ In this work, since we further employed models 3-5-5, 4-4-5, and 2-4-5 along with model 3-4-6, it is interesting to compare the vibrational properties of these newly introduced clusters with those reported previously.

Table V shows the vibrational frequencies associated with the two-, three-, and four-membered rings calculated for the present model clusters. We found that these ring modes are highly localized and decoupled from the motions of the extra-annular atoms. We see from Table V that the vibrational frequency associated with the three-membered ring in model 3-5-5 is in good agreement with that in model 3-4-6, implying that the vibrational frequency of the three-ring mode is almost constant irrespective of the type of the cluster. On the other hand, it appears that there is a slight scatter among the calculated frequencies of the four ring modes. For example, model 4-4-5 yields two rather different vibrational frequencies for the four-ring modes at 529 and 539 cm^{-1} ; two four-membered rings in this model almost equally contribute to these two types of breathing modes. It should be

TABLE V. Harmonic vibrational frequencies of the n -membered ($n=2,3,4$) silica rings mode calculated at the HF/6-31G(d) level.

| | ν_H^a | ν_T^b |
|------------------------|-----------|-----------|
| <i>Four-ring mode</i> | | |
| Model 3-4-6 | 531 | 526 |
| Model 4-4-5 | 529 | 525 |
| | 539 | 527 |
| Model 2-4-5 | 539 | 524 |
| <i>Three-ring mode</i> | | |
| Model 3-4-6 | 652 | 653 |
| Model 3-5-5 | 651 | 652 |
| <i>Two-ring mode</i> | | |
| Model 2-4-5 | 765 | 771 |
| | 771 | 778 |

^aVibrational frequencies calculated for the H-terminated clusters.

^bVibrational frequencies calculated for the T-terminated clusters.

noted, however, that if we replace all the surface H atoms by tritium (T) atoms, the two vibrational frequencies tend to get close to each other; the resultant frequencies (525 and 527 cm^{-1}) are comparable to the frequency of the four-ring mode of the T-terminated model 3-4-6 (526 cm^{-1}). This indicates that the splitting of the four-ring modes in model 4-4-5 results from an accidental degeneracy or a resonance between the ring modes and the surface OH motions. The possibility of such a degeneracy has already been pointed out in a previous paper.⁶ Model 2-4-5 also gives the four-ring mode at 539 cm^{-1} for the H-terminated cluster, which is somewhat higher than that of the corresponding frequency of model 3-4-6 (531 cm^{-1}). However, one sees a rather good correspondence between the frequencies of models 2-4-5 (524 cm^{-1}) and 3-4-6 (526 cm^{-1}) when the terminal H atoms are replaced by the T atoms. Thus, a slight discrepancy between the frequencies of the two H-terminated clusters may also result from the interaction between the four-ring modes and the surface OH motions.

Considering these things mentioned above, we can expect all the clusters employed in this work to give basically similar vibrational frequencies not only for the three-membered rings but also for the four-membered rings. This is consistent with the two sharp Raman features in the Raman spectrum of SiO_2 glass, seen at 495 and 606 cm^{-1} . Although the raw frequency values calculated at the HF level are systematically higher than the observed ones by about 10–12% because of the neglect of electron correlation,²⁶ the ratio of the two ring modes ($\sim 652/\sim 532 = \sim 1.23$ for the H-terminated clusters and $\sim 652/\sim 526 = \sim 1.24$ for the T-terminated clus-

ters) is in good agreement with that of the observed one (606/495 = 1.22). Thus we consider that the three- and four-ring modes obtained in the work indeed correspond to the observed two sharp Raman lines in SiO_2 glass, which further confirms Galeener's predictions.^{7,8}

It should be worth mentioning that the two-membered ring has several vibrational modes in the frequency region from ~ 760 to ~ 780 cm^{-1} (see Table V). If we take into account the systematic errors at the HF level, these vibrational are expected to occur in the frequency range from ~ 700 to ~ 730 cm^{-1} . However, the observed Raman spectrum of SiO_2 glass does not show any spectral feature in this frequency range. It is hence most probable that the two-membered rings or the edge-sharing units hardly exist in the Si—O—Si network in SiO_2 glass. This can be explained by the large strain energy of the highly constrained edge-sharing units mentioned above.

V. CONCLUSIONS

We obtained the HF strain energies of the two-, three-, and four-membered silica rings without using the Born-Haber cycle and transferability assumptions. All the four-membered rings in the present model clusters have puckered geometries, and their strain energy is almost zero (0.02 eV). This indicates that the four-membered ring can relax its possible strain energy by puckering. The strain energies of the three- and two-membered rings are calculated to be 0.26 and 1.85 eV, respectively, which are in reasonable agreement with the previous GGA predictions. Such good correspondence between the present HF and GGA calculations strongly suggests that the condensed environments have only a minor effect on the strain energies of these small-membered rings in SiO_2 glass. That is, as shown in Fig. 3, bonding wave functions around the small-membered silica rings are highly localized. The geometries and energies of the n -membered rings ($n=2,3,4$) will hence be governed by such localized potential energy surfaces, resulting in rather regular structures, although the two-membered ring will hardly exist in actual SiO_2 glass because of its large strain energy. Furthermore, in agreement with our previous calculations,⁶ the two sharp Raman lines at 495 and 606 cm^{-1} have been ascribed to breathing motions of oxygen atoms in the puckered four- and planar three-membered rings, respectively.

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