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On the hydrocarbon chemistry in dust producing rf plasmas

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In reactive low temperature molecular plasmas the formation of dust is a well known phenomenon [1-4]. Numerous properties of dusty plasmas and dust particles were extensively analysed in the last decade. This included dust formation, growth, astrophysical importance, build-up of strongly coupled systems, formation of voids and many other aspects. Based on reactions of hydrocarbon precursors, as e.g. acetylene or methane, polymerization processes can lead to the formation of particles with a diameter up to several hundreds of nanometres in the plasma volume.

However, relatively little is known about basic plasma chemical phenomena. In this contribution results of a spectroscopic study of dust forming rf plasmas, combining mid-infrared tuneable diode laser absorption spectroscopy (TDLAS) with Fourier transform infra-red (FTIR) and mass spectroscopy (MS) techniques. The measurements were performed in a radio-frequency (rf) capacitively-coupled parallel plate reactor working at 13.56 MHz [3, 4]. The power is coupled symmetrically to both electrodes. The electrodes have a diameter of 30 cm and are separated by 8 cm. The applied power was 15 W. During plasma operation the pressure was 0.1 mbar for typical flow rates of 8 sccm Argon, 0.5 sccm C_2H_2 and/or 1 sccm CH_4. (see [3, 4] for details). For the time resolved TDLAS measurement of molecular concentrations, a compact and transportable multi-component acquisition system (IRMA) combined with an optical long path cell for improved sensitivity has been used [5]. The growth process of the particles was monitored by means of FTIR spectroscopy and the evolution of the exhaust gas was simultaneously analysed with the help of a mass spectrometer.

With the help of the IRMA system a group of four stable species, C_2H_2, C_2H_4, CH_4 and CO together with the methyl radical were detected in the C_2H_2/CH_4-Ar rf plasma. Figure 1 shows a survey spectrum with two Q branch lines of the ν_2 fundamental of the CH_3 free radical. The concentrations of the monitored molecular species were found to be in the range of 10^{10} to 10^{14} molecules cm^{-3}.

In figure 2 an example of the temporal evolution of the concentrations of C_2H_2, CH_4 and CH_3 measured by TDLAS (upper panel) and of the absorbance at 5000 cm^{-1} measured by FTIR, representing the growth process of the particles (lower panel), are given as a function of time in the rf discharge. From figure 2, it can be seen, that after starting the plasma in an Ar-C_2H_2 gas mixture (t = 0), the degree of dissociation of the C_2H_2 precursor reached a value of about 95 %. The concentrations of CH_4 and CH_3 were below the detection limit. After about 10 min, the C_2H_2 flow was stopped and CH_4 was added as precursor. Under these plasma conditions the concentration of the produced species CH_3 and C_2H_2 were found to be in the range of 10^{11} and 10^{12} molecules cm^{-3}, respectively. After about 45 min, two alternative short admixtures of again C_2H_2 led to an increase of methane concentrations and to a simultaneous lowering of the methyl radical density.

In the lower panel of figure 2 the FTIR measurements reflect the periodicity of the growth process of the particles. From the beginning of the experiment the particles grow till they reach a critical size. Then they are lost from the plasma after about 43 min. The change in plasma conditions, in particular the sudden decrease of the electron energy (which increased during the dust particle growth) with the disappearance of the dust, clearly leads also to a reduced degree of dissociation of the precursor gas CH_4, while the density of C_2H_2 is also slightly enhanced. It should be mentioned, that without any oxygen admixture, the amount of CO were found to be in the range of 10^{13} molecules cm^{-3} in the plasma (not shown). Both molecules are being supposed to originate from the plasma interaction with the previously deposited layers on the reactor wall.

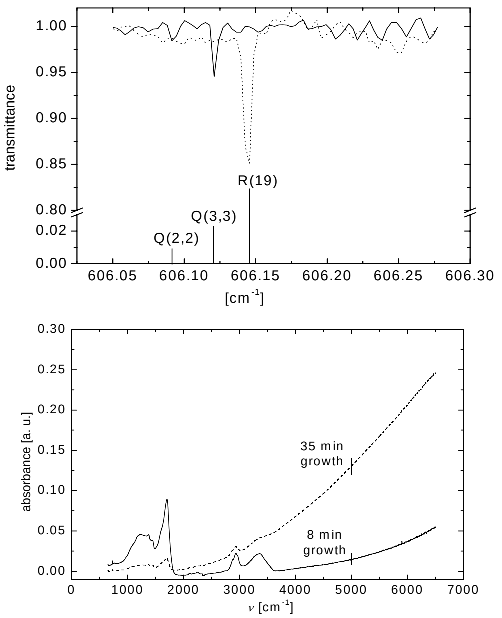

Fig. 1. Survey spectrum showing two Q branch lines of the ν_2 fundamental of the CH_3 free radical (upper panel). The spectrum represented by the dashed line is a calibration spectrum from N_2O. Lower panel: broad-band FTIR absorption spectra. To monitor the particle growth the temporal evolution of scattering signal at 5000 cm^{-1} is monitored.

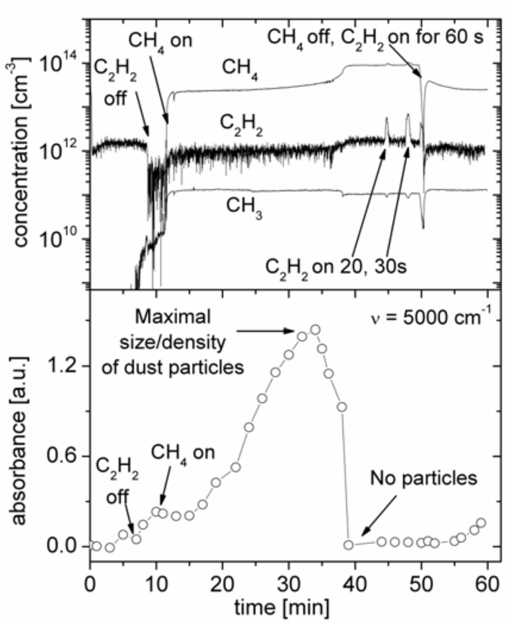

Fig. 2. Temporal evolution of concentrations of CH_4, C_2H_2 and CH_3 (upper panel) measured by TDLAS and of the absorbance at 5000 cm^{-1} (lower panel) measured by FTIR as a function of time in the rf discharge.

Acknowledgements

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