Gas-phase silica glass formation and structure: quantum-chemistry point of view.

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The first steps of synthesis play an important role in the formation of fumed silica particles during any kind of the CVD process. To study these processes we have used a supercluster approach in quantum chemistry. Due to different points of view on the nature of the high dispersed silica we have done quantum chemistry simulation of silica formation using 'technology following' method, which is based on the idea to simulate manufacturing process at the atomic level. To calculate large silica particles we used a sophisticated semiempirical method PM3. Some key systems were computed by ab initio methods. Each system was fully optimized, additionally force field and dipole moment derivatives have been evaluated. Both experimental IR and neutron inelastic scattering (INS) spectra were used to verify computational models. Following gas-phase technology of CVD silica glass producing process we have simulated different size cluster formation directly from molecules. During glass formation we have observed different cluster growth with completely amorphous structure. The main feature of amorphous structure is distributions of bond length, angle values, coordination numbers and atomic charges distributions. Detail investigation of the cluster structure shows the coordination numbers 3, 4, 5 and 6 for silicon atoms and 1, 2 and 3 for oxygen atoms. More detail results and discussion will be presented. Some results of glass formation will be presented as computer animation.

Methodology

There are two possible ways to produce nanosize particle: to condense small molecules or to divide a large bulk. Two high dispersed silica (fumed silica and silica fume) will be discussed as like as optical silica glass, obtained by CVD method. Following the near-CVD technology this presentation shows the first way: what will happen with small chemical active molecules in the flame. The reason of such approach is the fact that reaction happens in vapour phase, so the process of combining takes place and using crystalline model to simulate amorphous states of solid is an unrealistic.

To study space structure and properties of solids and their surface we have developed toolkit for the space structure and molecules-clusters vibration spectra simulation. There are a lot of methods to simulate space structure at the atomic level but the main question after simulation – how to verify obtained structure? – is still a problem.

This question becomes a big problem if small particles, amorphous or real surface are under study, when it is impossible to use standard structure methods such as X-raw or neutron diffraction. In order to solve this problem we have proposed to use vibration spectroscopy as a method to verify calculated structure with reality. It is well known that vibration spectra (infrared (IR), Raman and inelastic neutron scattering (INS)) are fingerprint for substance.

During simulation it is necessary to take in account two main component of simulation accuracy: the accuracy of computation method and accuracy of model to represent properties under study. As usual, accuracy of simulation will be not more, than minimal accuracy of these two components. Therefore, an unlimited accuracy increasing of only one component of a simulation method will not increase simulation result accuracy. As a sample it is possible to show that silicon dioxide molecule is not able to reproduce the properties of bulk silica due to small number of atoms and different electronic structure of small molecule and solid state.

To perform all these calculation we have used our new quantum chemical program QuChem [1] for semiempirical (PM3) simulation of space and electronic structure as like as other known packages (MOPAC, AMPAC and so on) and for data preparation for detailed normal coordinate analysis by our software package COSPECO [2.]

Silica simulation: from molecule to solid

The first steps of synthesis play an important role in the formation of fumed silica particles during any kind of the CVD process. To study these processes we used a supercluster approach in quantum chemistry. Due to different points of view on the nature of the high dispersed silica we have done quantum chemistry simulation of silica formation using 'technology following' method, which is based on the idea to simulate manufacturing process at the atomic level. Each system was fully optimised, additionally force field, dipole moment and polarizability derivatives have been evaluated. Experimental infrared (IR), Raman and neutron inelastic scattering (INS) spectra were used to verify computational models.

The next important point is the choice of starting space structure of cluster for simulation. Silica glass as like fumed silica, is amorphous and, therefore, it is difficult to understand discussions on crystal structure for amorphous state simulation. Especially, in a large extend the computations are made on clusters, the structure of which is based on quartz structure. For large simulation in molecular dynamics, for example, the starting point is quartz. When the temperature is increased, the disorder appears but after cooling local quartz structure reappears. This could be due to the choice of the potential or uncompleted simulation above the melting temperature. We would like to propose another way to simulate amorphous state of solids: to start rightly from the gas phase.

To simulate amorphous silica we have used 'Technology following' methodology [3]. It based on possible reproduction of condition of molecules during technological process. From our point of view all gas-phase silica synthesis processes like fumed silica production from silicon tetrachloride in oxygen-hydrogen flame, CVD silica glass production from silicon tetrachloride and free oxygen with external heating and silica fume production as by-product during silicon reduction from quarts in electrical arc furnaces are based on the similar chemical process with silicon dioxide molecule as a starting brick.

We have simulated reaction between silicon dioxide molecules with small number of molecules (up to 6 molecules in detail and some data more rarely). These data (fig. 1) show that the finale silica cluster structure is quite depended from the starting point. As result, we have a 'reaction tree', which can describe all products. It means that dependency of the collision condition the reaction pathway may leads to different results. Therefore, there are a lot of bifurcation points on the potential energy hypersurface where system chooses the active centre for reaction. As result, these bifurcation points generate cluster growth three. All clusters with the same number of atoms have slightly different heat of formation. After reaction between silicon dioxide molecules, when they concentration decreased, the silica clusters begin interact one with other without chemical reaction barrier (fig. 2). This process takes a place when active centres like one-coordinated oxygen atoms and three-coordinated silicon atoms cover cluster surface. If the reaction mixture contains small active molecules, which are able to saturate silica cluster surface (water and so on), the cluster condensation process will be terminated. In this case cluster surface will be covered by hydroxyl shell, which prevent bulk glass formation. This case we have observed during fumed silica producing, when number of water molecules is compatible with number of silicon dioxide molecules. As result of this technological process fine silica particles with hydroxyl shell come in. Water molecules react with surface and saturate it as it is shown in fig. 3. Fig. 4 shows structure of surface hydroxyl shell with H-bond between hydroxyl groups and their IR-spectrum in the region of hydroxyl group vibrations – 2700-4000 cm^{-1}. This simple structure describes experimental DRIFT spectrum for high-dispersed silica good enough. 'Free' hydroxyl group describes narrow peak at 3750 cm^{-1} with low intensity and half-width and H-bonded hydroxyl group describes wide and intense peak at 3650 cm^{-1}.

We have verified our models by different vibration spectroscopy experimental methods like inelastic neutron spectroscopy (INS), infrared (IR) and Raman. The data for cluster Si53OH with cristobalite structure are shown in the fig 5. To our opinion we have good enough reproduction of experimental data. The difference between experimental and computed data can be explained as a size and/or surface effects. The difference in Raman spectra due to silica cluster structure is cristobalite, but glass structure is more disorder. It means that glass structure is not crystal structure with defects, glass structure is amorphous state. More detailed data and discussion will be presented.

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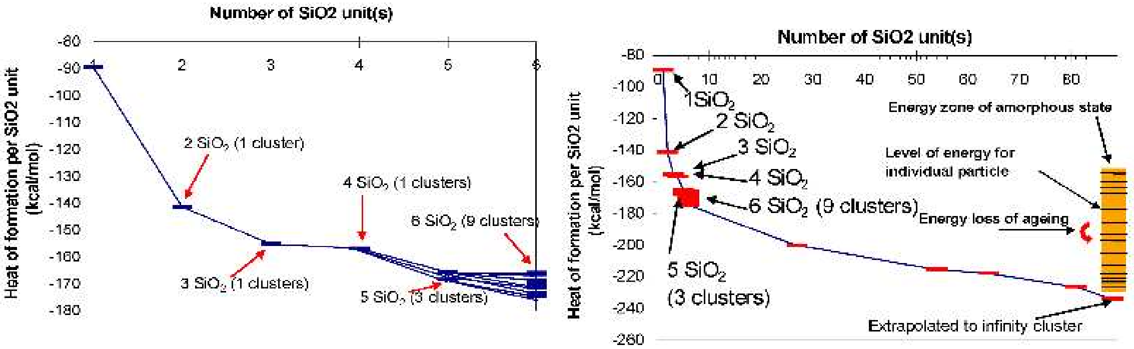

Fig. 1. Reaction three for small silica clusters - heat of formation as a function of number of silicon dioxide molecules (left fig – for small number of molecules and right fig. – for large number and extrapolation to infinity number of molecules).

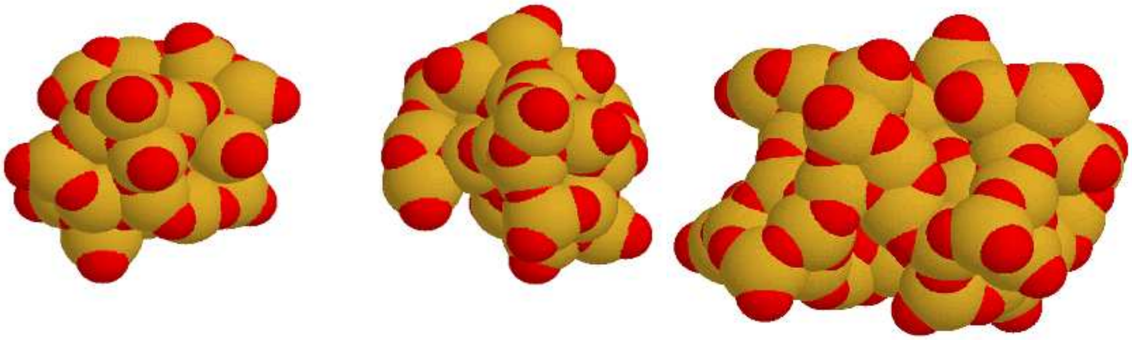

Fig. 2. Reaction between small silica clusters (left fig – starting point and right fig. – final point).

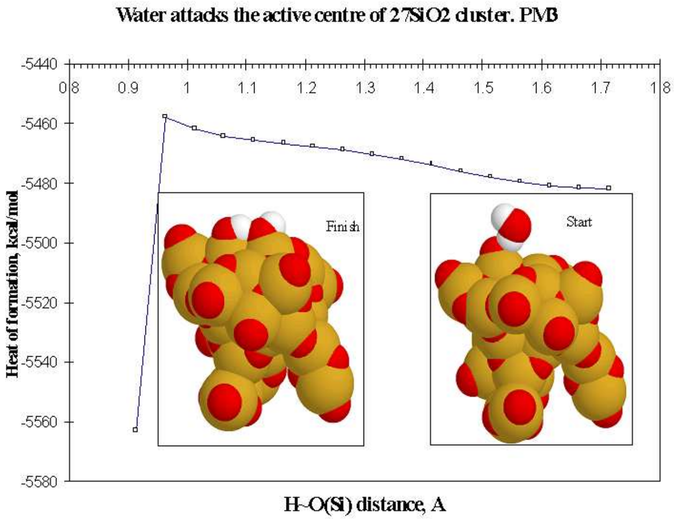

Fig. 3. Reaction between small silica clusters (27SiO$_2$) and water molecule – chemical reaction pathway (right fig – starting point and left fig. – final point).

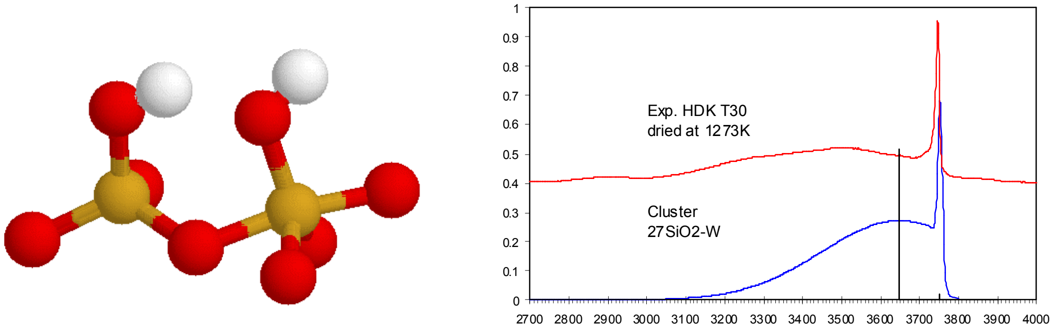

Fig. 4. Two surface hydroxyl groups on the small silica clusters (27SiO$_2$) with H-bond (left fig.) and their IR-spectrum for region 2700-4000 cm^{-1} (right fig. – blue line –calculated and red line – experimental data for fumes silica T30 /Wacker Chemie/).

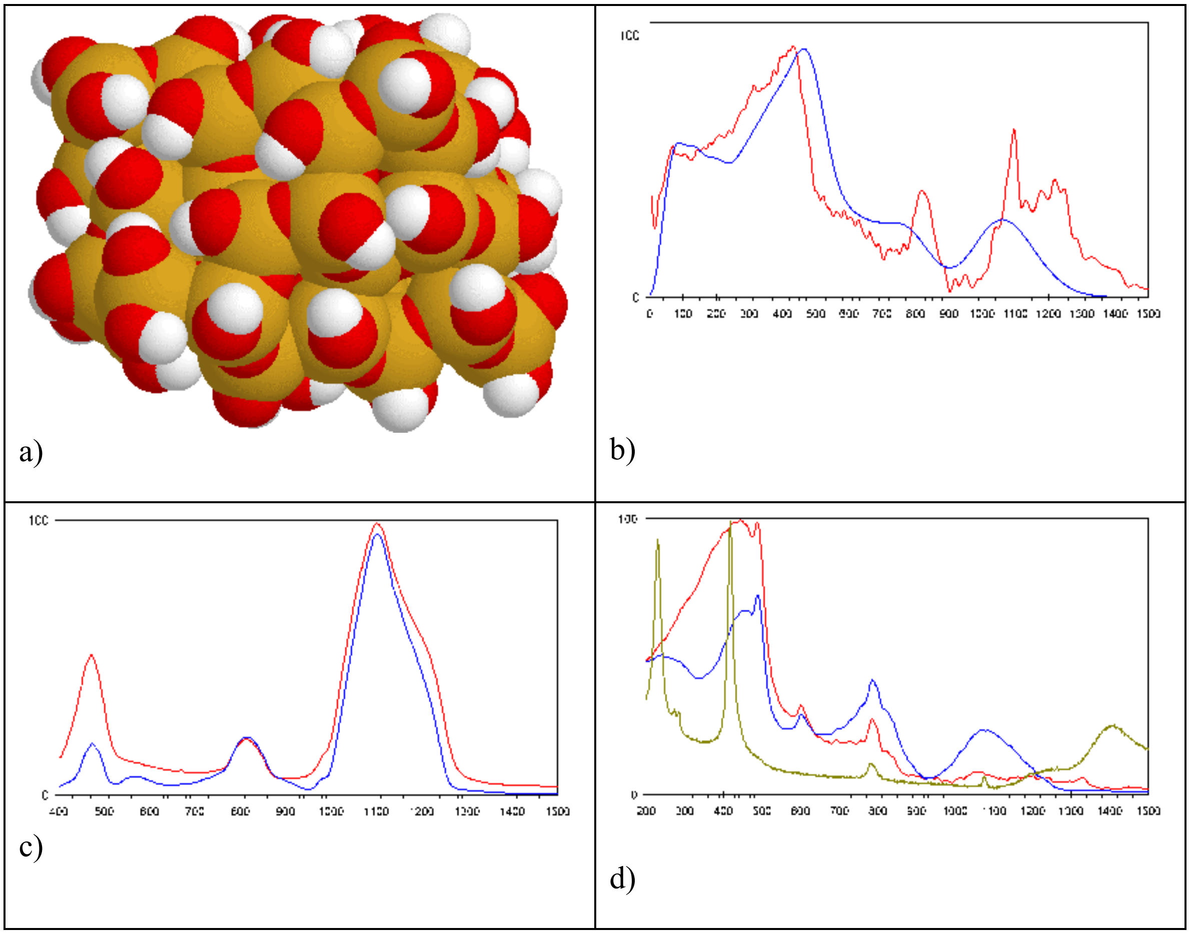

Fig. 5. Silica cluster Si53OH (a) and their INS (b), IR (c) and Raman (d) spectra.(red line – experimental data, blue line – calculated spectra, for Raman spectra green line is literature Raman spectra for cristobalit).