Journal of Physics: Conference Series **715** (2016) 012002 doi:10.1088/1742-6596/715/1/012002

Metal hydrides studied in gas discharge tube

I. Bozhinova, S. Kolev, Tsv. Popov, A. Pashov

Department of Physics, Sofia University, 5 J. Bourchier blvd., 1164 Sofia, Bulgaria

E-mail: pashov@phys.uni-sofia.bg

M. Dimitrova

Institute of Electronics, Bulgarian Academy of Sciences, Tsarigradsko schausee 72, 1784 Sofia, Bulgaria

Abstract. A novel construction of gas discharge tube has been tested for production of high densities of metal hydrydes. Its performance turned out to be comparable with the existing sources of the same type and even better. First results of the tests on NiH are reported and critically analysed. Plans for future modifiaction of the construction and application of the tube are discussed.

1. Introduction

The metal hydrides (especially FeH, CrH, NiH) are among the most abundant molecules that have been observed in the Sun spots [1, 2, 3] and in the atmosphere of other cold stars [4, 5]. Therefore the knowledge of their absorption spectra is important in order to identify them and this is one of the motivations for laboratory studies of this molecules. Moreover by using the Zeeman splitting of the rovibrational energy levels it is possible to make estimations on the magnetic field on the surface of space objects [6, 7]. The hydrides are specially suited for this, because their rotational constants are large and it is relatively easy to observe spectra with fully resolved rotational structure.

Many papers have been devoted to spectroscopic studies of metal hydrides (MH) (see for example [5, 8] and references therein). There are too main approaches for production of these molecules in laboratory conditions. The first utilizes a King type furnace and the molecules are produced by heating the metal up to 2500 - 3000 K in a H_2 containing atmosphere [9]. The second approach uses gas discharge tubes, where the metal is vaporized by sputtering [10, 11, 12]. The second approach has the advantages of producing molecules at lower gas temperatures (close to room temperature) with smaller Doppler broadening. The gas pressure is also lower ($\approx$ 1 torr compared with several tens torrs in the King furnaces) leading to smaller pressure broadening. On the other hand, the collisions with electrons allow higher rovibrational levels of the ground electronic state to be populated which makes the spectroscopic information more rich.

Some of the existing hollow cathode sources provide relatively high concentration of MH molecules, but in a small volume [12]. The current densities are high which leads to fast sputtering of the cathode and requires a cooling. Another construction of gas discharge source can be found in [10]. It consists of a long tubular cathode and a set of pin anodes placed in the centre of the tube. It overcomes the disadvantages of the hollow cathode source. It has large

absorption length and less sputtering of the cathode, but the emmision from the discharge fills the centre of the tube which makes laser-induced fluorescense (LIF) measurements, for example, difficult.

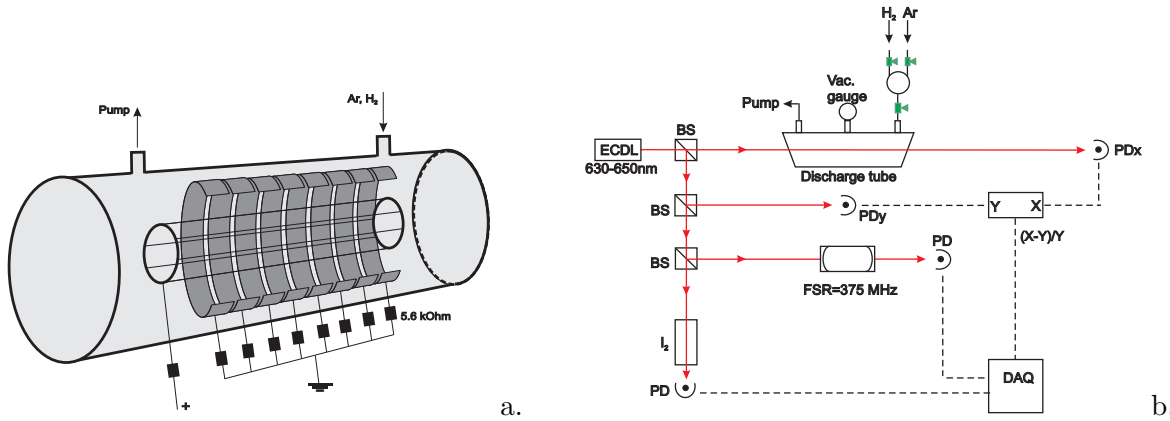


Figure 1. a. Scheme of the discharge tube and **b.** the experimental setup for absorption spectroscopy.

In this paper we present a different design of the discharge tube. It consists of a series of separated ring cathodes and an anode made of several rods forming a cylinder around the center of the tube (Figure 1a). At certain conditions (pressure and discharge current) it was shown that a dark zone is formed in the center of the tube when filled with Ar [13]. This observation motivated us to undertake a systematic study of this tube in order to figure out (i) whether it is suitable for production of high densities of MH and (ii) is it possible to produce molecules at the same conditions when a dark zone is formed in the center of the tube. This would make this tube an extremely attractive source for LIF spectroscopy. The present experiments were carried out with Ni cathodes, because several sources have been tested for NiH production [10, 11, 12] providing good ground for comparison.

2. Experimental setup and results

The discharge tube is made of 50 cm long pyrex glass tube. A total of 8 cathodes (a ring made of Ni 0.5 mm foil, 50 mm in diameter and 20 mm thick) are placed. The space between the rings is about 5-6 mm. Each ring is connected separately to the ground of the high voltage (HV) source via a blast resistor of 5.6 kOhm through a glass feedthrough. The anode consists of six Ni rods, 300 mm in length forming a cylinder with a diameter of 30 mm. The tube is closed with glass windows at a small angle with respect to the tube axes (to avoid back reflections to the laser source and interferences). The tube is equipped with two additional glass tube connections, where KF flanges are mounted for pumping out the tube and filling with buffer gas. The DC HV source is able to reach 1.5 kV and currents up to 250 mA. At these conditions and gas pressures down to 100 mtorr of H_2 and Ar we observed a very stable and homogenous discharge between the cathodes and the anodes.

The concentration of NiH molecules was monitored through their absorption in the red $B^2\Delta_{5/2}$-$X^2\Delta_{5/2}$ band starting from v''=0 in the ground state to v'=0 in the excited electronic B state. This band has been observed already by Brien et al. [11]. The authors give a list of frequencies of identified transitions in two isotopologues – ^{58}NiH and ^{60}NiH so it should be easy to set the laser to one of the absorption lines. The setup is shown in Figure 1b. The laser source is a commercial free running diode laser (635 nm or 650 nm) scanned in frequency by the current and the temperature. While the main laser beam passes the discharge tube and its

intensity is measured by the photodiode PDx, three other beams are split from it. The first one goes to PDy for calibration of the laser power. The second and the third are used for frequency calibration of the laser frequency by a confocal interferometer (free spectral range of 375 MHz) and a 300 mm long iodine cell at room temperature. All signals are collected and recorded by a Tektronix TDS 2024 digital oscilloscope.

After setting the laser frequency on a selected line from [11] the laser was scanned by ±10 GHz around it. At the same time various parameters of the discharge (gas composition, current, pressure) were changed searching for absorption signal. Initially we started with a gas mixture of 90 % Ar and 10 % H_2. This concentration was reported to be optimal in Ref. [10, 12]. The experiments have shown, however, that for the current discharge tube, NiH signals are obtained only in pure hydrogen atmosphere. Adding even small amounts of Ar destroys the absorption signals.

In Figure 2a a typical set of signals is shown. Along with the interference fringes and the iodine lines two NiH lines are seen in this scan (J″=8.5) belonging to different istopologues ^{58}NiH and ^{60}NiH. The NiH signals were very weak, corresponding to an absorbance of about 0.02 % (the strongest signals) and less. An estimate of the Doppler width is made $\Delta\nu_D = 0.027$ cm^{-1}, corresponding to gas temperatures of about 340 K, which sounds very reasonable.

From the measured absorption coefficient and the known absorption length L=250 mm the concentration of NiH molecules in a particular rovibrational level N_J was done through the following realtions:

$$\Delta I/I = \sigma(\nu_0) N_J L, \qquad \text{where} \qquad \sigma(\nu_0) = \frac{2\lambda^2 A_{00}}{8\pi\Delta\nu_D}\sqrt{\frac{\ln 2}{\pi}} \ . \tag{1}$$

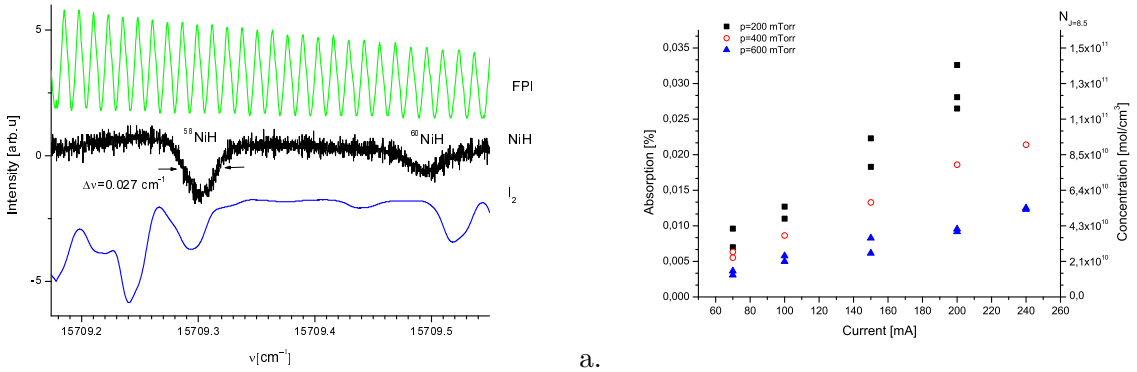
Here λ is the wavelength and A_{00} is the Einstein coefficient for spontaneous emission from the upper level (v'=0, $J' = 7.5$) to the lower level (v''=0, $J'' = 8.5$) of the electronic transition. We estimated this coefficient as follows. From Ref. [10] it is known that the lifetime of the rovibrational levels with $v' = 1$ of the $B^2\Delta_{5/2}$ state is about 1 μs. From [14] it is known that the overall LIF from the $B^2\Delta_{5/2}(v' = 1)$ levels is about 20 times more intensive than the fluorescence from $B^2\Delta_{5/2}(v' = 0)$. If we assume the induced fluorescense as a measure of the number of the excited molecules, we can estimate the transition ($v'' = 0 \rightarrow v' = 0$) as 20 times weaker than the ($v'' = 0 \rightarrow v' = 1$) one and consequently $A_{00} = A_{01}/20$.

Under this assumptions we can estimate the density of NiH molecules in the ($v'' = 0, J'' = 8.5$) state from eq. (1). We obtain a maximum concentration of $N_J \approx 10^{11}$ cm^{-3} for $J = 8.5$ and $N \approx 10^{12}$ cm^{-3} for the total density of molecules where a thermal distribution over the rovibrational levels is assumed (T=340 K). Although very rough this estimation shows the better performance of this source comparaed with other gas discharge sources, e.g. in Ref. [10] where the authors report a concentration of $N \approx 10^{10}$ cm^{-3}.

In order to optimize the working parameters of the tube, we measured the relative absorption of the same spectral line at different currents and pressures of Hydrogen. The measurements were carried out in the center of the tube and close to the anodes. While the increase of the absorption with the current is very close to linear, there is an optimal gas pressure at about 200 – 400 mtorr of hydrogen (see Fig. 2b). Within the uncertainty of our measurements we did not observe significant change of the absorption close to the anodes, so the distribution of NiH within the anode volume should be pretty homogenous.

3. Discussion

The presented configuration of discharge tube turned out to be a successful alternative of the existing sources for production of metal hydrides. The construction is not limited at length, so long absorption paths can be realized. Additional attractive feature of this tube is that there is no



a. b.

Figure 2. a. Typical absorption spectrum around 15709 cm^{-1}. This is the P(8.5) line in ^{58}NiH and ^{60}NiH). **b.** Dependence of the relative absorption of NiH in the center of the tube on the Hydrogen pressure.

current in its center and at certain conditions it can be dark. Unfortunately in case of hydrogen at the currents and gas pressures for maximum NiH production the central zone was bright. In parallel to the experiment we run a numerical simulation (a report will be presented elsewhere) which reproduces reasonably the experimental observations. At present we are optimizing the code and we will search for configuration with at least similar MH concentrations and dark central zone. One way is to study discharges in different hydrogen containing gases (for example CH_4, H_2O, NH_4). Another possibility is to change the geometry of the tube. Preliminary calculations and also practical consideration have shown that a dark zone can be achieved even at 200-400 mtorr of H_2 when the diameter of the cathodes is about two times larger. There is still another direction for future application of the new tube. We plan to study the possibility to insert the tube in a magnetic field in order to study the Zeeman splitting of the MH lines (especially FeH).

4. Acknowledgements

I.B. and A.P. acknowledge a partial support through the Sofia University grant 143/2012 and the National Scientific Fund of Bulgaria grant RILA 01/1/2011.

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