IR ABSORPTION SPECTROSCOPY OF FLUOROCARBON MOLECULES IN A DBD

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Abstract

IR diagnostics were performed in argon, nitrogen, dry air and admixtures of fluorocarbons. Fluorocarbons are usable to receive better hydrophobic properties of textile. In discharges in argon/nitrogen/(CF_4 or c-C_4F_8) mixtures CO, COF_2, HF, C_2F_6, and C_2F_4 molecules were found by applying IR absorption spectroscopy. In the case of discharges in argon/(CF_4 or C_2F_6) mixtures CF_3 radical was detected by means of emission spectroscopy.

1. Experimental set-up

The discharge is running in a cylindrical vessel (0.8 m diameter and 1.0 m long). For more details see our other report on this conference. The vessel can be evacuated to 10^{-2} mbar and filled with various working gases (around 0.5 to 1.5 bar). The interelectrode gap is usually flooded with a continuous gas flow (various gases and their mixtures) of up to 7.5 l_n/min at constant total pressure. The gas flow can be varied between 0.02 and 2 l_n/min Ar, 0.05 and 5l_n/min for N_2, 0.005 and 0.5 l_n/min for admixture gases. The total pressure is kept constant controlled by a valve and monitored by pressure gauge.

2. IR- diagnostics in mixtures of N_2 or Ar with fluorocarbon

Concentrations of various species were measured end-on by Fourier Transform IR (FTIR) absorption spectroscopy. The optical absorption length is in the order of 70 cm. Absorbances in the range between 10^{-2} and 1 could be measured. The absorbance is given by the relative change of the light intensity I_0 due to absorption, i.e. by $\Delta I/I_0$.
The detection of IR absorption spectra is a suitable method for the absolute density determination of different species in the gas discharge volume.
Nonthermal discharges in fluorocarbon molecules are very interesting subjects of investigations for some reasons. These molecules are used very often for industrial applications, for example plasma polymerization and plasma etching processes. Fluorocarbons are also known as a very fast quencher of charged particles by a fast attachment process. As a results of chemical reactions in fluorocarbon gases very active fluorine atoms and also radicals with fluorine atoms are produced. The diagnostics of fluorine atom, and radical densities depending on plasma processing parameters are a very important issue for understanding of plasma chemistry in discharges containing fluorocarbons. Optimization of the plasma polymerization process in nonthermal plasmas can be achieved by changing of gas composition and plasma parameters.

Identification of fluorine atom, and CF_x-radical densities are known by applying the emission spectroscopy and/or absorption spectroscopy in UV and visible ranges. The absolute CF_2 radical density, for example, was measured in a fluorocarbon plasma by UV absorption spectroscopy [1]. As an alternative method the IR absorption spectroscopy method can be used. The absolute density of CF_x (x=1-3) radicals was measured by applying very sensitive infrared diode laser absorption spectroscopy [2]. FTIR absorption spectroscopy is also available for this aim.

Fluorocarbons we used are: tetrafluoromethane (CF_4), hexafluoroethane (C_2F_6) and cyclo- octafluorobutane (c-C_4F_8). As it was shown in [2] the CF_x radicals are the main dissociation products of fluorocarbons in an ECR plasma. The concentrations of CF_2- and CF- radicals are higher by two orders of magnitude in discharges with admixtures of c-C_4F_8 compared to CF_4. The main product of CF_4 dissociation is the CF_3- radical. All mentioned CF_x- radicals in an ECR plasma are important precursors of polymer deposition. Therefore it is important to study the influence of the C/F ratio of the fluorocarbons used on the radical densities and also the radical kinetics in high density plasmas.

Typical IR spectra of Ar/CF_4, N_2/CF_4 and Ar (or N_2, or air)/c-C_4F_8 mixtures are shown in Figs. 1-3. In the figures not all the absorption bands are identified yet. We can identify C_2F_2 (1030 cm^{-1}), C_2F_6 (1116 cm^{-1}, CF_3- radical production and further recombination), CO molecules, and HF (fine structure in the absorption spectra in the range of a 3700-4200 cm^{-1}) in a mixture of N_2/CF_4. After relatively long time of discharge duration (35 min) the absorption band near 740 cm^{-1} was found. This band belongs to the "amorphous" polytetrafluoroethane (PTFE). As an accompanying product one can identify H_2O molecules (absorption in the range of a 1400-2000 cm^{-1}).

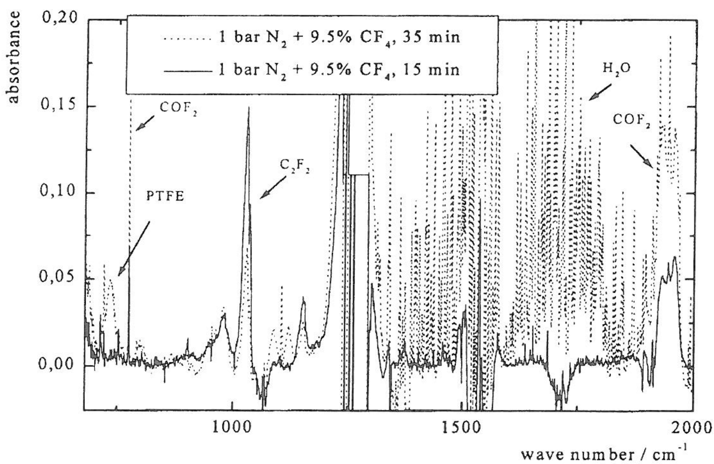

Fig. 1: IR-absorption spectra in N_2/CF_4-mixtures.

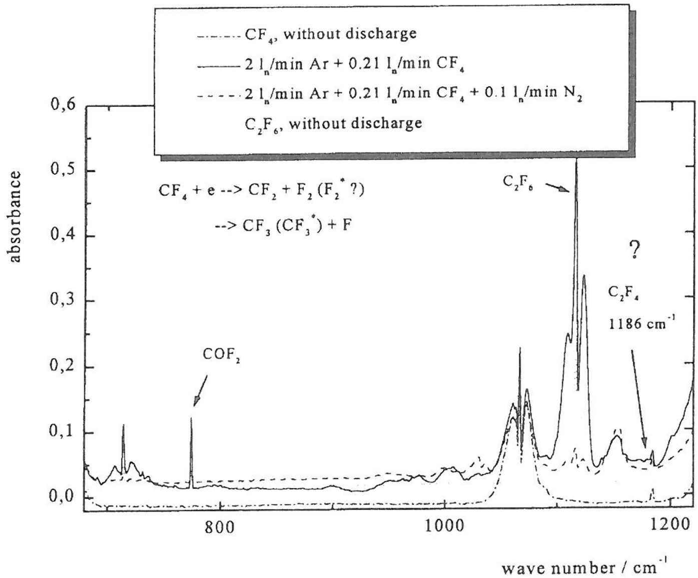

Fig 2: IR absorption spectra of Ar/CF_4 mixtures.

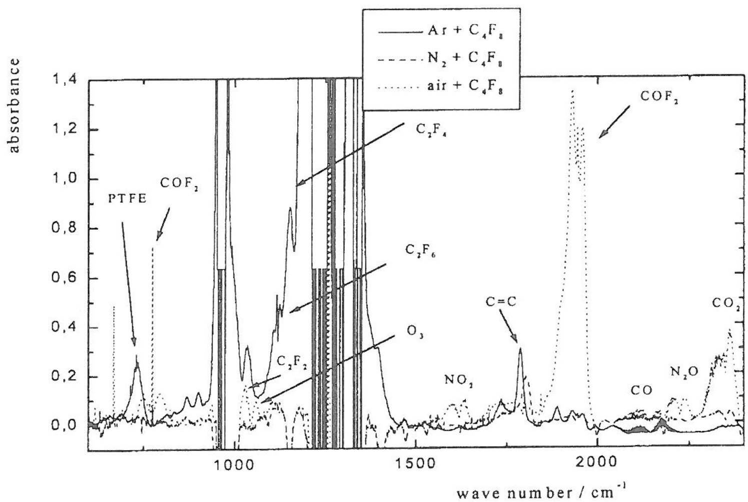

Fig. 3: IR absorption spectra in admixtures of 0.1 l_n/min c-C_4F_8 to 1 l_n/min Ar (or N_2, or air).

Water came out of the electrode surfaces and surfaces nearby due to the increase of the gas temperature (electrode temperature also), because the discharge is running for a long time with high power.

In a c-C_4F_8 discharge we detected following products: „amorphous" PTFE, CO, C_2F_6-molecules (1116 cm^{-1}, by CF_3- radical production and further recombination), C_2F_4 molecules (1186 cm^{-1} by direct dissociation of c-C_4F_8 and/or CF_2- radical production with further recombination [3]), and HF molecules. The densities of all mentioned products are increasing, if the discharge is running at a relatively high power and high c-C_4F_8 concentration. The small amount of COF_2 molecules as a product of these discharges could be also seen (774, and 1944 cm^{-1} bands). This molecule was observed as main product in a synthetic air/c-C_4F_8 mixture. In this mixture NO_2, CO, CO_2, O_3 and N_2O molecules are also seen.

By small admixture of nitrogen (only several percent in concentration) to Ar/ CF_4 mixture the intensity of the absorption band at 1116 cm^{-1} (C_2F_6) is strongly reduced. Simultaneously, the intensity of the emission band belonging to the CF_3- radical is also decreased. These results show that CF_3- radical is very fast quenched by chemical reaction with nitrogen (atoms, ions). Emission spectrum of CF_3- radical are shown on Figs. 4, 5. The very bright yellow emission (in the region 450-750 nm) which belongs to the CF_3- radical was found earlier by M. Suto [4].

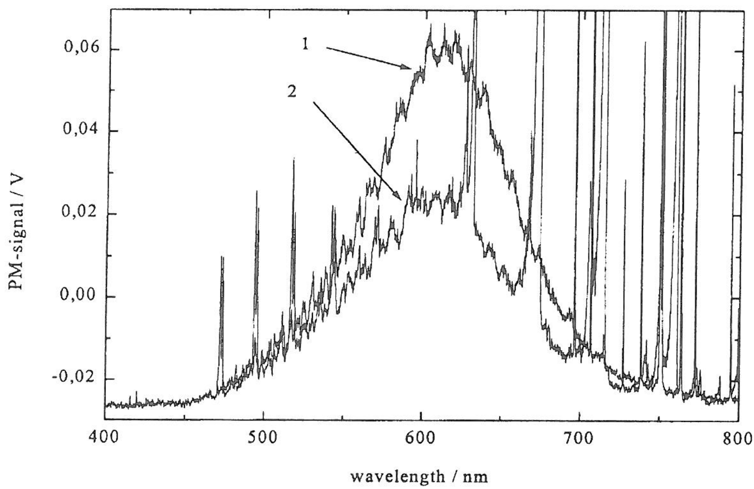

Fig. 4: Emission spectra of CF_3- radical, depending on N_2 concentration; 2l_n/min Ar + 0.21l_n/min CF_4, p = 1bar. 1- without N_2, 2- 0.08 l_n/min N_2.

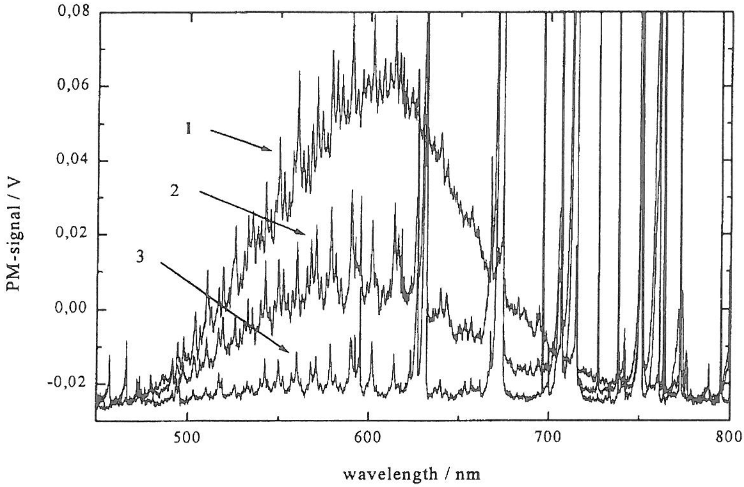

Fig. 5: Emission spectra of CF_3- radical, depending on the N_2 concentration; $1l_n/min$ Ar + $0.12l_n/min$ C_2F_6, p = 1bar. 1- without N_2, 2- 0.1 l_n/min N_2, 3- 0.2 l_n/min N_2.

References

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