Infrared Absorption Spectroscopic Studies of H₂ – Ar - N₂ - Microwave Discharges Containing Methane or Methanol

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Abstract

In this contribution tunable diode laser absorption spectroscopic (TDLAS) studies of hydrocarbon-containing H₂-Ar-N₂-discharges in a planar microwave reactor (f= 2.45 GHz, P=1.5 kW) under static conditions are presented. Measurements were performed using various ratios of H₂ to N₂ and small admixtures of some percents of methane or methanol at a discharge pressure of 1.5 mbar. TDLAS was used to determine the degree of dissociation of the precursor hydrocarbons methane or methanol as well as the concentrations of the produced molecules like acetylene, ethylene, ethane, hydro cyanic acid, ammonia and the methyl radical.

The degree of dissociation of methane was found to be between 70 to 95 %, showing a considerable increase at small nitrogen contents. Methanol dissociated almost completely (about 97 %) for all H₂-N₂-admixtures.

Introduction

Due to their favorable properties non-equilibrium molecular plasmas are of high potential for plasma processing resulting in growing interests in their volume chemistry. The online monitoring of stable plasma reaction products in chemical reactors, in particular the measurement of their ground state concentrations, is the key to an improved understanding of the plasma chemistry and the kinetics in these molecular discharges. This can be done by appropriate diagnostic methods, e.g. by absorption spectroscopy.

TDLAS in the mid infrared spectral region between 3 and 20 µm is a non-invasive technique for measuring number densities of stable molecules and radicals. Basically this diagnostic method is not restricted to a specific type of plasma. It was used to determine neutral gas temperatures [1] and to investigate dissociation processes [2-5]. Due to their small laser line width (about 10⁻⁴ cm⁻¹) the lead-salt diode lasers used in the mid infrared region are well suited for high resolution spectroscopy purposes, e.g. of low molecular weight free radicals and molecular ions [6-9].

One of the most successful applications of TDLAS is for studying the decomposition of hydrocarbons in a variety of PECVD processes. Recently, systematic investigations of plasma chemistry and kinetics in plasmas containing hydrocarbons have been published [2,10]. Outside of plasma diagnostics this technique has been used successfully in the field of atmospheric trace gas monitoring and for exhaust gas monitoring of on-road vehicles, e.g. refs. 11,12.

This contribution is focused on TDLAS studies in the mid infrared region which have been performed in a planar microwave reactor. Molecular species concentrations have been monitored in H₂-Ar-N₂-plasmas containing hydrocarbons, either methane or methanol, under static discharge conditions.
Experimental

The experimental set-up of the used TDL arrangement and the microwave reactor is shown in figure 1. Experimental details of this set-up can be found elsewhere. [2,13] The infrared diode laser beam entered the plasma chamber via a KBr window and passes twice through the plasma region. A monochromator in front of the HgCdTe detector was used as a mode filter. The absorption signal of the detector was amplified and transferred to a PC system. Measurements were performed under static conditions in a planar microwave reactor (f = 2.45 GHz, P = 1.5 kW) using various ratios of H₂ to N₂ and 7.2 % of methane or methanol with a discharge pressure of 1.5 mbar. In order to reduce the influence of gas transportation processes in the chamber, a specific measurement procedure was used [2]. The discharge was started under flowing conditions with the gas mixture of interest. When a stable plasma had been established the reactor was closed. After one minute the concentration measurements under static conditions were started.

TDLAS has been used to determine the degree of dissociation of the precursor hydrocarbons methane and methanol as well as the concentrations of the produced molecules acetylene, ethylene, ethane, hydro cyanic acid, ammonia and the methyl radical. The identification of the absorption lines and the measurement of their absolute positions was carried out using well documented reference gas spectra and an etalon of known free spectral range for wavenumber interpolation [14,15].

Results and Discussion

The degree of dissociation (figure 2) was determined from the measured concentrations of the precursor hydrocarbons before igniting the plasma and in the plasma under static conditions. It was found to be between 70 to 95 % for methane-containing plasmas, showing a considerable increase at small nitrogen contents. The methanol was determined to be dissociated almost completely (about 95 to 97 %) for all ratios of H₂ to N₂.

In H₂-Ar-N₂-plasmas containing methane concentrations of six stable molecular species as well as of the methyl radical were measured for various ratios of H₂ to N₂ (figure 3).
Ammonia and hydro cyanic acid showed to be main products of the plasma. The concentration of hydro cyanic acid in the discharges under static conditions increased for small nitrogen percentages reaching a maximum of about $5 \times 10^{14}$ molecules cm$^{-3}$ for nitrogen contents around 15%. The concentration of ammonia produced in the plasma showed a similar behavior with a maximum of about $1.5 \times 10^{14}$ molecules cm$^{-3}$ at the same H$_2$ to N$_2$ ratio. The concentration of the hydrocarbons C$_2$H$_2$ and C$_2$H$_6$ decreased for low nitrogen contents to values less than $1 \times 10^{13}$ molecules cm$^{-3}$. The C$_2$H$_4$ density was measured to be one order of magnitude lower. It showed a strong decrease for small nitrogen admixtures. The methyl radical concentration decreases from $1 \times 10^{13}$ molecules cm$^{-3}$ to $1 \times 10^{12}$ molecules cm$^{-3}$ with increasing nitrogen content.

The molecular concentrations in methanol-containing plasmas (figure 4) showed a comparable behavior. Although the degree of dissociation of this precursor hydrocarbon was higher, the concentration of hydro cyanic acid was found to be slightly lower compared to the methane case. Its concentration reached at maximum $2.5 \times 10^{14}$ molecules cm$^{-3}$. Methane was an additional product in the methanol-containing discharge. It had a concentration between $3 \times 10^{13}$ molecules cm$^{-3}$ and $3 \times 10^{14}$ molecules cm$^{-3}$. Ammonia as another final product in the discharge had a maximum concentration of about $9 \times 10^{13}$ molecules cm$^{-3}$. A higher amount of C$_2$H$_2$ and C$_2$H$_6$ was measured in methanol-containing plasmas. The concentrations of C$_2$H$_4$ and the methyl radical showed a strong decrease for small nitrogen admixtures.

**Outlook**

For further insight into plasma chemistry it is planned to measure concentrations of other radicals like NH$_2$ and CH$_2$. The improvement of the sensitivity will be achieved using a multipass setup at the discharge vessel. The experimental results are going to be used for modeling the plasma chemistry in the volume.
References