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Detection of rovibrationally excited molecular hydrogen in the electronic ground state via synchrotron radiation

S. Béchu,[1,a)] S. Aleiferis,[1,b)] J. Bentounes,[1,c)] L. Gavilan,[2] V. A. Shakhatov,[3] A. Bès,[1] P. Svarnas,[4] S. Mazouffre,[5] N. de Oliviera,[6] R. Engeln,[7] and J. L. Lemaire[8]
[1]*LPSC, Université Grenoble-Alpes, CNRS/IN2P3, F-38026 Grenoble, France*
[2]*LATMOS, CNRS UMR 8190, IPSL, Université de Versailles Saint-Quentin, F-78280 Guyancourt, France*
[3]*Topchiev Institute of Petrochemical Synthesis, Moscow 119991, Russia*
[4]*High Voltage Lab., Electrical and Computer Engineering Department, Rion-Patras 26504, Greece*
[5]*ICARE, 1c, Avenue de la recherche scientifique, 45071 Orléans, France*
[6]*DESIRS beam line, Synchrotron SOLEIL, Saint Aubin, 91192 Gif sur Yvette, France*
[7]*Department of Applied Physics, University of Technology, 5600 MB Eindhoven, The Netherlands*
[8]*Institut des Sciences Moléculaires d'Orsay (ISMO), CNRS - Université Paris-Sud, Université Paris-Saclay (UMR 8214), 91405 Orsay, France*

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We describe an original setup named SCHEME (Source of exCited HydrogEn MolEcules) designed to study the recombinative desorption mechanisms of H atoms on a surface by means of high-brilliance monochromatic synchrotron radiation (SR). H atoms are produced on electrically heated filaments under vacuum (in the absence of any discharge) and subsequently recombine on a surface to produce excited hydrogen molecules, namely, $H_2(v'', J'')$. Once these levels are produced, they are probed in the vacuum chamber with 5–40 eV (248–31 nm) SR-photons. A preliminary test with Krypton has demonstrated the feasibility of SCHEME to obtain simultaneously VUV-synchrotron radiation induced fluorescence and VUV-absorption signals with room-temperature gas. In order to evaluate the hydrogen molecule dissociation induced by the heated filaments, the absolute density of H atoms has been measured by VUV-absorption. At 1800 K and 100 mTorr, we estimated a dissociation degree of 10^{-4}, which corresponds to an absolute density of $1.8 \times 10^{17}\ m^{-3}$. VUV-absorption spectroscopy is shown to be a valuable tool to detect $H_2(v'', J'')$ molecules up to $v'' = 3$. Possible improvements of the experimental setup, to detect higher v'' levels, are suggested in the end of this paper. *Published by AIP Publishing.*
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The vibrational excitation of a H_2 molecule in its electronic ground state ($X^1\Sigma_g^+$) 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 ($v'' \geq 5$) and cold electrons (≤ 1 eV).[1] The vibrational excitation of a molecule can be caused by: (i) inelastic collisions between primary electrons ($T_e \geq 25$ eV) and ground state molecules;[2,3] (ii) recombinative desorption mechanisms (Langmuir-Hinshelwood, Eley-Rideal[4] and Harris-Kasemo) when atoms impinge on a surface and either react immediately or diffuse in a short time before reacting with already adsorbed atoms.[5,6]

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;[7,8] such studies are mandatory for the future programs ITER and DEMO;[9–11] (ii) for high-energy particle accelerator programs (European spallation source or CERN superconducting proton linac);[12–14] (iii) in astrophysics, where H_2 formation via negative ions is considered as a coolant in the early universe ($H^- + H \rightarrow H_2 + e^-$); vibrationally excited $H_2(v'', J'')$ molecules can overcome or diminish the activation barrier of various astrochemical reactions.[15] This letter presents an original setup designed to probe these excited states of the H_2 molecules by both fluorescence [vacuum-ultra violet (VUV)-synchrotron radiation induced fluorescence (SRIF)] and absorption spectroscopy using VUV synchrotron radiation (SR). It is worth mentioning that the characterization of $H_2(v'', J'')$ formed after recombination of H atoms on cold surfaces simulating interstellar grains has been the subject of many experimental studies.[16–18] These experiments use REMPI $2+1$ (resonantly enhanced multi-photon ionization at $2+1$ photons), while the main interest of the synchrotron radiation is to allow direct 1-photon characterization of $H_2(v'', J'')$.

Prior to the study of recombinative desorption mechanisms, experiments were conducted with Kr room-temperature gas. As Kr atom density can be estimated from the pressure and as a Kr atom optical transition exists close to the Ly-α line, krypton can be used for fine tuning, optimization, and calibration of the optical setup. The main claim of the present work lies in the application of a SR-based technique for determining operational windows that will allow the study of recombination desorption mechanisms.

The SCHEME (Source of exCited HydrogEn MolEcules) source has been installed on the end-station branch of the DESIRS (Dichroïsme Et Spectroscopie par Interaction avec le Rayonnement Synchrotron) monochromatic beam line.[19] The 200 gr/mm grating is employed here to obtain the highest photon flux (4×10^{13} photons s^{-1} at

[a)]Author to whom correspondence should be addressed: bechu@lpsc.in2p3.fr
[b)]Present address: Patras University, Rion-Patras 26504, Greece.
[c)]Present address: Abdelhamid Univ. IBN Badis, Mostaganem, Algeria.

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10 eV) with a slit opening of 30 μm and a spectral resolution of ~25 pm, optimal to distinguish the rotational J″ components and, in particular, the neighbouring R0 and R1 lines of $H_2(v'', J'')$. The vacuum chamber (VC) is a 120 mm diameter Pyrex-glass™ cylinder closed at both ends and encapsulated into a copper cylinder (see Fig. 1). This copper cylinder is cooled to a constant temperature (290 K). The Pyrex-glass and copper cylinder are placed into a third stainless steel cylinder (160 mm in diameter) to keep them under high vacuum (5×10^{-6} mbar base pressure). A turbo molecular pump (800 l/s) is directly connected to this cylinder. Holes (×8) drilled in the Pyrex-glass and in the copper tube allow the pumping of the inner volume of the VC. With this setting, the base pressure is reached within less than 2 h after venting. Three hot tungsten filaments, 0.1 mm in diameter and 120 mm in length, are placed in the glass chamber and are electrically heated to reach a moderate temperature (≤ 2000 K compared to the tungsten melting point of 3695 K) to avoid pollution due to tungsten evaporation. Under these conditions, the heated filaments partially dissociate H_2 molecules into atoms due to thermal and catalytic effects. Inside the VC chamber, facing the filaments, the present material under test (standard 304-L stainless steel) is mounted on the Pyrex-glass cylinder and maintained at the same temperature (290 K). The total surface of the material is 0.01 m^2 with a Pyrex-glass to stainless steel surface ratio of 5. As the recombination coefficient, γ, on the Pyrex-glass surface ($\gamma \sim 0.004$ at 290 K)[20,21] is much lower than the stainless steel one ($\gamma \sim 0.5$ at 240–300 K),[22] H atoms are adsorbed and recombine preferentially on the metal surface to form ground state excited $H_2(v'', J'')$. The synchrotron beam enters the VC through a MgF_2 window placed between the tuning fork chopper and the VC. The filament current and the surface temperature are stabilized before any measurement.

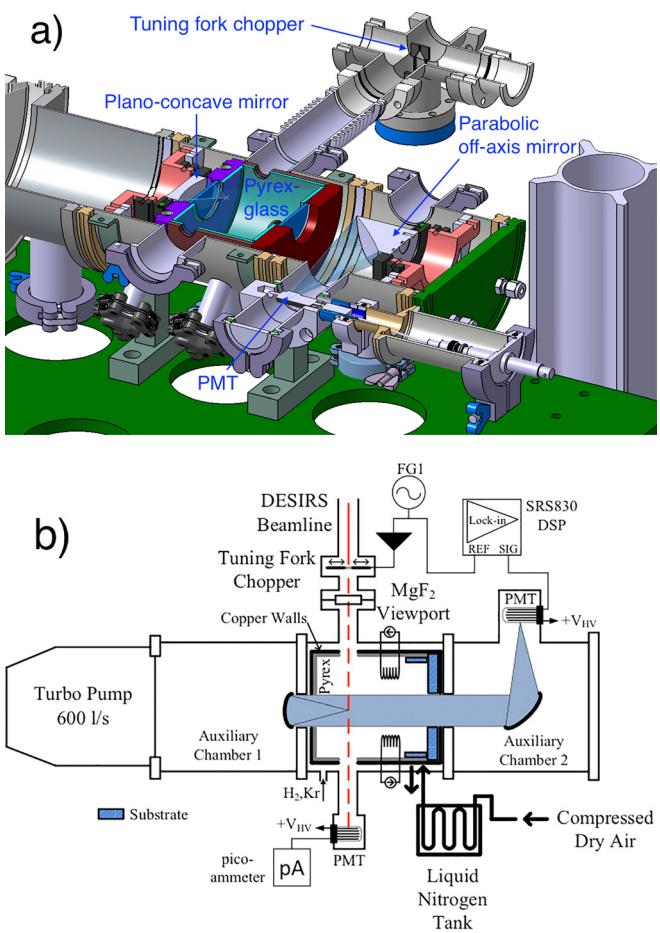


FIG. 1. Horizontal cuts of the SCHEME setup: (a) 3D drawing and (b) schematic. The Pyrex-glass cylinder is housed in a copper cylinder and is closed by MgF_2 windows. Holes, observable in the Pyrex-glass and in the copper tube, are drilled to place three heated filaments in the chamber and for pumping. The third heated filament is out of the cutting plane in (b). The red discontinuous line refers to the synchrotron beam line. The beam enters either a VUV PMT or a VUV spectrometer using the same PMT.

For SRIF spectroscopy, the optical setup comprises a short focal length concave mirror and an off-axis parabolic mirror, both VUV enhanced. The collection of the fluorescence light is made perpendicular to the SR radiation wave vector. The two ends of the VC have an aperture diameter of 50 mm to allow light collection by the concave mirror placed on the left and by the off-axis mirror placed on the right (see Fig. 1). Both mirrors are protected from tungsten heating and/or evaporation by 2 mm thick MgF_2 windows. A solar blind photomultiplier tube (PMT Hamamatsu R1259) is placed at the focal point of the parabolic mirror. In addition, the SR is chopped by a tuning fork (see Fig. 1) oscillating at constant frequency (130 Hz) for phase-sensitive detection using a lock-in amplifier (SR830 - Stanford Research Ltd).

For absorption spectroscopy, the light of the SR beam, which is selectively absorbed by $H_2(v'', J'')$ molecules, enters directly a PMT (R1259) or the slit of a low resolution (0.5 nm) VUV monochromator equipped with the same PMT and used to completely remove the filament-originated visible light which perturbs the signal of the solar blind detector which is the same as PMT. The latter has a spectral response between 115 and 195 nm and is biased at −900 V, resulting in a gain of 6.5×10^5.

The effect of a specific surface material on the production of $H_2(v'', J'')$ exited states has been investigated by using stainless steel 304-L as a test material. Following a rigorous methodology, two reference measurements are performed: (i) measurement of the Kr absorption line (at 123.6 nm) or induced fluorescence at a controlled pressure and (ii) measurement of the H atom density in the VC.

After a fine-tuning, optimization, and calibration of the optical setup with room-temperature Kr gas, the SCHEME experimental setup allows the simultaneous acquisition of an induced fluorescence signal (with the use of the lock-in amplifier) and an absorption spectrum (with the use of a picoammeter) of the 123.6 nm Kr-atom line, as shown in Fig. 2. It also gives the possibility to monitor the transparency of the thin MgF_2 windows, which are placed perpendicular to the SR beam to protect the mirrors, by measuring the intensity of these spectra obtained at a definite pressure.

Figure 3 shows the absorption spectrum of the Ly-α line. For these lowest wavelengths, only the absorption spectrum has been detected. Despite the use of phase-sensitive detection, the SRIF signal was too weak to be recorded. The attenuation of the signal induced by the MgF_2 windows, and the PMT, is 36% higher for the Ly-α (121.6 nm) than that for the Kr radiation (123.6 nm), and the reflectivity for the two mirrors is 3% lower for hydrogen. Hence, the total attenuation is therefore ~50% higher for the Ly-α than that for the Kr

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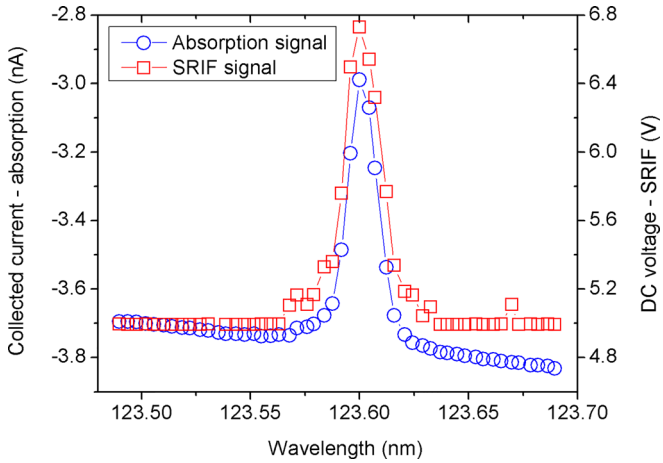


FIG. 2. Simultaneous records of the SRIF signal and absorption spectrum of the Kr atom at the 123.6 nm line (pressure: 10 mTorr and slit opening: 10 μm).

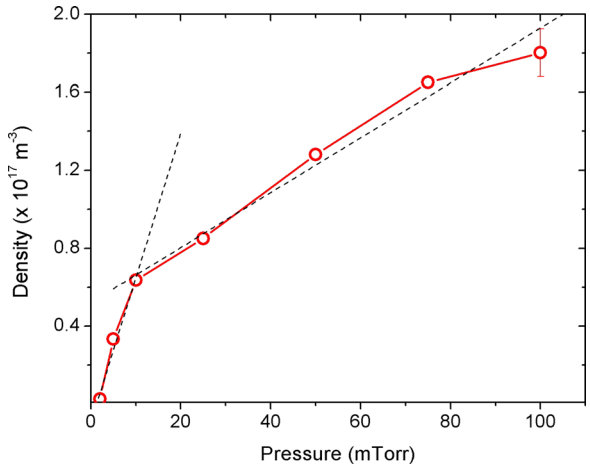


FIG. 4. Absolute density of H atoms, obtained by absorption spectroscopy, as a function of pressure; the temperature of filaments is 1800 K.

radiation. Consequently, the H atom density has been evaluated through VUV-absorption which gives a higher sensitivity. Even though the resolution of the 200 gr/mm grating is too low to evaluate the Doppler broadening of the line as performed by Niemi *et al.*[23] for oxygen and nitrogen atomic lines with a high resolution Fourier-transform spectrometer, a Gaussian curve fits well to the measured line profile (Fig. 3). Integration of this line is used to get the normalized absorbance and subsequently the H atoms density in the VC. Figure 4 presents the absolute density of H atoms as a function of the H_2 inlet pressure (error bar is calculated from several measurements at 100 mTorr). It can be pointed out that the variations of the density present two linear parts: the first one, steeper, between 2 and 10 mTorr and the second one from 10 to 100 mTorr. As depicted by Zheng *et al.*,[24] several mechanisms are responsible for the dissociation probability of hydrogen molecules on hot tungsten wires in similar working conditions. However, investigation of these mechanisms is beyond the scope of this letter. At 100 mTorr, a H atom density of 1.8×10^{17} m^{-3} is obtained, corresponding to a degree of dissociation of 1×10^{-4}. Hence, even though the dissociation degree is weak, the electrically heated filaments produce a controllable quantity of H atoms. This is mandatory to study the mechanism of recombinative desorption.

The variation in H atom density as a function of the temperature of the filaments, presented in Fig. 5, shows a linear increase. The density of H atoms at 2000 K, extrapolated from the linear variation of the atom density, is 2×10^{17} m^{-3}. Hence, one can expect an increase of 20% of the atom density when the temperature is set at its maximum, 2000 K, instead of 1800 K (as employed for long duration experiments). Investigations concerning recombinative desorption have been mainly conducted at 100 mTorr and 1800 K to expose the material under test to the highest density of atoms while minimizing evaporation of tungsten.

Figure 6 shows the transition of the first J″ levels of the R- and P-branches of the $^1\Sigma^+$ B-$^1\Sigma^+$ X (v′ = 1-v″ = 2) transition for two filament temperatures (1800 K and 2000 K) at 100 mTorr. These results clearly demonstrate the feasibility of measuring the vibrational population in the ground state (here, v″ = 2 and also for v″ = 3 with a much lower signal-to-noise ratio) of $H_2(v'', J'')$ molecules created in the VC chamber. In this case, the investigated material was stainless steel (standard 304-L) maintained at 290 K and mounted on

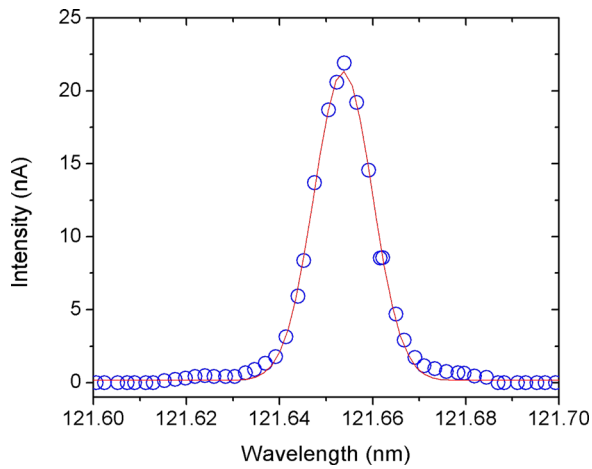


FIG. 3. Absorption spectrum of the Ly-$_\alpha$ line (pressure: 100 mTorr, slit opening: 10 μm, and temperature of filaments: 1800 K). The red line is a Gaussian fit, base line subtracted.

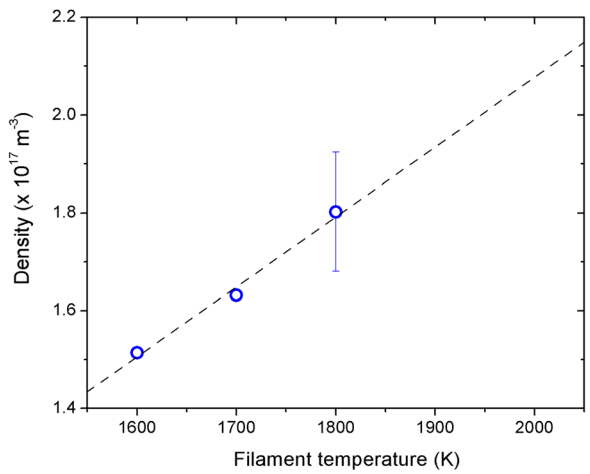


FIG. 5. Absolute density of H atoms, as a function of filament temperature; pressure: 100 mTorr.

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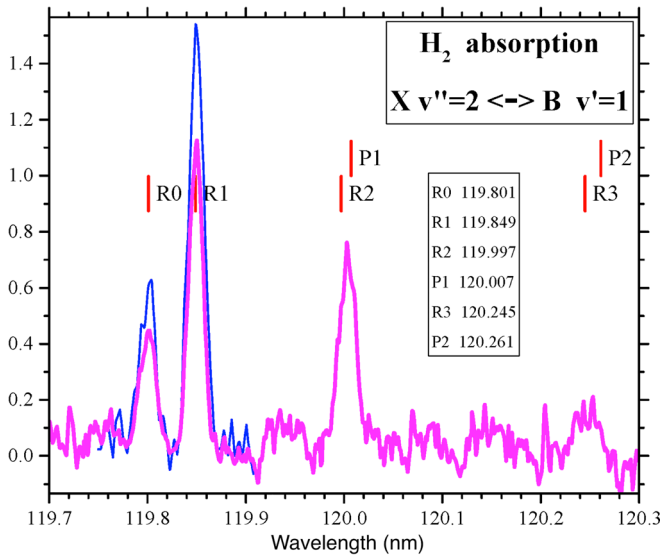


FIG. 6. Absorption spectra of H_2 molecules (in nA) for tungsten filaments heated at 1800 K (pink line) and 2000 K (blue line). At 2000 K, the spectrum ranges from 119.75 nm to 119.92 nm only because the beam time allocation ended (pressure: 100 mTorr and slit opening: 30 μm).

the Pyrex-glass facing the heated filaments. The effect of the filament temperature, at the same pressure, is obvious on R0 and R1 absorption lines. An increase of nearly 30% of the absorption spectrum is due to an equivalent augmentation of the H atom density in the VC chamber, as shown in Fig. 5. These atoms recombine with other atoms, already adsorbed on the stainless steel surface, and desorb into excited molecules. It confirms, as stressed by Hall *et al.*[25] and Umemoto *et al.*,[26] a creation of $H_2(v'', J'')$ molecules by recombinative desorption of H atoms on the tested material, stainless steel in that case, and a negligible excitation due to the collisions of molecules on the hot filament surface.

In this letter, we show that with the experimental setup SCHEME, we can simultaneously obtain a VUV-SRIF and a VUV-absorption signal for Kr gas at room temperature and pressures ranging from 1 up to 100 mTorr. VUV-absorption allows the measurement of the absolute density of H atoms as a function of pressure and filament temperature. These results, concerning H atoms, drive our choice of experimental working conditions: 100 mTorr and 1800 K (in the continuous mode) and 2000 K (for a narrow wavelength range scan) for the study of the recombinative desorption mechanisms. This study demonstrates the possibility of probing these mechanisms by using synchrotron radiation for absorption spectroscopy. However, the low signal to noise ratio, the lack of safe zero reference measurements, and the fact that the R0/R1 ratio at 1800 K and 2000 K was not consistent prevent us from obtaining even an estimation of the $H_2(v'', J'')$ population. As a consequence, we are planning to improve the setup: (i) by using a better H_2 dissociation method, a plasma source for example; and (ii) by decreasing the spectral line width of the SR, using a 2400 gr/mm grating which is available for the DESIRS-6.65 m monochromator. Hence, recombinative desorption mechanisms would be enhanced and a higher sensitivity of VUV-absorption would be reached to obtain results on higher v'' and J'' levels of the of $H_2(v'', J'')$ molecules.

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