PROCEEDINGS OF SCIENCE

Cosmic dust formation at cryogenic temperatures

Gaël Rouillé*[a], Serge A. Krasnokutski[a], Melinda Krebsz[b], Cornelia Jäger[a], Friedrich Huisken[a] and Thomas Henning[c]

[a] *Laboratory Astrophysics Group of the Max Planck Institute for Astronomy at the Friedrich Schiller University Jena, Institute of Solid State Physics*
Helmholtzweg 3, 07743 Jena, Germany
[b] *Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences*
45 Budaörsi street, 1112 Budapest, Hungary
[c] *Max Planck Institute for Astronomy*
Königstuhl 17, 69117 Heidelberg, Germany
E-mail: cornelia.jaeger@uni-jena.de

Within a project aimed at studying the formation of interstellar silicates in dense molecular clouds, we have carried out experiments on the accretion of SiO molecules at cryogenic temperatures using SiO-doped superfluid He nanodroplets and solid Ne matrices. Mass spectrometry revealed the formation of Si_xO_x oligomers in the doped droplets, i.e., at a temperature of 0.37 K. Therefore the reactions that produce the oligomers have no energy barrier at their entrance channel. Reaction energies were experimentally determined and the results of theoretical calculations were found to be consistent with the measurements. Absorption spectroscopy at UV and mid-IR wavelengths was performed at various stages of the annealing of SiO-doped Ne matrices and after their complete evaporation. It showed that the matrices were actually doped with Si_xO_x (x = 1–3) species which disappeared during annealing to be replaced with a condensate characterized by a broad IR spectrum peaking near 9.5 μm. High-resolution transmission electron microscopy and energy-dispersive X-ray spectroscopy investigations showed that the condensate had on the whole a homogeneous, amorphous structure and the formula SiO. Still, the study of the IR spectra indicated some degree of disproportionation which increased during warming from 8 to 294 K. We have concluded that SiO molecules can accrete at temperatures as low as 13 K into a solid compound. These preliminary experiments have demonstrated the relevance of the techniques to the study of accretion at low temperature. More particularly their results allow us to envisage the formation of silicates in the interstellar medium.

The Life Cycle of Dust in the Universe: Observations, Theory, and Laboratory Experiments
18-22 November, 2013
Taipei, Taiwan

*Speaker.

PoS(LCDU 2013)047

1. Introduction

Silicates are a major component of interstellar dust [1]. As they may grow in dense molecular clouds where temperatures are of the order of 10 K [2], we have started a project to study the formation and growth of silicates at cryogenic temperatures. In a first stage we have investigated the condensation of SiO molecules, which represent a major gas-phase carrier of the element Si in dense clouds [3]. Two techniques have been employed depending on the size of the condensation products. The formation of Si_xO_x (x = 2–3) oligomers has been studied using SiO-doped superfluid He droplets, while that of micrometer-sized SiO grains has been examined by annealing and evaporating SiO-doped Ne matrices.

Since the results of the experiments with doped He nanodroplets have been reported and analyzed in detail in Ref. [4], they are only briefly presented here. This work focuses on our experiments with doped Ne matrices, more specifically on the characterization of the SiO grains produced in these experiments. It closes with conclusions on the possible formation of silicates in the ISM.

2. Experimental

We have conducted experiments on the condensation of SiO at cryogenic temperatures using two media, namely, He nanodroplets and Ne matrices. The He nanodroplets are superfluid and have a characteristic temperature of 0.37 K. In contrast, the Ne matrices are solid and can be formed at temperatures as high as $\sim$7 K. They can be annealed to allow the diffusion of dopants, though within a limited range of temperatures and with losses due to evaporation, since pure Ne sublimates at $\sim$8 K [5].

In a dedicated vacuum apparatus, He nanodroplets were formed into a beam and directed toward an oven in which SiO powder was heated up. As they passed through the oven, the nanodroplets picked up SiO molecules released by the heated powder. In general, molecules are rapidly embedded in the He nanodroplets and cooled down to 0.37 K. Thus, any reaction between picked-up species takes place at this temperature, indicating that its entrance channel does not have an energy barrier. While mass spectrometry is generally applied to detect the revealing products of the reaction, it can also be used to determine the energy of the reaction. A detailed description of the experimental procedures is given in Ref. [4].

When working with Ne matrices, SiO molecules were produced by shooting at an SiO pellet with a pulsed laser source. It emitted photons with a wavelength of 266 nm in pulses of 5 ns duration at a rate of 10 Hz. The pulses carried an average energy of $\sim$1.7 mJ. As repeated shots formed a hole 0.45 mm in diameter at the surface of the target, the laser beam was shifted every minute so as to avoid drilling through the target. Together with an excess of Ne atoms, the vaporized species were deposited onto a KBr substrate placed $\sim$55 mm away in front of the target and kept at 6.3 K through the action of a cryocooler. The Ne flow was set to 5 standard cubic centimeters per minute. Thus, Ne matrices were formed that contained isolated SiO molecules as well as oligomers, as verified by absorption spectroscopy in the UV and mid-IR domains. Reactions between the embedded SiO molecules and oligomers were made possible by annealing the matrices until their complete evaporation. This was done by heating the substrate gradually up to 13 K. Spectra were measured during the annealing procedure and also while the substrate warmed

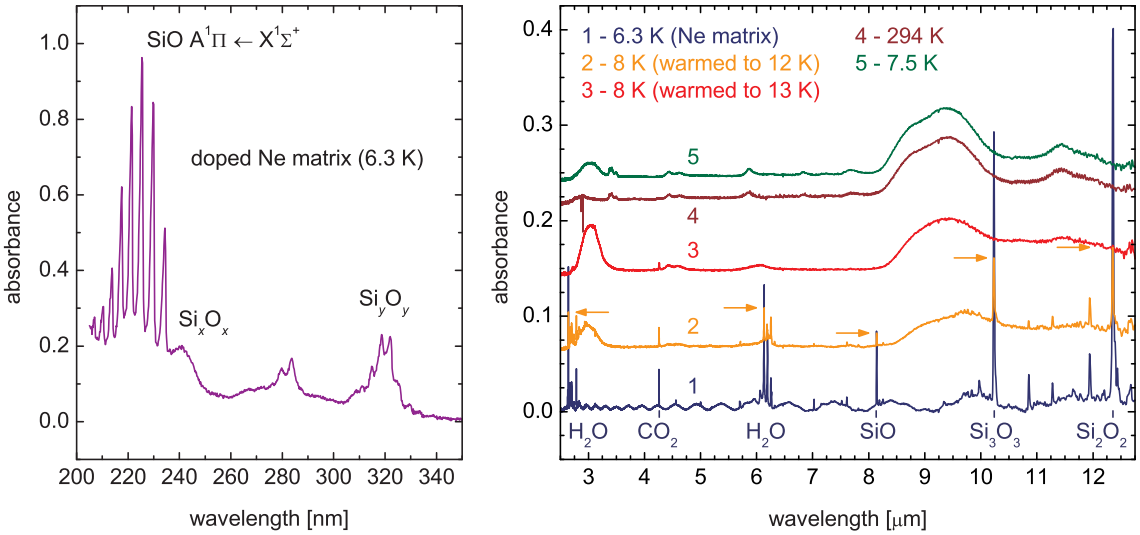

Figure 1: (Left) Ultraviolet absorption spectrum of a Ne matrix doped with SiO molecules and oligomers. It was measured after depositing material for 11 min. (Right) Infrared absorption spectrum of the same matrix after 31 min of growth, with spectra measured at different temperatures after partial and complete evaporation of the Ne atoms. The sequence of measurements is indicated with numbers. In spectrum number 2, arrows mark band maxima. A vertical offset is applied to the spectra for clarity.

up to room temperature. Measurements at wavelengths longer than 12.75 μm were obscured by noise and could not be used.

3. Results and discussion

3.1 Experiments with He nanodroplets

The results of the experiments in which He nanodroplets were doped with SiO molecules have been presented in detail in Ref. [4]. Briefly, the formation of Si_xO_x compounds was observed and attributed to reactions that took place inside the nanodroplets, not only between SiO molecules, but also between SiO molecules and oligomers after the latter were formed. Thus, the absence of an energy barrier at the entrance channel of the corresponding reactions has been inferred. Moreover, reaction energies of 178 and 291 kJ mol^{-1} have been experimentally determined for the reactions SiO + SiO $\rightarrow$ Si_2O_2 and SiO + Si_2O_2 $\rightarrow$ Si_3O_3, respectively. The values are consistent with the results of theoretical calculations in which a cyclic structure was given to the oligomers [4].

3.2 Experiments with Ne matrices

Concerning our experiments with Ne matrices, the initial presence of isolated SiO molecules and oligomers in the solid Ne medium was verified by absorption spectroscopy as illustrated with Fig. 1 (see also Ref. [4]). In the UV domain, isolated SiO molecules were identified by measuring the $A^1\Pi \leftarrow X^1\Sigma^+$ band system [6]. Other features at UV wavelengths were tentatively attributed to Si_xO_x compounds as their intensity increased at the beginning of the annealing procedure, before decreasing [4]. In fact, the presence of SiO oligomers, formed during deposition, could be

expected, as reported by Khanna et al. in a similar study with N_2 matrices [7]. Accordingly, measurements in the mid-IR region revealed the presence of the SiO, Si_2O_2, and Si_3O_3 species (Fig. 1). They were identified using the assignments made by Khanna et al. [7].

Figure 1 shows that, after a first annealing of a doped matrix and the partial evaporation of the Ne atoms, the sharp lines of the isolated molecules and oligomers had lost their intensity. At the same time, a broad feature had appeared, extending from $\sim$8.2 μm toward longer wavelengths. After complete evaporation of the Ne atoms at 13 K, and cooling to 8 K, the broad feature remained. The maximum of absorbance corresponds to a band peaking at $\sim$9.5 μm. It is accompanied by a secondary maximum at $\sim$11.4 μm. We attribute this band to a solid condensate formed by the accretion of the Si_xO_x species.

After warming up to 294 K, a shoulder could be clearly discerned at $\sim$8.7 μm on the side of the strongest band and the secondary maximum at $\sim$11.4 μm became sharper. Around 10.7 μm, however, the absorbance decreased. To verify that these changes were not caused by a simple dependence of the spectral properties of the condensate on the temperature, we cooled it back down to 7.5 K, without breaking the vacuum. The spectrum remained essentially the same as it was at 294 K with the shoulder still visible. Consequently, we have attributed the evolution of the band profile upon warming to a structural modification, e.g., the disproportionation of SiO, in addition to the disappearance of the underlying libration band of water ice. This band extends from 10 μm toward longer wavelengths and peaks at 12.8 μm (see, for instance, Ref. [8]). It should disappear like the other bands of water ice seen at 3.05 and 6.04 μm in the low-temperature spectrum.

The present spectra are in agreement with those obtained by Khanna et al. [7] by annealing a similarly doped N_2 matrix from 32 to 50 K. The comparison with literature data reveals that the condensate gives a spectrum similar to that of Si_2O_3, which is characterized by a band at 11.4 μm [9, 10, 11]. Considering the spectrum measured at room temperature, an attribution of the corresponding peak to silanol groups (Si–OH) would not be consistent with the weak OH stretching feature observed between 2.5 and 3.3 μm [11]. On the other hand, a contribution from the bending modes of oxidized SiH groups, the presence of which is indicated by the small bands at 4.5 μm, is not to be neglected [12].

Following each experiment, we observed the presence of white, micrometer-sized grains on the substrate. The larger grains actually looked like film fragments. As revealed by high-resolution transmission electron microscopy (HRTEM) and energy-dispersive X-ray (EDX) spectroscopy, the condensed material had a homogeneous, amorphous structure with a composition close to SiO. A HRTEM image is displayed in Fig. 2. The two techniques, however, have limitations and our equipment would not allow us to distinguish amorphous concentrations of Si atoms or even crystalline domains if the latter were as small as 1 nm. The question arises because commercial SiO, such as the powder we pressed to prepare our pellets, has been found to be disproportionated into Si and SiO_2 nanometer-sized domains [13, 14].

In the absence of other data, whether the accretion of SiO molecules and oligomers led to a disproportionated condensate must be found out by examining the IR spectra. One observes that the band at 9.5 μm coincides in position with the transverse and longitudinal modes of the Si–O–Si asymmetric stretching vibrations observed in amorphous SiO_2 (see, for instance, Ref. [15]). Moreover, we have noted the Si_2O_3 character of the condensate. Consequently, we infer that, just after formation, still at low temperature, the condensate is disproportionated to some extent. The

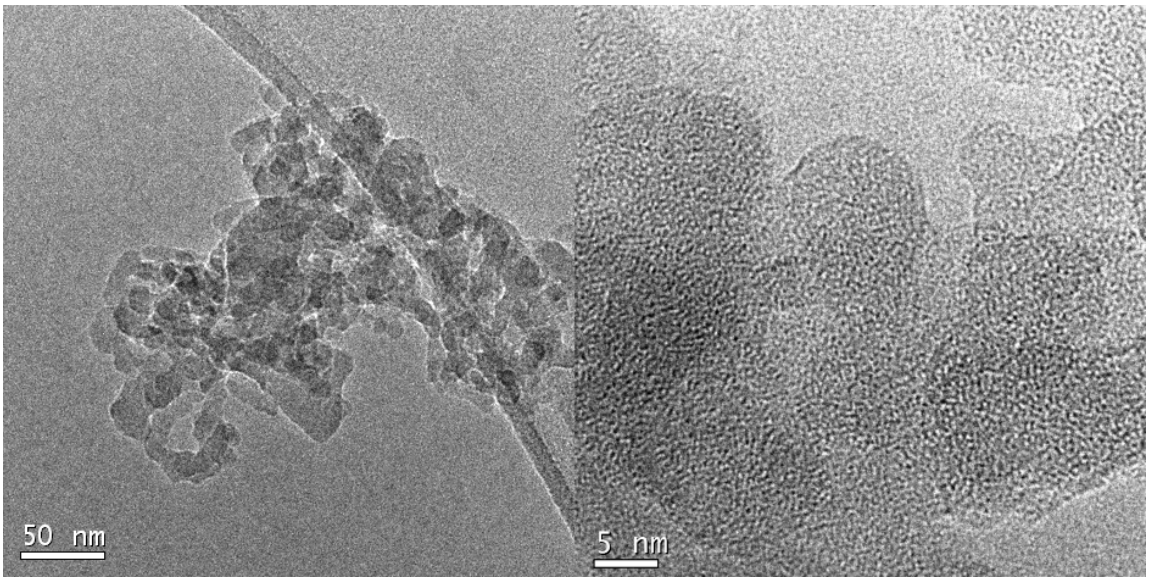

Figure 2: HRTEM images of a grain from an SiO condensate obtained by annealing and evaporating an SiO-doped Ne matrix. The grain agglomerates have a fluffy morphology and the solid structure appears as homogeneous and amorphous within the limits of the technique.

variations in the spectrum upon warming to room temperature are interpreted as the result of a further disproportionation of the condensate, with a strengthening of the Si_2O_3 character.

4. Conclusions

In dense molecular clouds, the condensation of silicates would proceed through the accretion of cold gas-phase species onto the even colder surface of small grains acting as seeds. In our experiments, the accreting species are initially hot because of the vaporization procedure. By isolating them in He nanodroplets and in Ne matrices, we cool them to relevant temperatures before they can interact. In addition, we gain the opportunity to verify the nature of the vaporized species. We have found that Si_xO_x (x = 2, 3) oligomers are obtained through barrierless reactions between SiO molecules. Moreover, these molecules can accrete into a solid, amorphous compound, forming strong chemical bonds at temperatures as low as 13 K. Thus, interstellar SiO molecules can be expected to accrete, likely contributing to the formation of silicates since the fingerprint of interstellar SiO grains, disproportionated or not, has not been reported. Other O atom-carrying species must accrete along with SiO to obtain the Si-to-O ratio of silicates. Of course, Mg and Fe atoms must also be caught in the accretion process. All the necessary substances are abundant in molecular clouds. The next question to answer is how foreign elements and substances, especially the abundant carbonaceous species, are prevented from interfering with the formation of silicates. It can be proposed that these species that get adsorbed on the surface of a growing silicate are desorbed rapidly enough not to interfer with the growth process. While the substances forming the silicates form relatively strong bonds, the other substances must be weakly attached, allowing their efficient removal, for instance, by the action of interstellar UV photons. Consequently, the cold

condensation of silicates may already take place in diffuse clouds with low temperature as well as in low-density regions of molecular clouds.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft through project No. He 1935/26-1 of the Priority Program 1573 "Physics of the Insterstellar Medium". M. K. is grateful for the award of an Eötvös Scholarship of the Hungarian State.

References

[1] Henning, T., *Cosmic silicates*, 2010, ARA&A, 48, 21

[2] Herbst, E., *The chemistry of interstellar space*, 2001, Chem. Soc. Rev., 30, 168

[3] Herbst, E., Millar, T. J., Wlodek, S., & Bohme, D. K., *The chemistry of silicon in dense interstellar clouds*, 1989, A&A, 222, 205

[4] Krasnokutski, S. A., Rouillé, G., Jäger, C., Huisken, F., Zhukovska, S., & Henning, Th., *Formation of silicon oxide grains at low temperature*, 2014, ApJ, 782, 15

[5] Meier, J., Wittich, G., Classen, J., & Hunklinger, S., *Desorption behavior of quench-condensed argon-neon mixtures*, 2002, Phys. Rev. Lett., 88, 016104

[6] Hormes, J., Sauer, M., & Scullman, R., *The vacuum ultraviolet absorption spectrum of SiO in rare gas matrices*, 1983, J. Mol. Spectrosc., 98, 1

[7] Khanna, R. K., Stranz, D. D., & Donn, B., *A spectroscopic study of intermediates in the condensation of refractory smokes: Matrix isolation experiments of SiO*, 1981, J. Chem. Phys., 74, 2108

[8] Öberg, K. I., Fraser, H. J., Boogert, A. C. A., Bisschop, S. E., Fuchs, G. W., van Dishoeck, E. F., & Linnartz, H., *Effects of CO_2 on H_2O band profiles and band strengths in mixed H_2O:CO_2 ices*, 2007, A&A, 462, 1187

[9] Ritter, E., *Zur Kenntnis der SiO- und Si_2O_3-Phase in dünnen Schichten*, 1962, Optica Acta, 9, 197

[10] Day, K. L., & Donn, B., *Condensation of nonequilibrium phases of refractory silicates from the vapor*, 1978, Science, 202, 307

[11] Hagenmayer, R. M., Friede, B., & Jansen, M., *Structural studies on amorphous Si_2O_3 and $H_2Si_2O_4$ by means of diffraction using high energy photons*, 1998, J. Non-Cryst. Solids, 226, 225

[12] Tsu, D. V., Lucovsky, G., & Davidson, B. N., *Effects of the nearest neighbors and the alloy matrix on SiH stretching vibrations in the amorphous SiO_r:H ($0 < r < 2$) alloy system*, 1989, Phys. Rev. B, 40, 1795

[13] Hohl, A., Wieder, T., van Aken, P. A., Weirich, T. E., Denninger, G., Vidal, M., Oswald, S., Deneke, C., Mayer, J., & Fuess, H., *An interface clusters mixture model for the structure of amorphous silicon monoxide (SiO)*, 2003, J. Non-Cryst. Solids, 320, 255

[14] Schulmeister, K., & Mader, W., *TEM investigation on the structure of amorphous silicon monoxide*, 2003, J. Non-Cryst. Solids, 320, 143

[15] Gunde, M. K., *Vibrational modes in amorphous silicon dioxide*, 2000, Physica B, 292, 286