

Modeling Optical and Electronic Properties of Silica Nano-Clusters in Silicon Rich Oxide Films

N.D. Espinosa-Torres^{1,*}, J.F.J. Flores-Gracia¹, J.A. Luna-López¹, A. Morales-Sánchez²,
J.L. Sosa-Sánchez¹, J.C. Ramírez-García³

¹ Centro de Investigaciones en Dispositivos Semiconductores, CIDS-ICUAP-BUAP Puebla México

² Centro de Investigación en Materiales Avanzados S. C. Unidad Monterrey-PIIT, 66600 Apodaca,
Nuevo León, México

³ Facultad de Ciencias Químicas, BUAP Puebla, México

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Quantum effects are very important in nano scale systems such as molecules and clusters constituted of particles from a few to hundreds or a few thousands of atoms. Their optical and electronic properties are often dependent on the size of the systems and the way in which the atoms in these molecules or clusters are bonded. Generally, these nano-structures display optical and electronic properties significantly different of the bulk materials. Silica agglomerates expected in Silicon Rich Oxide (SRO) films have optical properties, which depend directly on size, and their rationalization can lead to new applications with a potential impact on many fields of science and technology. On the other hand, the room temperature photoluminescence (PL) of Si : SiO₂ or Si : SiO_x structures usually found in SRO has recently generated an enormous interest due to their possible applications in optoelectronic devices. However, the understanding of the emission mechanism is still under debate. In this research, we employed the Density Functional Theory with a functional B3LYP and a basis set 6-31 G* to calculate the electronic and optical properties of molecules and clusters of silicon dioxide. With the theoretical calculation of the structural and optical properties of silicon dioxide clusters is possible to evaluate the contribution of silica in the luminescent emission mechanism experimentally found in thin SRO films. It was found that silica contribution to the luminescent phenomenon in SRO thin films is less important than that of the silicon monoxide agglomerates because the number of silica structures, which may show emission in the visible spectrum, is much lower [1], compared to the number of silicon monoxide structures which emit in this region.

Keywords: Nano-crystals, Silicon oxide clusters, Silicon-rich oxide, Luminescence, Spiro-Union, Moieties.

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1. INTRODUCTION

Many researchers have proposed various models to understand the origin of photoluminescence (PL) in silicon rich oxide (SRO) films at room temperature, and some are agree that the Quantum Confinement Effect (QCE) in nanocrystals increases the band gap and modifies the selection rules for radiative transitions. This confinement raises PL of nanocrystals sizes below five nm above the band gap in the visible region. However, QCE cannot explain by itself the behavior of all SRO films at different concentrations [2]. Lioudakisa et al. [3] have suggested the contribution to the PL phenomenon by localized states in the interface between the silicon nanocrystals and the amorphous silica matrix. In addition, Dianov [4] suggest that defects and vacancies in the oxide are responsible for the manifestation of PL in visible region.

Some experimental results published about SRO films deposited by Low Pressure Chemical Vapor Deposition (LPCVD) show that the wavelength of the excitation states (and therefore their energy), the intensity and curve shape of PL spectra of SRO films, depend of the silicon excess.

The structural disorder of some atoms and the compositional variations found in SRO films, induce the generation of localized states in the interface between the crystal and the silica matrix. Energetically, the states that exist at the surface of the nanocrystals are

between the frontiers orbitals [the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO)]. The actual energy position of these states depends on the dimensions or extension of the distorted surface.

The most intense light emission observed in SRO films obtained by LPCVD technique has been reported in films with approximately 5 % excess silicon, but silicon nanocrystals were not observed in those films [5]. Consequently, in SRO films with low silicon excess (< 5 at. %) the emission characteristics should be associated to oxidation states, probably silica amorphous nanoclusters consisting of two-membered-rings (2 MR), three-membered-rings (3 MR), four-membered-rings (4 MR) and hybrid species of some of them [6]. Rather, the interaction between silicon oxygen compounds, or agglomerates of such molecules, could be responsible of or at least contribute in some way to the emission in SRO-LPCVD films.

In this work, we calculated theoretically the IR, UV-Vis and Raman spectra of a selected set of silica agglomerates and they were compared with the experimental results found in the literature for SRO films deposited by LPCVD. The equilibrium energy calculated of several proposed SiO₂ nanostructures at ground state and the six first excitation states result very useful to evaluate the possible contribution to the PL from different silica nanostructures present in SRO films.

* siox130@gmail.com

Only reasonably small size $(\text{SiO}_2)_n$ moieties could emit in the visible region in the nano-structures based on silicon dioxide. The expected emission could be attributed to the effects of stress in these structures contrasting with nanostructures of silicon monoxide, where relatively large moieties (with 13 or more silicon atoms), could emit in the visible region of the spectra due to a significant reduction in the difference of energy between the frontier orbitals [1].

2. THEORETICAL CHEMICAL MODEL

Regardless of the fact that it is not possible to solve the Schrödinger equation analytically for many electron systems, the molecular properties calculated using Density Functional Theory (DFT) [7] should reproduce suitably the corresponding experimental quantities. The less severe the restrictions to the theoretical model, the better the correlation between the experimental and the calculated results.

Any theoretical model proposed to explain the luminescent phenomenon found in SRO films must meet certain conditions. Most importantly, the model should predict a unique energy of the ground state and the number of unpaired electrons and the number of electrons (among other molecular properties) must be calculated using only the type and position of the nuclei involved. A model should not resort, in any way, to “chemical intuition”. Also, it is important, as far as possible, that the magnitude of the error of the calculated energy should increase approximately in proportion to the molecular size, that is, the model should be “size consistent”. Then, the reaction energies can be properly described when it is feasible to anticipate that. Somewhat less important, but highly desirable, is that the model should be “variational”; this means that the calculated energy be as closest as possible to the exact (Schrödinger) energy.

Finally, a model needs to be “practical”, that is, able to solve not only to very simple or idealized systems, but also to problems which are actually of interest and that could be more complicated.

The DFT developed by Hohenberg, Kohn and Sham is one approach for the treatment of electron correlation. Density functional models have “at their heart” the electron density, $\rho(r)$, as opposed to the many electron wave functions, $\Psi(r_1, r_2 \dots)$. There are both distinct similarities and distinct differences between traditional wave function based approaches and electron density based methodologies. As far as similarities are concerned, first the essential building blocks of a many electron wave function are single electron (molecular) orbitals, which are directly analogous to the orbitals used in density functional methodologies. Secondly, from a Self-Consistent Field (SCF) approach, both the electron density and the many electron wave functions are constructed, this requires nearly identical matrix elements [8].

DFT theory considers that the sum of the exchange and correlation energies between electrons in a uniform electron gas can be exactly calculated, knowing only its density. Moreover, Kohn-Sham propose that the ground-state electronic energy (E) as a sum of the kinetic energy, E_T , the electron nuclear interaction energy, E_V , the Coulombic energy, E_J , and the exchange / correlation energy, E_{xc} .

$$E = E_T + E_V + E_J + E_{xc} \quad (1)$$

Except for E_T , all components depend on the total electron density, $\rho(r)$.

$$\rho(r) = 2 \sum_i^{\text{orbitals}} |\psi_i(r)|^2 \quad (2)$$

Here, ψ_i are the so-called Kohn-Sham orbitals and we must estimate the summation over pairs of electrons. Within a finite basis set used (B3LYP-6-31G* density functional calculation of energy preceded by Hartree-Fock 3-21G calculation of geometry) the energy components can be written as follows.

$$E_T = \sum_{\mu}^{\text{basis}} \sum_{\nu}^{\text{functions}} \int \phi_{\mu}(r) \left[-\frac{1}{2} \nabla^2 \right] \phi_{\nu}(r) dr \quad (3)$$

$$E_V = \sum_{\mu}^{\text{basis}} \sum_{\nu}^{\text{functions}} P_{\mu\nu} \sum_A^{\text{nuclei}} \int \phi_{\mu}(r) \left| \frac{Z_A}{|r-R_A|} \right| \phi_{\nu}(r) dr \quad (4)$$

$$E_J = \frac{1}{2} \sum_{\mu}^{\text{basis}} \sum_{\nu}^{\text{functions}} \sum_{\lambda}^{\text{functions}} \sum_{\sigma} P_{\mu\nu} P_{\lambda\sigma} (\mu\nu|\lambda\sigma) \quad (5)$$

$$E_{xc} = \int f(\rho(r), \nabla\rho(r), \dots) dr \quad (6)$$

where ZA is the nuclear charge, r -RA is the distance between the nucleus and the electron, P is the density matrix and $(\mu\nu|\lambda\sigma)$ are two-electron integrals and f is an exchange / correlation functional, which depends on the electron density and perhaps it depends on the gradient of density as well.

The density functional models are particularly attractive for the calculations executed on large molecules, where the cost of second order Moller-Plesset (MP2) models may be prohibitive, and where Hartree-Fock semi-empirical calculations may not be sufficiently accurate. Some of the silicon dioxide structures evaluated are “large molecules”.

In addition, the density functional models are very useful for calculations with high accuracy on inorganic and organic-metallic systems, where Hartree-Fock models may not be sufficiently accurate and where the cost of LMP2 and MP2 models are generally prohibitive.

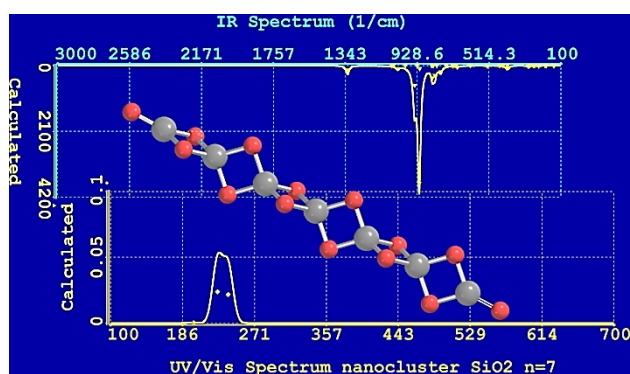
Due to their chemical nature, silicon is considered an inorganic material. Therefore, DFT models can be used to study the $(\text{SiO}_2)_n$ chemical bonds present in the SRO films. Finally, thermo chemical calculations, in particular, those that involve explicit chemical bond making or breaking, and absolute activation energy calculations can also be solved employing density functional. The study of the thermo-chemical properties is very useful to assess the stability of the various proposed structures.

3. ANALYSIS AND DISCUSSION OF THE RESULTS OBTAINED *IN SILICO*

Nayak et al. [9] have found that nanostructures $(\text{SiO}_2)_n$ type chains with $n \leq 6$ are thermodynamically more stable forms of silica. We have calculated optoelectronic and structural properties including IR and UV-Vis spectrum, of linear structures with two member rings (2 MR), with a number of silicon atoms from $n = 4$ to 16. Table 1 shows the obtained energy values and other properties calculated for the previously cited structures and they are compared with those reported in the literature, finding a good agreement [10]. Fig. 1 shows the luminescent emission and the FTIR spectra

Table 1 – Energies and Band Gap calculated for silica nanostructures type chains (SiO₂)_n with two member rings (2 MR)

Number of Silicon atoms	Energy of Activation, eV	Band Gap, eV	HOMO, eV	LUMO, eV
4	-47897.10	5.828	-9.08	-3.25
5	-59873.43	6.306	-9.12	-2.82
6	-38.17*	10.993*	-9.08	-2.70
7	-83824.76	6.384	-9.07	-2.66
8	-95800.40	6.41	-9.06	-2.64
9	-107776.08	6.42	-9.06	-2.63
10	-119751.72	6.43	-9.05	-2.61
11	-131727.40	6.44	-9.05	-2.61
12	-143703.04	6.44	-9.05	-2.60
13	-155678.72	6.44	-	-
14	-167648.47	-	-	-
15	-179630.04	6.45	-9.05	-2.60
16	-191605.37	6.45	-	-
17	-203581.37	5.83	-9.08	-3.25

**Fig. 1** – IR and UV-Vis spectra calculated for 2 MR linear Silica Structure, $n = 7$

obtained by the simulation of a molecule formed with seven SiO₂ bonds. This structure has an emission peak in the violet at approximately 227.42 nm and the most intense peak in the IR absorption spectra correspond with the wavenumber of 917 cm⁻¹. For small silica chains (with less than seven silicon atoms) a small shoulder appears in UV spectra near 200 nm, it vanishes as the structure size increases (spectra not shown). The IR absorption spectra of nano-structures type 2 MR shown an intense peak in the range of 875-952 cm⁻¹ ascribed to the Si-O stretching vibration mode.

Table 2 shows some of the most relevant results obtained for silica nanostructures type 2 MR. It may corroborate that these silica nanostructures emit in the violet region of the spectrum (~227 nm). FTIR of nanostructures type 2 MR fits well with equation:

$$\varphi = 1123n^{-0.09}$$

Where φ is the wave-number (cm⁻¹), n is the number of silicon atoms.

By the other hand, using a basis set B3LYP/6-31G*, the theoretical IR and UV-Vis spectra for Linear Spiral Moieties -LSM- with pairs silicon atoms, for $n = 4, 6, 8 \dots 18$ were evaluated. Fig. 2 presents specific results for $n = 6$ silicon atoms.

The calculated LSM nanostructures show emission in the violet region with two overlapped peaks located in the range of 241 to 269 nm. The highest emission intensity shifts to visible as the size of the structure

increases, and the separation of excitation states will increase, this in turn will give rise to greater emission (see Table 3).

Table 2 – Optical parameters calculated for silica nanostructures (SiO₂)_n type chains with two member rings (2 MR)

Number of Silicon atoms	Wavenumber of main peak in FTIR, cm ⁻¹	Wavelength of more intense peak in UV-Vis, nm
4	1096	246.25
5	952	228.02
6	1398	-
7	917	227.42
8	907	227.27
9	897	227.27
10	891	227.14
11	884	227.14
12	880	227.05
13	875	227.18
14	-	227.10
16	867	227.05

The symmetric and anti-symmetric components of the three fundamentals modes of the Si-O vibration bonds in silica nanostructures can be identified in the FTIR absorption spectra.

The rocking vibration mode of SiO chemical bonds correspond with wavenumber between 875 and 915 cm⁻¹. The bending mode appears in the range from 1000 to 1140 cm⁻¹ (this is the most intense frequency of vibration in all cases) and finally, the stretching vibration mode is in the range of 1305-1328 cm⁻¹.

Table 3 shows IR and UV-Vis results obtained for LSM type silica nanostructures. In addition to the exhaustive work on the silica nanostructures constituted from fewer membered-rings, other small silicon dioxide nano-agglomerates has been simulated to provide additional useful information about oxidation states as responsible of the PL phenomena. It has also calculated IR and UV-Vis spectra for cyclic silica nanostructures. These nanostructures would be formed by the rupture of the two double Si = O bonds located at the ends of linear molecules and the formation of two new Si-O single bonds (see Fig. 3).

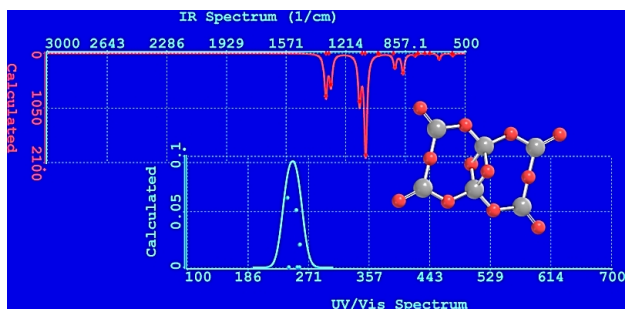


Fig. 2 – IR (up) and UV-Vis theoretical spectra (down) evaluated for silica structure 4 MR SUL

Table 3 – Calculated optical parameters for silica nanostructures (SiO₂)_n type LSM with four member rings (4 MR)

Number of Silicon atoms	Wavenumber of main peak in FTIR, cm ⁻¹	Wavelength of more intense peak in UV-Vis, nm
4	1140 and 1320	269.02
6	1095	241.25
8	1052	241.25
10	1022	253.16
12	1000	252.91
14	986	252.73

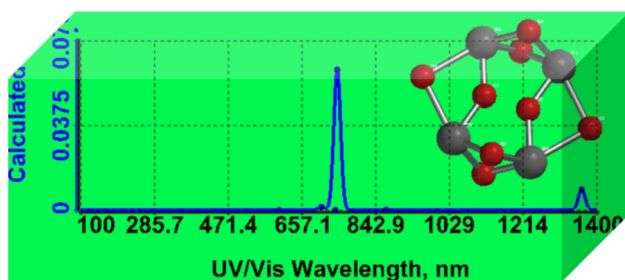


Fig. 3 – UV-Vis spectra computed for cyclic 2 MR Silica nanostructure with four silicon atoms

Table 4 shows optical parameters calculated for cyclic silica nanostructures. When the chain is very small, that means four or five silicon atoms, the cyclic structure will be more stressed increasing the possibility of emission in the visible region of the spectrum.

As observed in Fig. 3, the molecule with $n = 4$ silicon atoms has a very intense emission in the red, with a low emission intensity in the orange region of the spectrum containing two overlapping excitation states (600.04 and 869.73 nm) and a low emission intensity in the near infra-red (1362.14 nm).

The nanostructure with $n = 5$ silicon atoms, shown in Fig. 4, may produce a relatively large intensity in the UV, because this nanostructure has 4 excitation states in the range from 341.76 to 436.07 nm. In addition, a moderate emission in the wavelength of 465.31 nm and a less intense emission in the green at 514.08 nm are expected.

Fig. 5 shows the highest emission intensity for different sizes of cyclic molecules with silicon atoms numbers from $n = 4, 5, 6...$ to 16. In this particular case, the results obtained show that the emission in the visible spectrum is limited to very small molecules up to five silicon atoms. Molecules with a number of silicon atoms greater than 12 apparently can emit only in the UV or have no emission.

Table 4 – Calculated optical parameters for cyclic silica nanostructures (SiO₂)_n with two member rings (2MR).

Number of Silicon atoms	Wavenumber of main peak in FTIR, cm-1	Wavelength of more intense peak in UV-Vis, nm
4	698	745.84
5	830	353.15-514.08
6	921	279.97-314.37
7	876	274.32
8	927	225.73
9	899 y 929	245.24
10	919	220.63
11	918	213.91
12	908	208.65

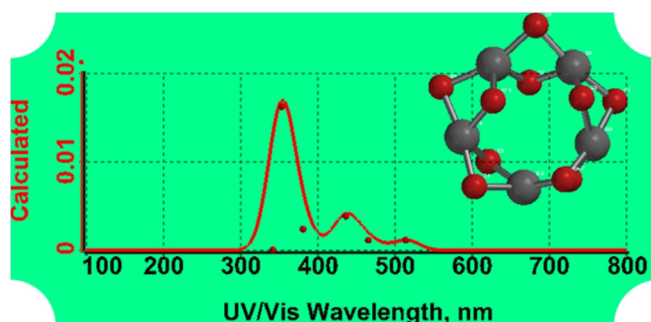


Fig. 4 – *In silico* UV-Vis spectra for a cyclic Silica agglomerate with 5 silicon atoms

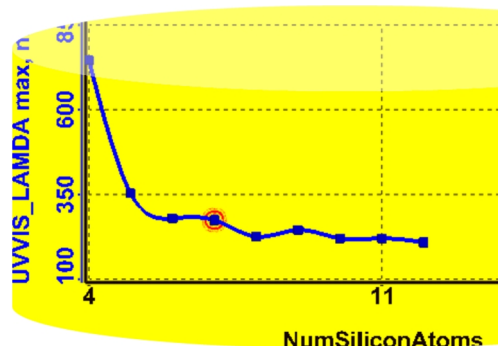


Fig 5 – λ_{max} , vs. Number of Silicon Atoms for Silica nanostructures 2 MR cyclic

Fig. 6a exhibits the structure of cyclic silica nanostructures for twelve silicon atoms and twelve rings of two members each (2MR). This is a molecular ring based on 2 MRs optimized by Zhang [10].

In this particular case the molecular rings could be formed joining the Non Bridging Oxygen (NBO) end groups of a chain of a moiety as shown in Fig. 1 (2MR-based chain). The molecular rings based on edge-sharing 2 MRs are extraordinarily different from bulk crystalline and amorphous silica. Due to the full coordination for all atoms, they cannot form a continuous three dimensional network from side to side with chemical bonds between rings. With the lengthening of the nano-agglomerate, although the stress in the molecular rings caused by the formation of cycles of the (SiO₂)_n chain is quickly released [10], an intrinsic internal stress due to the spiro-links remains on the individual components [11, 12, 13].

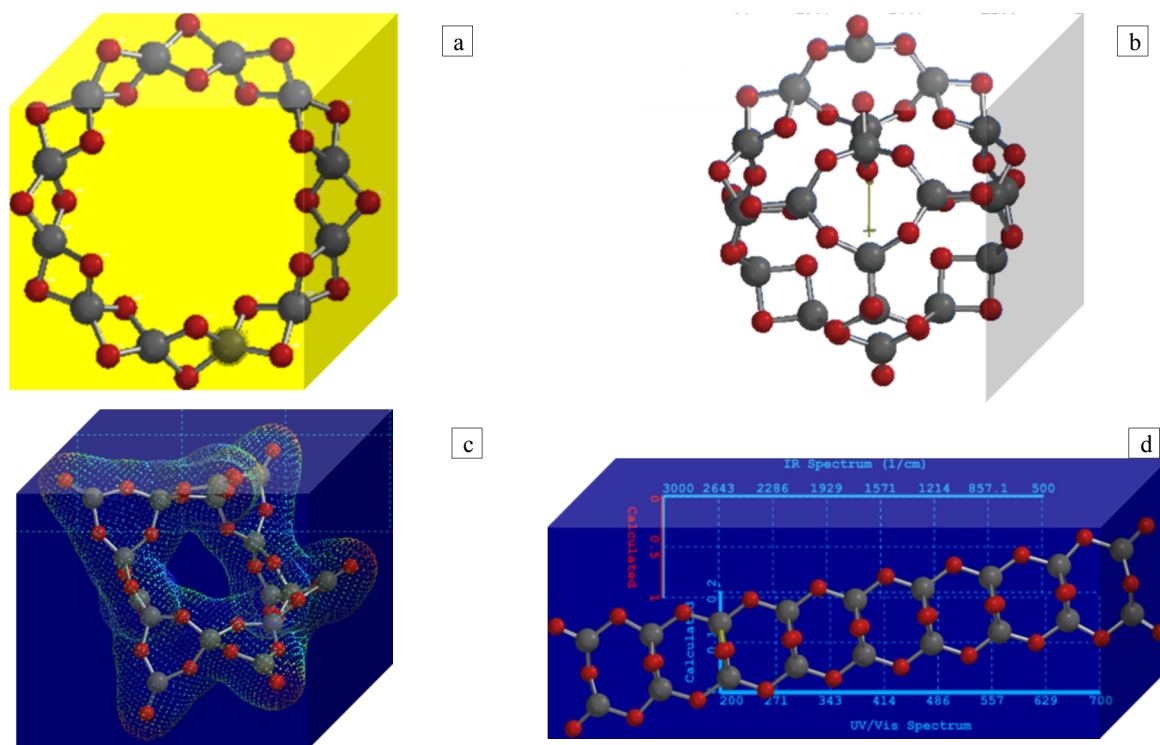


Fig. 6 – Different nano-structures of silica nanoclusters: a) 2 MR $n = 12$, b) 4 MR SiO₂ $n = 20$, c) 3 MR SiO₂ $n = 16$, d) SU-2 MR SiO₂ $n = 18$

A silica nanostructure with twenty silicon atoms constituted of five rings of four members each is shown in Fig. 6b.

We calculated the energy, the IR, UV-Vis and Raman spectra and the geometry of some 3 MR-silica based clusters with $n = 9, 10, 13, 16$ and 30 silicon atoms (Zhao and Zhang [14, 15] described previously these structures). Particularly, it was computed the geometry of nano-agglomerates from 4, 6 and 8 chain links with three-member-rings (3 MR) each. These nanostructures have $n = 9, 10$ and 13 silicon atoms, respectively. Unlike 2 MR-based molecular chains, 3 MR-based molecular chains have a nonlinear arrangement (a curved configuration) and when $n = 16$, the chain tends to joint on the edges to form a ring without any cyclic stress.

With respect to 2 MR, in 3 MR-based molecular rings some structural advantages are noticed: first, there is not additional stress, secondly they have less intrinsic strain than 2 MR rings, and finally, the 3 MR-based agglomerates can be extended to a continuous 3-D network analogous to crystalline silica. There is still an energetic disadvantage, the 3 MR-based molecular rings contain more NBO groups and for this reason these nanostructures can be extendable and then form multi-rings. A particular case is depicted in Fig. 6c, in which the individual links are jointed in an external loop with 16 silicon atoms and 32 oxygen atoms. This structure has 8 loops and corresponds to that early suggested by Zhao and Zhang [14, 15]. We found an alternative structure for the 3 MR moiety with 16 silicon atoms (not shown here).

Finally, the Fig. 6d shows a particular structure called spiro-union [6]. This structure is quite similar to Fig. 2, but it features 18 silicon atoms. There are four

particular characteristics that in our point of view will help to rationalize the structure of such moieties:

- The chain consists only of even- n SiO₂ units;
- It possesses a much larger radial size and thus it is shorter and more compact than 2MR chains;
- Structures as large as those shown in Fig. 6d, tend to be slightly curved, with poor symmetry and problems with convergence during iteration procedures and
- The silicon atoms divide into two parallel arrays by Bridging Oxygen (BO) atoms.

Fig. 7 displays the Raman spectra calculated for a 4 MR SiO₂, silica nano-agglomerate with 20 silicon atoms. The two highest emission peaks correspond to the wavenumber of 769 and 1261 cm⁻¹. Additional peaks with less intensity in 376 cm⁻¹, overlapping in the range of 501-521 and in 1240 cm⁻¹ were also predicted. Laughlin and Joannopoulos [16] reported that the peaks at 450, 800 and 1050 cm⁻¹ in the vibrational density of states correspond to the rocking, bending, and stretching normal bond modes of a SiO₂ nano-agglomerate in agreement with Bell and Dean original classification scheme [17]. In addition, Gaskel and

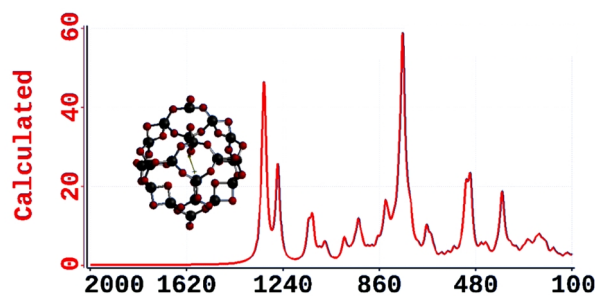


Fig. 7 – Raman Spectra calculated for silica nano-structures 4 MR SiO₂ $n = 20$

Johnson [18] have shown that the Si-O-Si bond angle variation in an amorphous network is the mayor cause of widening of these peaks. In our results, we obtain a shift of $\sim 52 \text{ cm}^{-1}$ with respect to those values, and this could be attributable to the size of the nanoagglomerates.

4. CONCLUSION

Quantum confinement effects and structural defects are mechanisms known as likely responsible for the phenomenon of luminescence. The calculations in this

research indicate that the effects of stress on small SiO_2 nanoagglomerates, as well as considerations of geometry and size in the evaluated nanostructures could contribute to the emission in the visible region of thin films of non-stoichiometric silicon oxides.

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