Plasma polymerized nanoparticles as astro-analogues

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Abstract

We present plasma polymerized spheroidal dust particles produced in RF discharge under low pressure, using C\(_2\)H\(_2\) as precursor. The in-situ infrared (IR) spectra of nanoparticles reveal all characteristics identified with dust in the interstellar medium of our galaxy. The influence of oxygen and nitrogen in the growth environment on the IR fingerprint spectra was studied. The dominance of the nitrogen bands over the hydrocarbon bands was observed, the 3.4 µm feature diminishing in the presence of the HCN feature. This result opens the question if the absence of the 3.4 µm band in dense cloud spectra results from a HCN band which itself is hidden by water ice.

Introduction

Dust particles are ubiquitous in space, including e.g. diffuse and dense interstellar media (ISM), nova ejecta, the outflow of red giant stars and accretion disks, proto-planetary nebula etc. Even though interstellar gas dominates the mass fraction by 100:1, the interstellar dust plays an important role: dust regulates star formation, catalyzes molecule production and reprocesses UV and optical radiation.

A useful tracer of the carbonaceous component of dust is the C-H stretching vibrations from aliphatic hydrocarbons observed in absorption at 3.4 µm throughout the Galactic diffuse ISM (DISM). An important tool for the interpretation of astronomical infrared (IR) data and the understanding of the observed phenomena is the availability of IR spectra gained from laboratory investigations on analogue materials. The crucial criteria in the IR spectra of interstellar dust which analog laboratory candidates must meet in order to be considered good interstellar matches have been identified [1] and we present here new results of laboratory investigations following these criteria. Measurements with different gas mixtures are also presented. The existence of nitrogen in both gas and solid phase is clearly seen in observational IR spectra, especially in dense molecular clouds where interstellar ices form [2,3]. In the case of diffuse ISM, however, the elemental nitrogen is present in the gas phase with no obvious solid state component. Nitrogen depletion from the gas phase into the dust
was also shown to be very low and insensitive to changes of physical conditions of the environment [4,5] (the interstellar nitrogen abundance in the local Milky Way is about 80% of the solar value). Therefore, it was interesting to introduce nitrogen to our discharge and investigate the variations of the chemical properties of the particles.

**Experimental Set-Up**

The investigations were performed in a capacitively-coupled parallel plate reactor, symmetrically driven by radio frequency power (RF) at 13.56 MHz. The electrode system consists of two plain stainless steel electrodes, 30 cm in diameter and separated by 8 cm. The reactor was operated at room temperature, with a gas mixture of acetylene, argon and/or nitrogen/oxygen gas. The total gas pressure was about 0.1 mbar. The characteristic pumping speed of the system gives a mean gas residence time of about 1 min. The applied RF power was 10-50 W measured before the match-box. The details of the experimental set-up are given elsewhere [6]. Infrared (IR) absorption spectroscopy was used to monitor the dynamics of the dust formation as previously described [6,7].

**Experimental results and discussion**

Figure 1 presents in-situ FTIR spectra resulting from our experiments with spherical particles polymerized in hydrocarbon (acetylene) plasmas with argon as a carrier gas. As a precursor gas, acetylene (C$_2$H$_2$) undergoes instantaneous polymerization [8] in the plasma, thus enabling very efficient and reproducible dust growth [6]. C$_2$H$_2$ has been suggested as a precursor for dust formation in circumstellar media, e.g. in the disk regions of red giant stars [9], and is a possible origin for the PAH formation that may take place in the carbon rich circumstellar shells [10]. The laboratory-dust spectra reveal weak OH (3300 cm$^{-1}$) and carbonyl (1700 cm$^{-1}$) stretch bands, strong aliphatic CH stretch bands (centered around 2940 cm$^{-1}$) and correlated weaker CH deformation bands (1450 and 1375 cm$^{-1}$), as well as traces of aromatic compounds (3050 and 885 cm$^{-1}$). In our work we followed the criteria for “suitable” analogs as given by Pendleton & Allamandola [1, 7]. For example, the important feature at 2940 cm$^{-1}$ (3.4 µm) from plasma polymerized hydrocarbon nanoparticles matches very well in every subfeature the spectrum observed from the interstellar dust towards the Galactic centre Source IRS 6E (see Fig. 2)[1,7,11]. Further investigations were performed on the carbonyl and OH groups by admixture of oxygen in the argon-acetylene gas mixture. These bands are in interstellar media either very small or not observed - like the dotted spectra of analog on Fig 3.
Figure 1: FTIR spectrum of the particles grown in Ar:C\textsubscript{2}H\textsubscript{2}=8:0.5 sccm plasma

Figure 2: Comparison of 3.4 µm feature obtained from the laboratory dust to the astronomical observations towards Galactic Centre (circles)

We show (see solid line in Fig. 3) that even small amounts of oxygen (1%) are responsible for the strong increase of the corresponding broad bands around 3300 cm\textsuperscript{-1} (OH band) and 1700 cm\textsuperscript{-1} (carbonyl band).

Figure 3: Comparison of two IR spectra obtained in Ar:C\textsubscript{2}H\textsubscript{2}=8:0.5 sccm mixture (dots) and Ar:C\textsubscript{2}H\textsubscript{2}:O\textsubscript{2}=8:0.5:0.08 sccm (solid line)

Figure 4: Comparison of two IR spectra obtained in Ar:C\textsubscript{2}H\textsubscript{2}=8:0.5 sccm mixture (dots) and N\textsubscript{2}:C\textsubscript{2}H\textsubscript{2}=8:0.5 sccm (solid line)

Investigations with the nitrogen admixture are presented in the Figure 4 as a comparison of the spectra obtained in argon/acetylene and the nitrogen/acetylene discharge. The spectrum with nitrogen as carrier gas is dominated by a strong, broad absorption peak centred at about 1625 cm\textsuperscript{-1} (6.15 µm). According to Gonzalez et al. [12], this peak may be attributed to N–sp\textsuperscript{2} C vibrations, which indicates the presence of nitrogen atoms bonded to the skeleton of the dust particles. Secondly, there is a strong and broad feature with the maximum peaking at 3332 cm\textsuperscript{-1} (3.0 µm). In the case of astronomical observations, the 3.0
µm feature is dominated by the water ice. Our laboratory experiment allows us to study this feature in the absence of water ice. Therefore, we can identify this broad peak as NH stretching vibrations from an HCN band. The striking result is that the main absorption feature at 2940 cm\(^{-1}\) (3.4 µm) in the mixtures without nitrogen is drastically weakened in comparison to the HCN bands in nitrogen-acetylene mixtures. There is a possibility that some amount of the carbon and hydrogen content that would otherwise produce the 3.4 µm feature goes into making HCN. The question arises if the absence of the DISM 3.4µm aliphatic hydrocarbon band in dense cloud spectra [13,14] could possibly result from production of the HCN band which would be hidden by the strong 3.1 µm water ice band in dense clouds [7]. This intriguing idea will be, however, the subject of further investigation. Another broad peak located around 2165 cm\(^{-1}\) (4.62 µm) corresponds to the astronomical XCN/OCN\(^{-1}\) band [5, 14]. This broad absorption feature can be identified as stretching vibrations of C≡N bonding, nitrile or isonitrile.

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References