Neutral and cationic free-space oxygen-silicon clusters \( \text{SiO}_n \) (1 < \( n \) ≤ 6), and possible relevance to crystals of \( \text{SiO}_2 \) under pressure

G. Forte\(^a\), G. G. N. Angilella\(^{b,c,d,e,*}\), V. Pittalà\(^a\), N. H. March\(^f,g\), R. Pucci\(^b,d\)

\(^a\)Dipartimento di Scienze del Farmaco, Facoltà di Farmacia, Università di Catania, Viale A. Doria, 6, I-95126 Catania, Italy
\(^b\)Dipartimento di Fisica e Astronomia, Università di Catania, 64, Via S. Sofia, I-95123 Catania, Italy
\(^c\)Scuola Superiore di Catania, Università di Catania, Via S. Nullo, 5/i, I-95123 Catania, Italy
\(^d\)CNISM, UdR Catania, 64, Via S. Sofia, I-95123 Catania, Italy
\(^e\)INFN, Sæz. Catania, 64, Via S. Sofia, I-95123 Catania, Italy
\(^f\)Department of Physics, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium
\(^g\)Oxford University, Oxford, UK

Abstract

Motivated by the theoretical study of Saito and Ono (2011) on three crystalline forms of \( \text{SiO}_2 \) under pressure, quantum-chemical calculations on various free-space clusters of \( \text{SiO}_n \) and \( \text{GeO}_n \) for 1 < \( n \) ≤ 6 are reported here. Both neutral and cationic clusters have been examined, for both geometry and equilibrium bond lengths. Coupled clusters and correlation-corrected MP2 calculations are presented. For the cations, we emphasize especially the structural distortions occurring in removing degeneracies.

PACS: 31.15.Ne, 36.40.Qv

1. Introduction

The background to the present study is to be found in the theoretical work of Stenhouse et al. in this Journal \([1]\). This dealt with scattering...
intensities and partial structure factors in vitreous silica, both X-ray and neutron diffraction experiments being invoked. Our interest in the present Letter focusses on the electron density distribution in free-space clusters such as SiO$_2$, SiO$_4$, and SiO$_6$. This quantum-chemical study has been directly motivated by the theoretical work of Saito and Ono [2] on different crystalline forms of SiO$_2$ under pressure (see also [3] on vitreous silica). In addition to our calculations on the above three neutral clusters of the form SiO$_n$, we have also considered cationic free-space clusters of this kind.

2. Free-space cluster SiO$_2$ by Hartree-Fock (HF) theory

All the clusters studied in this work have been first considered in free space, by performing geometry optimization within the coupled cluster approximation with single and double excitations (CCSD) [4, 5, 6]. Correlation-corrected MP2 calculations were then carried out for the optimization. In all the calculations, performed by means of the Gaussian 09 software [7], the 6-31 basis set, supplemented by polarization and diffuse functions (6-31G+**), was used.

Fig. 1 shows the way in which an O$_2$ molecule, at a fixed bond length 1.21 Å, is brought up to a single Si atom in the neutral cluster SiO$_2$. The distance $d$ was varied from 2 Å to 1.75 Å at intervals of 0.05 Å. Table I reports the HF energies for singlet, triplet, and quintet spin states. While O$_2$ still retains its spin density at the largest distance $d_1 = 2$ Å, the triplet state energy lying below the singlet value, a crossover in energy taking place around 1.85 Å; at 1.75 Å separation the singlet state clearly lies lowest.
Table 1: Energies in Fig. 1 as a function of distance $d_1$, for different spin states.

| $d_1$ (Å) | $E$ (Hartree) |
|-----------|---------------|
|           | singlet       | triplet       | quintet      |
| 2.00      | −439.104      | −439.118      | −439.013     |
| 1.95      | −439.112      | −439.122      | −439.002     |
| 1.90      | −439.121      | −439.125      | −438.990     |
| 1.85      | −439.129      | −439.127      | −438.976     |
| 1.80      | −439.137      | −439.128      | −438.960     |
| 1.75      | −439.144      | −439.128      | −438.941     |

Table 2: Bond lengths and angles for optimized low-lying isomer of SiO$_4$, as shown in Fig. 2.

| distance (Å) | angle (°) |
|--------------|-----------|
| 1–2          | 1.729     | 2–1–3 82.25 |
| 1–3          | 1.729     | 2–1–4 108.5  |
| 1–4          | 1.639     | 2–1–5 108.5  |
| 1–5          | 1.639     | 4–1–5 130.14 |

3. Neutral free-space clusters SiO$_4$

Fig. 2 calculated by HF theory, shows what we consider to be the low-lying isomer of the free-space cluster SiO$_4$. The geometry of this present proposal for the ground state is recorded in Table 2. It is seen that there are two SiO distances which we determine to be 1.64 Å and 1.73 Å respectively. The corresponding angles range from 82.3° to 130°, via the (almost) tetrahedral angle of 109°. It is already relevant to make some contact with the crystalline calculations of Saito and Ono [2] (see especially their Table II). These workers show that at ambient temperature and pressure, the ground-state structure $\alpha$-quartz ($q$-SiO$_2$ in their Table II) has two slightly different bond lengths 1.60 Å and 1.61 Å, with angles near the tetrahedral value $\sim$ 110°. Above a pressure of 2 GPa, a rutile structure ($r$-SiO$_2$) is formed, and Table II records two SiO bond lengths of 1.75 Å and 1.79 Å, which are at least fairly near to our predicted second bond length 1.73 Å for the free-space SiO$_4$ cluster in Fig. 2. Angles were not recorded however for $r$-SiO$_2$ in their Table II.

We shall return briefly to our further results pertaining to SiO$_4$ clusters when we summarize our calculations on cationic free-space clusters below.
4. Neutral free space cluster of a Si atom with six surrounding O atoms

Fig. 4a shows first a neutral cluster in which atom 1 is Si and tetrahedral angles for 4 surrounding O atoms are assumed. The energy and bond distances are recorded in Table 3, the larger distance 1–2 and 1–3 being around 2.3 ± 0.1 Å, compared with 4 shorter bond lengths around 1.66 ± 0.01 Å. Table 4 shows how variation of the geometry away from the tetrahedral angle 109.5° entering Table 3 lowers the HF energy by ∼ 0.008 Hartree, with the cluster form depicted now in Fig. 4b. We note briefly that in Table II of Ref. [2], the longest bond length recorded is for r-SiO$_2$, and is 1.81 Å. We have also considered the stability of the neutral cluster SiO$_6$ with respect to an isolated Si atom plus two ozone molecules O$_3$, finding a relative energy
difference of $\Delta E = -0.373$ hartrees.

5. Some less detailed results with the Si atom replaced by Ge in free-space neutral clusters

Prompted by the solid-state theoretical calculations presented by Saito and Ono [2], we have also studied GeO$_n$ clusters, though in somewhat less detail than their Si counterparts. One of the configurations of the free-space neutral cluster is depicted in Fig. 5 for GeO$_6$. The bond distances and angles are collected in Table 5 for comparison with SiO$_6$ for the neutral cluster shown in Fig. 4b.

6. Singly-charged positive ion clusters SiO$_4^+$ and GeO$_4^+$

Having treated the neutral clusters of SiO$_n$ in some detail, we felt it of interest in longer terms to estimate bond length distortions due to ionization for both SiO$_4^+$ and GeO$_4^+$. We note first that if we were dealing with the free-space tetrahedral molecule silane, then we could appeal to experiment for the symmetry of the cation SiH$_4^+$ (see, e.g., Ref. [8]).

We show therefore in Fig. 6 the proposed structures for these neutral SiO$_4$ and cationic clusters SiO$_4^+$ from the present quantum-chemical technique.

| $n$ | $E(O)$ | $E(Si)$ | $E(Si + nO)$ | $E(SiO_n)$ | $\Delta E$ |
|-----|--------|---------|--------------|------------|-----------|
| 2   | -74.940| -289.017| -438.897     | -439.244   | -0.346    |
| 4   | -74.940| -289.017| -588.777     | -589.384   | -0.607    |
Table 4: Shows geometries of low-lying isomers of SiO$_6$ depicted in Fig. 4.

|          | distance (Å) | angle (°) |
|----------|--------------|-----------|
| SiO$_6$ (Fig. 4a), $E = -739.4260$ Hartree |              |           |
| 1–4      | 1.647        | 5–1–4     | 109.5     |
| 1–5      | 1.669        | 5–1–6     | 109.5     |
| 1–6      | 1.67         | 5–1–7     | 109.5     |
| 1–7      | 1.679        |            |           |
| 1–2      | 2.195        |            |           |
| 1–3      | 2.377        |            |           |
| SiO$_6$ (Fig. 4b), $E = -739.4343$ Hartree |              |           |
| 1–4      | 1.664        | 5–1–4     | 123.07    |
| 1–5      | 1.664        | 5–1–6     | 84.77     |
| 1–6      | 1.664        | 5–1–7     | 123.07    |
| 1–7      | 1.664        |            |           |
| 1–2      | 2.208        |            |           |
| 1–3      | 2.208        |            |           |

Bond lengths and angles are correspondingly recorded in Tab. 5. Analogous results are then shown in Fig. 5 and Tab. 7 for neutral GeO$_4$ and cationic clusters GeO$_4^+$. In the light of the earlier discussion, we note in particular that now two bond lengths are in evidence, the longer being 2.2 Å for GeO$_4^+$.

Additionally in Table 8 we record our calculations of the Mulliken charges, which demonstrate the expected shift of electronic charge from Ge to the O nuclei, due to the high electronegativity of the latter atom.

We conclude this section by recording for both GeO$_4$ and GeO$_4^+$ the one-electron self-consistent field eigenvalues for these neutral and also charged clusters (Tab. 9). As with the bond lengths, even though we are not dealing with stable gas phase molecules like SiH$_4$ and its cation, there are parallels...
Table 5: Bond lengths and angles for optimized low-lying isomer of GeO$_6$, as shown in Fig. 5.

| distance (Å) | angle (°) |
|-------------|-----------|
| 1–7         | 2.333     | 3–7–4 | 123.54 |
| 2–7         | 2.333     | 3–7–5 | 130.04 |
| 3–7         | 1.797     | 3–7–6 | 78.84  |
| 4–7         | 1.797     |       |        |
| 5–7         | 1.796     |       |        |
| 6–7         | 1.797     |       |        |

Figure 6: (Color online) Low-lying isomers predicted theoretically for neutral SiO$_4$ and cationic SiO$_4^+$, the total ground-state energies being $E = -589.3844$ and $E = -588.8507$ a.u., respectively. Bond lengths and angles are given in Tab. 6.

with the Jahn-Teller removal of degeneracy.

7. Summary

Our major conclusion from the present theoretical study concerns the predicted low-lying isomers for the neutral free-space clusters SiO$_n$ ($1 < n \leq 6$), and in briefer fashion for the corresponding Ge clusters. As stressed in Sec. 1, the immediate motivation was afforded by the recent theoretical work of Saito and Ono [2] on three different crystal structures of SiO$_2$ under pressure (see also our own early study on diffraction from vitreous silica in [1]). It is to be hoped that our present results will stimulate experimental studies on the free-space clusters SiO$_n$ for small $n$, and possibly also on the comparison between the electron density distribution in crystalline SiO$_2$ under pressure with vitreous SiO$_2$, also under compression.
|        | distance (Å) | angle (°) |
|--------|--------------|-----------|
| SiO\textsubscript{4} |              |           |
| 1–2    | 1.63         | 2–1–4     | 137.12    |
| 1–3    | 1.63         | 2–1–5     | 137.13    |
| 1–4    | 1.63         | 2–1–3     | 62.24     |
| 1–5    | 1.63         |           |           |
| SiO\textsubscript{4}\textsuperscript{+} |             |           |
| 1–2    | 1.729        | 2–1–4     | 108.5     |
| 1–3    | 1.729        | 2–1–5     | 108.52    |
| 1–4    | 1.639        | 2–1–3     | 82.25     |
| 1–5    | 1.639        |           |           |

Table 6: Bond lengths and angles for neutral cluster SiO\textsubscript{4} and cation SiO\textsubscript{4}\textsuperscript{+}, as shown in Fig. 6.

Acknowledgements

The authors thank Dr Saito for correspondence and for providing them with unpublished supplementary information to Ref. [2]. They also thank Dr Tse for providing them Ref. [3] prior to publication, and for useful discussions. NHM is partially supported by the University of Antwerp (UA) through the BOF-NOI, and wishes to thank Professors D. Lamoen and C. Van Alsenoy for thereby making possible his continuing affiliation with UA. NHM also thanks Professors R. Pucci and G. G. N. Angilella for generous hospitality during his stay in Catania.

References

[1] B. Stenhouse, P. J. Grout, and N. H. March, Phys. Lett. A 57, 99 (1976).
[2] S. Saito and T. Ono, Japanese J. Appl. Phys. 50, 021503 (2011).
[3] M. Wu, Y. Liang, J.-Zh. Jiang, and J. S. Tse, in course of publication ..., ... (2011).
[4] J. Cizek, Adv. Chem. Phys. 14, 35 (1969).
[5] G. D. Purvis III and R. J. Bartlett, J. Chem. Phys. 76, 1910 (1982).
[6] G. E. Scuseria, C. L. Janssen, and H. F. Schaefer III, J. Chem. Phys. 89, 7382 (1988).
Figure 7: (Color online) Low-lying isomers predicted theoretically for neutral GeO$_4$ and cationic GeO$_4^+$, the total ground-state energies being $E = -2375.9477$ and $E = -2375.4176$ a.u., respectively. Bond lengths and angles are given in Tab. 7.

[7] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision A.1, Gaussian, Inc., Wallingford, CT, 2009.

[8] A. Krishtal, C. Van Alsenoy, and N. H. March, in course of publication ... (2011).
|   | distance (Å) | angle (°) |
|---|--------------|-----------|
| **GeO$_4$** | | |
| 1–2 | 1.770 | 2–1–4 | 140.31 |
| 1–3 | 1.770 | 2–1–5 | 57.32 |
| 1–4 | 1.770 | 2–1–3 | 140.35 |
| 1–5 | 1.770 | | |
| **GeO$_4^+$** | | | |
| 1–2 | 1.755 | 2–1–4 | 120.58 |
| 1–3 | 1.755 | 2–1–5 | 95.9 |
| 1–4 | 1.755 | 2–1–3 | 118.13 |
| 1–5 | 2.252 | | |

Table 7: Bond lengths and angles for neutral cluster GeO$_4$ and cation GeO$_4^+$, as shown in Fig. 7.

| SiO$_4$ | SiO$_4^+$ | SiO$_6$ | GeO$_4$ | GeO$_4^+$ |
|--------|----------|--------|---------|----------|
| Si     | 2.458    | Si     | 2.440   | Ge       | 2.416    |
| O      | −0.615   | O      | −0.600  | O        | −0.604   |
| O      | −0.615   | O      | −0.600  | O        | −0.604   |
| O      | −0.615   | O      | −0.474  | O        | −0.020   |
| O      | −0.615   | O      | −0.474  | O        | −0.600   |
| O      | −0.020   | O      | −0.600  | O        | −0.084   |
| O      | −0.020   | O      | −0.020  | O        |          |

Table 8: Mulliken charges in free space neutral and cationic clusters.
| GeO₄       | GeO₄⁺      |
|------------|------------|
| -405.39349 | -405.63174 |
| -52.29426  | -405.63137 |
| -46.38488  | -52.53368  |
| -46.38488  | -52.53365  |
| -46.38119  | -46.62474  |
| -20.68764  | -46.62464  |
| -20.68758  | -46.62181  |
| -20.6875   | -46.62164  |
| -20.68743  | -46.62148  |
| -7.34623   | -46.62147  |
| -5.32489   | -21.00925  |
| -5.32489   | -21.00894  |
| -5.32224   | -20.92582  |
| -1.80179   | -20.92566  |
| -1.80075   | -20.9248   |
| -1.80075   | -20.88442  |

Table 9: One-electron eigenvalues of both GeO₄ and GeO₄⁺ (atomic units).