HYDROGEN LINE BROADENING IN AFTERGLOW OBSERVED BY MEANS OF EPR[1]

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This paper concerns the unusual hydrogen line broadening in electron paramagnetic resonance (EPR) spectrum. We study hydrogen line in the afterglow of a microwave discharge in hydrogen with a small amount of oxygen admixture. A strong increase of the hydrogen EPR line width and concentration of H atoms with increasing amount of oxygen in the discharge was observed.

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1 Introduction

There are already studies (e.g. [1, 2]) on line shapes of atomic hydrogen (Balmer lines H_α and H_β) using optical emission spectroscopy (OES) in various discharges. In these studies there was typically used hydrogen mixed with certain noble gases and Doppler-broadened line shapes were identified.

Because our study is focused on processes in afterglow by means of EPR spectroscopy [3], we tried to find broadening of hydrogen line in EPR spectrum. It was shown [4] that a small amount of another gas added into the discharge could significantly change the dissociation of parent gas. The admixture can change both the reactions in the volume and the recombination coefficient on the walls. In the case when the oxygen was added into the hydrogen a strong influence on line intensity, width and integral (proportional to concentration) was observed.

2 Experimental

Schematic drawing of the experimental setup is presented in Fig. 1. We operated with microwave discharge in hydrogen (constant flow-rate 30 sccm) with oxygen admixture (flow-rate varied 0–5 sccm) in a quartz tube with inner diameter of 13 mm. The discharge burnt in a surfatron cavity powered by a magnetron working at 2.45 GHz.

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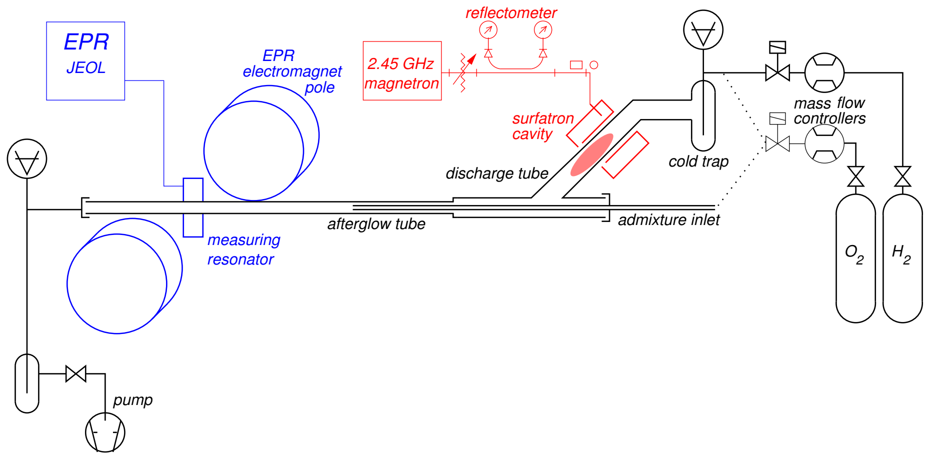

Fig. 1. Schema of experimental apparatus.

The mixture flew through surfatron cavity to 1m long quartz afterglow tube with inner diameter of 8 mm. The admixture was injected either into the afterglow tube by means of capillary or to the main gas upstream from the discharge. The distance between the end of discharge cavity and the center of measuring EPR resonator was 30 cm, end of the capillary (when it was used) was 23 cm after the end of discharge cavity. The hydrogen atom density was measured by means of EPR spectrometer. Operating pressure was around 130 Pa. Power fed into the plasma was 20 W.

3 Electron paramagnetic spectroscopy

This method is based on resonance absorption of microwave energy by the transitions between Zeeman split levels. For this the existence of non-zero magnetic momentum and the presence of external magnetic field are necessary. This method is non-invasive and gives the ability to study the radical reactions with high sensitivity. As discharges and their afterglow contains a lot of radical species, it is often advantageous to use EPR method to measure their concentration [5].

We employed electron paramagnetic resonance spectrometer JEOL JES-3B operating in X-band to measure the concentration of atomic hydrogen. The EPR spectrum of hydrogen (ground level ${}^2S_{1/2}$ consists of two lines which are centered around g=2 and are separated by 5×10^{-2} T (for approx. 10 GHz spectrometer). The absolute concentration was calculated from H line integral using calibration by O_2.

4 Results

In the afterglow we measured the atomic hydrogen concentration, line width and intensity of hydrogen EPR absorption line in two experimental arrangements. First, hydrogen with a small amount of oxygen admixture was fed into the discharge, and second we injected oxygen by a capillary into the pure hydrogen afterglow.

4.1 Oxygen added to the discharge

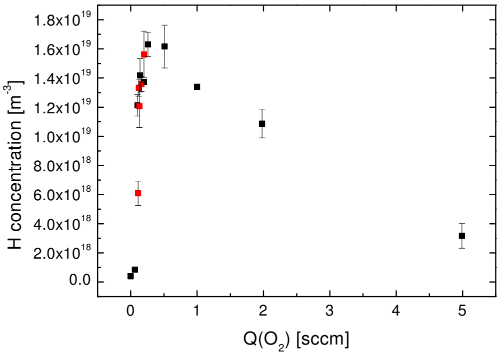

Fig. 2. Dependence of H-atom concentration on flow-rate of oxygen added into the discharge. $Q(H_2) = 30$ sccm.

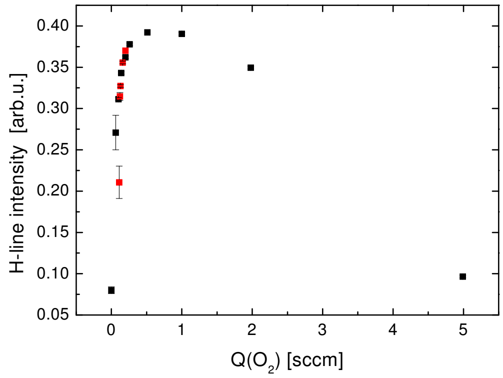

Fig. 3. Dependence of H-line intensity on flow-rate of oxygen added into the discharge. $Q(H_2) = 30$ sccm.

When we added small amount of oxygen admixture into the hydrogen discharge, we observed (see Fig. 2) rapid growth of atomic hydrogen concentration with increasing oxygen flow-rate. Oxygen increases the dissociation degree of hydrogen in the discharge. After the maximum we observed decrease due to dominating recombination processes.

We can see in Fig. 3 similar dependence of atomic hydrogen line intensity on oxygen flow rate as in the case of hydrogen concentration.

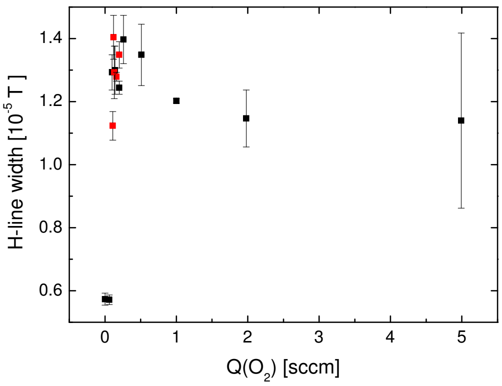

Fig. 4. Dependence of H-line width on flow-rate of oxygen added into the discharge. $Q(H_2) = 30$ sccm.

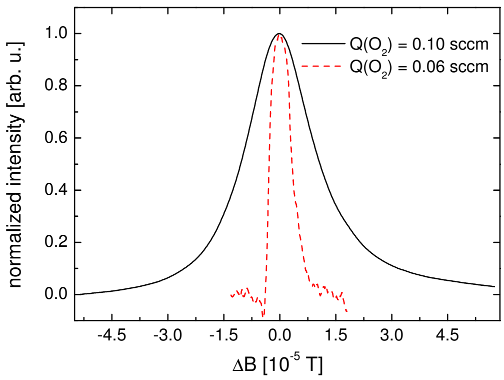

Fig. 5. H-line broadening for two oxygen flow-rates (added into the discharge). Line center is at $0,3293$ T, $Q(H_2) = 30$ sccm. The curves were normalized to unity.

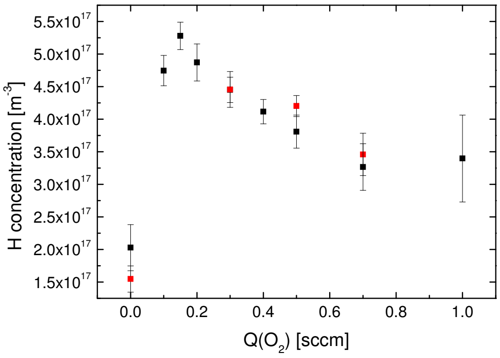

Fig. 6. Dependence of H-atom concentration on flow-rate of oxygen added into the hydrogen afterglow. $Q(H_2) = 30$ sccm.

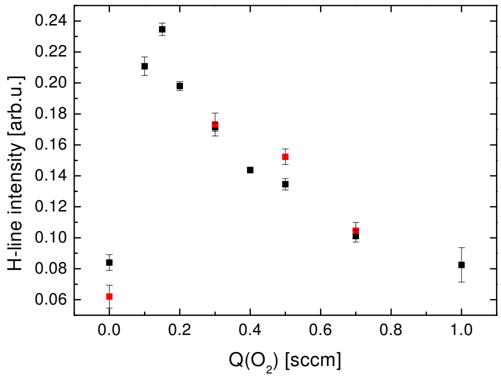

Fig. 7. Dependence of H-line intensity on flow-rate of oxygen added into the hydrogen afterglow. $Q(H_2) = 30$ sccm.

The Fig. 4 shows pronounced dependence of atomic hydrogen line width on increasing oxygen flow rate. After the sharp maximum we see again a decrease of the line width. Typical hydrogen EPR line has Lorentzian line shape. Our broadened hydrogen line also matched Lorentzian profile with high accuracy. In the Fig. 5 one can see the comparison of the broadest and narrowest line shape observed. Narrow line recorded at lower admixture flow is weak and therefore strongly affected by noise.

4.2 Oxygen added to the afterglow

When we add oxygen into pure hydrogen afterglow, we observe (see Fig. 6) similar dependence of hydrogen concentration on oxygen flow-rate as in previous experimental arrangement. Maximum is moved to lower oxygen flow-rate and maximum hydrogen concentration decrease by a factor cca 30. In comparison with hydrogen line intensity in the Fig. 7 we can see greater errors due to noise which affects integral more than intensity.

We assume the growth being caused by reaction of oxygen with hydrogen metastable molecule or vibrationally excited molecules [3]. When the source of atomic hydrogen is depleted the recombination processes begin to be important.

Line widths of hydrogen in this experimental setup were nearly constant (mean value was $(4.13 \pm 0.06) \times 10^{-6}$ T) and no anomalous broadening was observed. This indicates that for processes leading to broadening of H-line in the afterglow the presence of oxygen in the hydrogen discharge is necessary.

5 Discussion

We assume that the growth of atomic hydrogen EPR line width is caused by high velocities of absorbing hydrogen atoms. As the neutral gas temperature is close to room temperature, it means that hydrogen atoms are suprathermal. On the assumption that we have Boltzmann velocity distribution, the Doppler-broadening leads to a Gaussian profile of spectral lines. However, in our case we observe broadened line with Lorentzian line profile. The collision broadening is improbable because H-line width is pressure independent (S states should not broaden by collisions). Moreover when we used nitrogen instead of oxygen we did not observe any hydrogen line broadening. So one possibility is that H atoms velocity distribution is not Boltzmannian. In this case the typical Gaussian shape is not necessarily produced. If we suppose that narrowest hydrogen line width is the natural line width convoluted with apparatus function, we can calculate the H atom velocity needed for observed maximum broadening. As the real velocity distribution function is not known we can only estimate that the effect is comparable to the case when the H atoms have temperature approx. 1700 K.

The observation of excessive EPR H-line broadening in the afterglow of microwave-driven plasma is unexpected because of room temperature of plasma afterglow. It means that hydrogen atoms require a source of kinetic energy.

A source of energy must be in chemical reactions between hydrogen and excited oxygen. We guess that molecular hydrogen metastable triple states [6] play important role in energy storage as they are weakly bonded and can be easily dissociated.

The mechanism of this anomalous hydrogen line broadening, in spite of being observed in optical spectra by many authors, is still not clear. Some authors suppose interaction between particles and electrode surface in the plasma sheaths. The mechanism proposed by Djurović and Roberts [2] is the production of fast H atom from electric field-accelerated H_2^+. However, this hypothesis is based on the existence of strong electric fields (typical in sheaths) which are absent in our microwave plasma experiment.

In microwave plasma Mills [1] explained hydrogen line broadening by the release of energy from atomic hydrogen by resonant nonradiative energy-transfer mechanism. His explanation is based on existence of very controversial *resonance-transfer plasma* and *hydrino atom* which is hydrogen with hypothetical binding energy higher than 13.6 eV.

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