Study of the rovibrational levels of ground state excited hydrogen molecules by laser photodetachment and emission spectroscopy

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Abstract: We aim to probe the rovibrational levels of ground state excited hydrogen molecules by means of laser photodetachment and emission spectroscopy. These excited molecules are produced by recombinative desorption on the surface of a material, converted in negative ions by dissociative attachment. Different working conditions (materials and surface temperature) will be investigated and the effects of these conditions on the density of negative ions and the distribution of the first vibrational levels will be studied.

Keywords: rovibrational ground state molecules, recombinative desorption mechanisms, negative ions, hydrogen plasma, emission spectroscopy

1. Introduction

Vibrational excitation of an H2 molecule in its electronic ground state (X1Σg state) is the first step prior to the formation of a negative ion, H-, via dissociative attachment (DA). DA is a mechanism that involves highly excited states (v'' > 6) and cold electrons (< 1 eV). Vibrational excitation of a molecule is either caused by: i) inelastic collisions between primary electrons (T_e > 25 eV) and ground state molecules; ii) recombinative desorption mechanisms (Langmuir-Hinshelwood, Eley-Rideal and Harris-Kasemo) when atoms impinge on the surface and react immediately or after a short diffusion with adsorbed atoms [1,2].

Negative ions are of great relevance in many fields: i) in nuclear fusion, dedicated programs have been set up to design efficient H- negative ion sources [3,4]; such studies are mandatory for the future programs ITER and DEMO; ii) for high-energy particle accelerator programs (European spallation source or CERN superconducting proton linac); iii) in astrophysics, once H2 is rovibrationally excited, it can radiatively relax and emit a photon, which may escape from an interstellar cloud and cool the gas. H2 formation is considered as a coolant in the early universe, and the rate coefficient of the associate detachment (AD) reaction (H- + H → H2 + e-) has been experimen tally measured [5]. Augundez et al. [6] argued that vibrationally excited H2* molecules can overcome or diminish the activation barrier of various chemical reactions in molecular astrophysics.

We are focussing our interest on vibrationally excited H2* molecule by studying negative ions and emission lines in the visible range (600-630 nm).

2. Diagnostics of rovibrationally excited molecules

Two types of diagnostics could be employed to measure the population in the different excited rovibrational levels of the ground state: i) recording the fluorescence after promoting H2*(v'',J'') into a higher excited electronic state and ii) recording the ion current after ionization of the ground state excited molecule. Both are complex and very expensive to setup.

To circumvent these difficulties we employ laser photodetachment (1064 nm) in combination with optical emission spectroscopy. Negative ion, H-, produced via dissociative attachment (DA) and probed by photodetachment are related to highly excited states (v'' > 6) while emission spectroscopy scans lower levels (v'' < 4).

3. Laser photodetachment

The laser beam (ø 4 mm) is generated from a Nd:YAG 1064 nm laser (Quantel - Brilliant, 5 ns pulse width, 150 mJ/pulse). Here, the energy density is 50 mJ/cm2 and the probe bias is 25 V, i.e. 10 V above the plasma potential.

These conditions ensure saturation of the photodetached electron current pulse, which is measured with a wideband current transformer (Pearson electronics, 2877) connected to a LeCroy WaveSurfer 44Xs oscilloscope (400 GHz – 2.5 GSamples/s).

4. Emission spectroscopy

The lower vibrational states of the electronic ground state of the molecular hydrogen (v"< 4) will be inferred on the basis of the measured neutral gas pressure and the translational temperatures determined from Doppler-broadened line profiles [7].

For these measurements we use a Horiba Jobin-Yvon HR1000, 1 m of focal length, 0.01 nm of resolution, near
UV and visible range (350 – 900 nm). A spectrum obtained in ROSAE III plasma source is presented in Fig. 1.

![Normalized emission spectra of the microwave discharge in range of the wavelength 601 – 608 nm.](image)

**5. Source of vibrationally excited H$_2^*$ molecules**

The H$_2^*(v'',J'')$ source, named SCHEME for Source of exCited HydrogEn MolecEules, consists of a tungsten filament surrounded by a Pyrex surface, cooled at a constant temperature of 220 K, and a sample holder, cooled (220 K) or heated (370 K). When maintained at a moderated temperature (~ 1500 K) the heated filament partially dissociates H$_2$ molecules into atoms and does not evaporate onto the Pyrex surface and the studied material. The sample holder and the disk of studied material are bored. This small aperture controls the H$_2^*(v'',J'')$ flow rate delivered inside ROSAEIII.

The SCHEME source is connected to ROSAEIII (both have the same axis). A plasma source, employed only for the cleaning process of the Pyrex and the surface of the material, is set close to the filament. Hydrogen-argon (80-20 %) plasma allows both chemical and mechanical cleaning. Hence, a realistic comparison between different materials could be drawn from this study. As the Pyrex surface is maintained cold [8], H atoms only adsorb and recombine on the surface of the material to form ground state excited H$_2^*(v'',J'')$ molecules.

![Schematic of the source SCHEME.](image)

**6. Source of electrons**

The ROSAE III plasma source, already presented [4], briefly described below is used as a source of electrons to convert H$_2^*(v'',J'')$ into negative ions by DA mechanism (cold electrons Te < 1 eV) and to excited from the ground state to upper states which decay in the visible range. ROSAEIII has proven its ability to furnish electrons of different energies by using different working conditions. ROSAE III is implemented with a network of four dipolar ECR sources has been set on the top flange on a circle of 76 mm in diameter. The network is driven from a single microwave power supply of 1.2 kW (2.45 GHz) by dividing its microwave power into four equal parts. The axial distance, on the source symmetry axis, between the mid plane of the dipolar sources and the injection of the exited molecules is 200 mm.

**7. Expected results**

The Pyrex surface will be kept cold (220 K) to drastically decrease the recombination of H atoms on its surface. Theoretical works [1,2] have suggested, and previous experiments [9] have confirmed, that H$_2^*(v'',J'')$ molecules could escape from surfaces, by recombinative desorption, in high ro-vibrational levels at different yields depending of the material and of its temperature [9,10]. Hence, using the surfaces of different materials at two temperatures (cold 220 K and hot 370 K), we expect to compare recombinative desorption yield of materials for different exited states and involved mechanisms.

Three materials will be investigated: graphite (HOPG), tantalum and stainless steel. Graphite and tantalum have already proven, by indirect diagnostics, their ability to produce excited molecules [11]. Stainless steel, a conventional material used for vacuum chambers, will be used as a reference surface. The variation of the surface temperature will help to demonstrate which formation mechanism dominates; that is, either the diffusion of H atoms on the surface, namely the Langmuir-Hinshelwood mechanism and, to a lower extend, the Harris-Kasemo mechanism, or the direct reaction with already adsorbed atoms, Eley-Rideal mechanism.

**8. References**