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Determination of the rotational population of H_2 and D_2 including high-N states in low temperature plasmas via the Fulcher-α transition

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ABSTRACT

Vibrational and rotational excitation of the hydrogen molecule can significantly affect molecular reaction rates in low pressure low temperature plasmas, for example for the creation of H^-/D^- ions via the dissociative attachment process. In general, the rotational population in these discharges is known to be non-thermal with an overpopulation of states with high rotational quantum number N. In contrast to a sophisticated direct measurement of the rotational distribution in the $X^1\Sigma_g^+, v=0$ state, it is demonstrated that the determination can also be carried out up to high-N levels rather easily via optical emission spectroscopy utilizing the Fulcher-α transition of H_2 and D_2. The measured rotational populations can be described with a two-temperature distribution where the cold part reflects the population according to the gas temperature of the discharge. This has been verified by using the emission of the second positive system of nitrogen as independent gas temperature diagnostic. The hot part where the rotational temperature reaches several thousand Kelvin arises most probably from recombinative desorption of hydrogen at the discharge vessel wall where parts of the binding energy are converted into rotational excitation. Neglecting the hot population – what is often done when using the Fulcher-α transition as gas temperature diagnostic – can lead to a strong over-estimation of T_{gas}. No fundamental differences in the rotational distributions between hydrogen and deuterium have been found, only the hot rotational temperature is smaller for D_2 indicating an isotope-dependency of the recombinative desorption process.

1. Introduction

For hydrogen discharges, it is well known that rovibrational excitation of the H_2 molecule can have a significant impact on several molecular reaction rates. The correct consideration of these processes plays a key role for a detailed understanding of these plasmas, for example concerning H^- or D^- densities in negative hydrogen ion sources [1]. In the plasma volume, H^-/D^- ions are formed by dissociative attachment of electrons to the hydrogen molecule. For H_2 (D_2), the reaction rate increases by five (seven) orders of magnitude if the molecule is vibrationally excited to a state with the vibrational quantum number $v=5$ ($v=6$) [2]. Rotational excitation has an analogous effect as the rate is only dependent on the total internal energy of the molecule and not on the exact fraction of the energy in the particular rotational or vibrational modes [3].

In low pressure hydrogen discharges the rotational levels in the electronic ground state are known to be

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populated in a non-thermal way: Rotational states with low rotational quantum number follow a Boltzmann distribution according to the gas temperature of the discharge whereas those levels with high quantum number are overpopulated by several orders of magnitude (see for example [4–9] for hydrogen and [10–12] for deuterium). Different processes that could contribute to the overpopulation in general have been evaluated in detail in [9]. It turned out that the reaction behind the overpopulation – which is present in all vibrational states – is most probably recombinative desorption of hydrogen at the wall of the discharge vessel where parts of the energy from the exothermic reaction are converted into rotational excitation.

Despite the high overpopulation of the rotational states and its potentially considerable influence on the molecular reaction rates, direct measurements of rovibrational populations in the electronic ground state are rarely carried out. This arises from the fact that rather complex and expensive diagnostic methods such as coherent anti-Stokes Raman scattering (CARS) spectroscopy [7,10,11], resonantly enhanced multi-photon ionization (REMPI) [4], VUV laser absorption spectroscopy [5,6] or laser induced fluorescence (where the laser radiation is generated via stimulated anti-Stokes Raman scattering) [8,9] are required.

In contrast, the determination of the rotational population of the $v=0$ level in the electronic ground state presented in this paper is based on optical emission spectroscopy measurements of the Fulcher-α transition ($d^3\Pi_u \rightarrow a^3\Sigma_g^+$). This emission band is located in the visible spectral range and is routinely evaluated for obtaining the gas temperature of a discharge from the rotational population of the $d^3\Pi_u$ state since Lavrov's pioneering work [13–15]. Typically, these measurements are restricted to levels with rather low rotational quantum numbers. In this paper, the evaluation of the Fulcher-α transition is extended to the first twelve (for D_2 13) rotational levels what allows an easy assessment of the non-thermal part of the rotational population. It should be noted that such a distribution may also alter the direct correlation between the rotational temperature and the gas temperature T_{gas} in general [16]. In order to check if T_{gas} corresponds to the rotational temperature of the low lying states, measurements with varying nitrogen admixtures to hydrogen and deuterium plasmas have been carried out. From the evaluation of the emission arising from the second positive system of nitrogen, a reliable value for the gas temperature can be obtained [16].

2. The Fulcher-α transition of molecular hydrogen

The Fulcher-α spectrum which arises from the transition from the $d^3\Pi_u$ into the $a^3\Sigma_g^+$ state is located between 520 and 770 nm but the most intense part lies at 590–650 nm. It is typically the most intense emission of the hydrogen molecule in low pressure plasmas why it is often utilized for diagnostics concerning the rotational or vibrational population. Details of the Fulcher-α transition and the properties of the involved electronic states have been described extensively multiple times (see for example [17,14]), therefore only the most important facts are given in the following. The upper electronic state is split into the $d^3\Pi_u^+$ and $d^3\Pi_u^-$ states because of λ-doubling. Due to optical selection rules, the Q branch of the Fulcher-α transition originates only from the $d^3\Pi_u^-$ state whereas the P and R branch originate from the $d^3\Pi_u^+$ state. The latter two branches are not considered in the present investigation as the $d^3\Pi_u^+$ state is strongly perturbed by other electronic states [18,19] leading to anomalies in the intensities of the emitted lines [20].

In the upper $d^3\Pi_u^-$ state, the dissociation limit of H_2 to H (1s) and H(2s) is located between the energy levels of the vibrational states $v'=3$ and $v'=4$ [21,22]. Predissociation leads to non-radiative decay of the states and therefore the Fulcher-α emission gets considerably weaker for transitions involving states with $v' \geq 4$ [23]. For deuterium the limit is between the states $v'=4$ and $v'=5$ and transitions from $v' \geq 5$ are much weaker [18]. Therefore, the evaluations carried out in this paper are restricted to the vibrational states $v'=0, 1, 2$ and 3 both for deuterium and hydrogen. In addition, only the diagonal vibrational transitions with $v'=v''$ are considered as they represent the most intense emission bands within the electronic transition. Fig. 1 shows an exemplary Fulcher-α emission spectrum of hydrogen where the position of the Q lines from the first four diagonal vibrational transitions are depicted. The line positions have been taken from [24]. Fig. 2 shows the same spectrum but for deuterium, the line positions have been taken from [25]. Due to the larger mass of the deuterium molecule, the wavelength separation of the individual emission lines is smaller in comparison to hydrogen. A zoom into the region just above 600 nm is depicted in Fig. 3 in order to demonstrate that the individual lines of the Fulcher-α transition are well resolved both for H_2 and D_2 with the utilized spectroscopic setup (see Section 4 for details on the setup). This is important for the detailed evaluation described in this paper.

In low pressure low temperature discharges, the $d^3\Pi_u^-$ state is predominantly populated by electron impact excitation out of the ground state $X^1\Sigma_g^+$ [14,17]. It has been shown that the selection rule $\Delta N=0$ holds for this

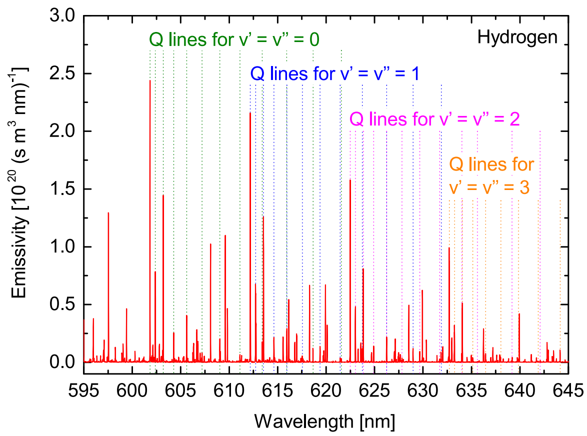

Fig. 1. Example spectra of the Fulcher-α emission of hydrogen recorded in an ICP operated at 1 Pa with an RF power of 600 W. The Q lines of the first four diagonal vibrational transitions ($v'=v''$) considered in the evaluations are depicted.