Formation of Silicate Grains in Circumstellar Environments: Experiment, Theory and Observations

A. W. Castleman, Jr.[*] S. N. Khanna[†] A. Ali[‡]

February 3, 2006

Abstract

SiO is one of the most abundant reacting oxygen bearing condensable gas-phase species in molecular astronomical regions. Based on laboratory smoke condensation experiments and analysis of end products, it was conjectured that silicate formation in the circumstellar envelopes surrounding M-type giants begins with the formation of pure SiOx clusters. There are no direct and almost no experimental studies on the role of molecular processes on formation of silicates in high temperature clouds.

In contrast to previous identification of amorphous disordered nature of silicates, the most recent infrared space observatory (ISO) observation shows the widespread presence of crystalline silicates throughout the galaxy. The "nominal" molecules of observed crystalline silicates such as forsterite (MgO)2(SiO2) do not exist in the gas-phase. The growth of crystalline silicates occurs by heterogeneous chemistry in unique catalytically active pathways through gas-surface interactions at high temperatures. Thus one of the most fundamental questions in grain formation studies is which one among the high-temperature condensable gas-phase species is going to nucleate first at a significant condensation rate to provide a molecular surface(cluster) enabling condensed phase growth of minerals.

In an attempt to resolve this critical question on condensation processes and the formation of cosmic silicates, samples of silicon and its oxides have been laser ablated under a series of different ambient environments. During the course of laboratory experiments an unexpected chemically anomalous composition of (SiO)x(SiO2)y was observed in both neutral and ionic clusters. The beams of molecular clusters are detected by ultrafast multiphoton ionization process in a time-of-flight reflectron mass spectrometry using femtosecond pulsed lasers. The observed anomalous compositions in SiOx clusters and their formation kinetics must be

---

[*] Departments of Chemistry and Physics, The Pennsylvania State University, University Park, PA 16802, USA.

[†] Department of Physics, Virginia Commonwealth University, Richmond, VA 23284-2000

[‡] Solar System Exploration Division, Astrochemistry Laboratory,NASA, Goddard Space Flight Center, Greenbelt, MD 20771 ashraf.ali@ssedmail.gsfc.nasa.gov

taken into account, prior to a mechanism is invoked for or an argument is presented against the role of SiO molecules in chemical models of formation of circumstellar silicates.

The gradient corrected density-functional theoretical studies have been carried out on the geometry, electronic structure and stability of SixOy clusters. It is found that the structures of the ground states of small SixOx clusters containing upto 4 units are single rings. The Si-Si bond appears first at Si5O5, and starting at this size, the elementary rings begin to assemble into multiple rings that eventually lead to cages. It is shown that the ground state structures at larger sizes have a central core of pure Si atoms decorated by outer shell of SiO2 units. The results of our investigations on the stability of SixOx-1 and SixOx+1 species will also be presented. In particular, we will examine the specific chemical processes in which the properties of SiOx clusters are involved, and could lead to the formation of SiO2 from the abundant SiO molecules in circumstellar space.

The present findings offer an expectation that a quantitative understanding of the chemistry of formation of silicate grains and nanoparticles in interstellar dust models may be reached through coordinated efforts of infrared observational astronomy, and the union of large-scale quantum theoretical calculations and laboratory spectroscopy and dynamics experiments of the type reported here.