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Lyman transitions of high rovibrationally excited H_2, HD and D_2 molecules

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ABSTRACT

Energies and probabilities of Lyman transitions of high rovibrationally excited H_2, HD and D_2 molecules have been measured and compared with calculations. The experimental results are obtained from laser-induced fluorescence spectra that have been recorded in the spectral range from 60500 to 83500 cm^{-1}, covering 2/3 of the hydrogen Lyman band system. The necessary vacuum-UV radiation is produced by stimulated anti-Stokes Raman scattering, providing a widely tunable radiation source with narrow spectral bandwidth to resolve single Lyman transitions. The highest internal energies of detected hydrogen isotopologues are close to the dissociation limit. This extends the available data base of Lyman transitions from and to higher rotational states ($J > 10$) of HD and D_2.

1. Introduction

The HD molecule is the simplest two-electron system to be considered after H_2 and therefore of interest for quantum mechanical calculations beyond the Born–Oppenheimer approximation. After H_2 and CO, HD is the third most abundant molecule in the interstellar medium and therefore relevant in astrophysics [1]. The HD density gives a measure of the H/D ratio in the universe, which is an important parameter in cosmology, e.g., for cooling processes of gas clouds and for the understanding of star formation [2]. HD was also detected in the atmosphere of gas planets [3,4]. Moreover, it is considered as a probe for detecting mass variation effects on a cosmological time scale [5]. On the other hand, D_2 has not been detected in the interstellar medium so far, because almost all D is bound in HD molecules due to the high H/D ratio [6].

In experimental fusion reactors, when driven by mixtures of H_2 and D_2, HD and D_2 molecules were found as recombination products in the cooler regions, i.e., in front of surfaces exposed to the plasma core [7–9]. While in space only the lowest rovibrational states of molecular hydrogen are occupied due to the low temperature, hydrogen molecules can be excited to high vibrational v and rotational J states in technological plasmas [7,8,10]. These high excitations are due to several processes, among them surface association of hydrogen atoms leading to the formation of a rovibrationally excited molecule (e.g., $H_{gas} + H_{surf} \rightarrow H_{2,gas}$). Association processes are widely studied in surface science, where rovibrationally excited hydrogen molecules were found to be formed by surface association reactions in experiment and models [11,12].

Since Mie observed Lyman transitions in the vacuum-ultraviolet (VUV) emission spectrum of an H_2/HD/D_2 containing argon lamp in 1934 [13], subsequent investigations concentrated mainly on improvements in sensitivity and accuracy of the detection [1,14–18]. Infrared Fulcher band emission measurements of H_2/HD/D_2 molecules followed by Dieke and Blue in 1935 [19], and more recently the visible and infrared emission spectrum has been studied by Aguilar et al. [20], Bailly and Vervloet [21]. The electronic and vibrational transition probabilities for $B^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ and $C^1\Pi_u \rightarrow X^1\Sigma_g^+$ transitions of H_2, HD and D_2 were determined by electron-excitation by Geiger and Schmoranzer [22]. A review on the electronic spectrum of deuterium molecule is available in [23] and recently, the electronic excited emission spectra of H_2 and D_2 were studied by Abgrall et al. [40] and Ajello et al. [1]. Finally, additional experimental data on the emission of D_2 in the VUV spectral range were presented by Roudjane et al. for $D^1\Pi_u \rightarrow X^1\Sigma_g^+$, $D'^1\Pi_u^- \rightarrow X^1\Sigma_g^+$ and $B'^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ bands [6,24].

Measurements of VUV spectra of HD in the interstellar medium require observatories in space, which became available only recently with the Copernicus and FUSE satellites [2,25–27]. In laboratory experiments molecular hydrogen densities were measured rovibrationally resolved by means of (resonance-enhanced) multiphoton ionization [12,28], a technique that requires low pressures and is difficult to be applied to an ionized gas like a plasma. Low lying rovibrational states of HD with $v < 3$ were detected by coherent anti-Stokes Raman scattering (CARS) [29,30]. The detection of densities of higher rovibrational states ($v > 1$) requires not only an efficient source of highly excited molecules, but also a broadband spectroscopic technique in the VUV with a narrow bandwidth to resolve single transitions. Stimulated anti-Stokes Raman scattering (SARS) is such a technique that has already been applied to the

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detection of rovibrationally excited H_2 [31–34], but only very recently to HD and D_2 molecules [10].

In this paper we present the detection of Lyman transitions of HD and D_2 from and to high rovibrationally excited states. The identification of the transitions and the determination of their transition energies become possible by comparison with an extension of earlier calculations toward higher rotational states ($J > 10$).

2. Spectroscopy on Lyman transitions of H_2/HD/D_2 molecules

Lyman transitions of rovibrationally excited hydrogen molecules have been detected by means of laser induced fluorescence (LIF). The necessary narrow bandwidth radiation in the VUV spectral range is produced by stimulated anti-Stokes Raman scattering (SARS), a technique described in detail before [31–36]. A scheme of the spectroscopic setup is shown in Fig. 1. Tunable laser radiation in a wavelength range from 436 to 470 nm is provided by a dye laser (Sirah Precisionscan), which is pumped by a frequency tripled Nd:YAG laser (Spectra Physics GCR230) operated at a repetition rate of 10 Hz. The dye laser radiation is frequency doubled in a Beta Barium Borate crystal resulting in pulses of 5 ns duration and with energies of 5–10 mJ in the spectral range from 218 to 235 nm and a bandwidth of 0.15 cm^{-1}. This beam is focused into a Raman cell, filled with 250 kPa of hydrogen gas, which is cooled by liquid nitrogen to enhance the SARS process [33,35]. The high laser intensity in the focus enables the SARS process producing laser-like coherent Stokes (S) and anti-Stokes (AS) beams. The beams are subsequently shifted in frequency by the vibrational Raman shift of H_2 (4155.22 cm^{-1}) and reduced in energy due to the non-linear SARS process. The fourth to ninth AS cover a range from 115 to 165 nm, i.e., about 2/3 of the spectral range of the hydrogen Lyman band system (see Fig. 2). However, the detectability of a transition depends on the density of a molecule in the lower state and on the transition probabilities of the excitation process and of the spontaneous emission back to the ground state. The wavelength range

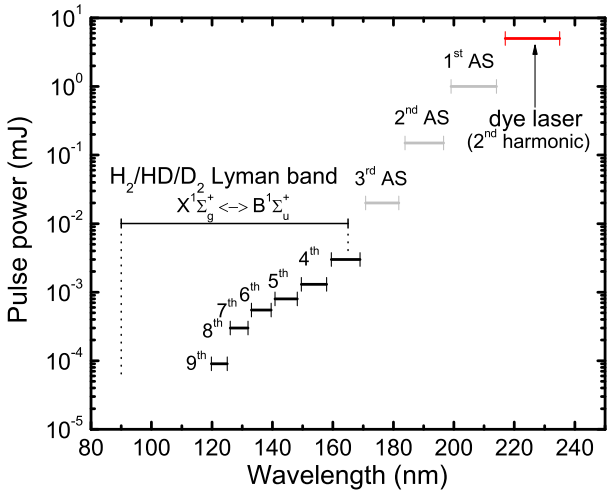

Fig. 2. Wavelength and pulse energy distribution of the anti-Stokes beams produced in the Raman cell.

lower than 110–115 nm is not accessible due to the non-availability of transparent windows in this spectral range. Thus, the Lyman transitions detected by this spectroscopic setup are limited to transitions of hydrogen molecules with internal excitations higher than about 1 eV, i.e., $(v,J) > (2,5)$ in case of H_2, $(v,J) > (2,9)$ in case of HD and $(v,J) > (4,9)$ in case of D_2.

Rovibrationally excited H_2, HD and D_2 molecules are produced in a cascaded arc [37,38], which provides a partially ionized and dissociated hydrogen plasma jet. The arc is driven by a current of 45 A and a power input of about 7 kW (see Fig. 3). Hydrogen gas flows through the plasma channel with a total flow rate of 3000 sccm (1.25×10^{21} s^{-1}) under sub-atmospheric pressure of about 9 kPa. Pure H_2 or D_2 gas is used as well as 50:50 mixtures

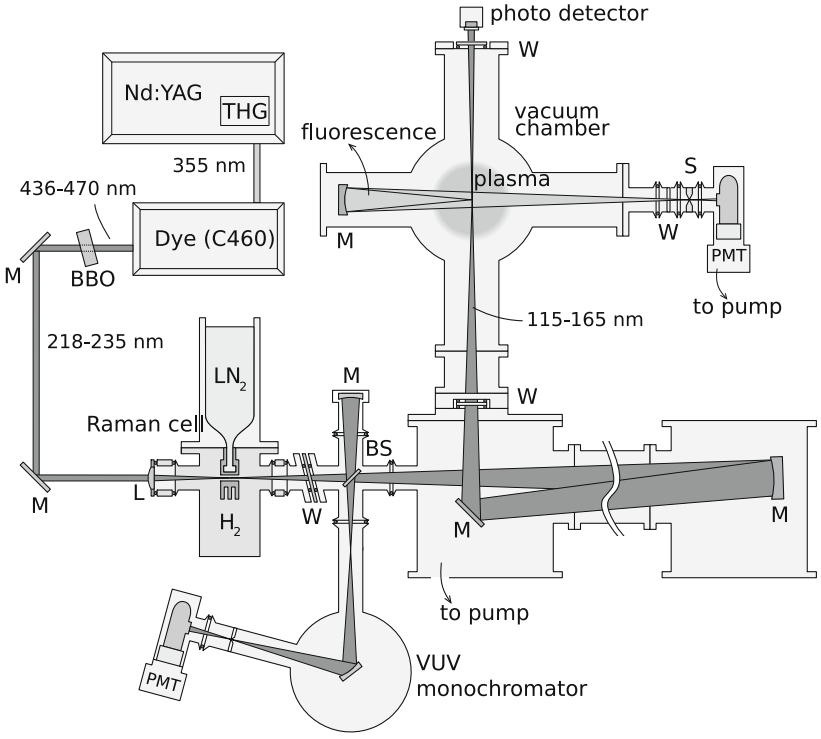

Fig. 1. Scheme of the spectroscopic setup showing the conversion of the laser frequency along the beam path and the LIF setup within the vacuum chamber (M – mirror, L – lens, W – window, BS – beam splitter).