High-resolution laser spectroscopy on H_2 at 97–98 nm

P. C. Hinnen[1,2], W. Hogervorst[1], S. Stolte[2], W. Ubachs[1]

[1] Laser Centre Vrije Universiteit, Department of Physics and Astronomy, De Boelelaan 1081-1083, NL-1081 HV Amsterdam, The Netherlands
[2] Department of Chemistry, De Boelelaan 1081-1083, NL-1081 HV Amsterdam, The Netherlands
(Fax: +31-20/444-7899)

Abstract. A narrowband tunable eXtreme UltraViolet (XUV) laser source is used for a high resolution study of the Lyman $(B^1\Sigma_u^+ - X^1\Sigma_g^+)$ band system of molecular hydrogen. Seven rotational transitions of two vibrational bands, (10,0) and (11,0), in the wavelength range from 97.2–98.3 nm have been investigated for the first time under sub-Doppler molecular beam conditions. A calibration procedure using the I_2 standard in the visible yielded an absolute frequency accuracy of 0.02 cm^{-1}. The obtained H_2 transition frequencies provide a calibration standard in the extreme ultraviolet wavelength region.

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High-resolution spectroscopy with tunable lasers was initially restricted to the visible and infrared wavelength domain. With the advance of high-power, pulsed dye lasers frequency doubling and sumfrequency mixing in birefringent crystals were shown to be efficient methods for the production of tunable UV laser light. Transparency and phase-matching properties of these non-linear materials are, however, limited and at present tunable pulsed radiation at power levels of $\approx$ mJ/pulse may be generated to just below 200 nm [1]. In the domain of the vacuum-ultraviolet ($\lambda < 200$ nm) nonlinear wave mixing in noble gases [2], molecular gases [3] or metal vapors [4] has been applied to produce coherent radiation, but the power levels obtained are below the µJ/pulse level. Amongst others Hilbig and Wallenstein and Hilber et al. [5, 6] have shown that two-photon resonant sum- and difference-frequency-mixing processes in noble gases are clean, elegant and rather efficient methods to generate short wavelength radiation. Particularly, the application of pulsed gas jets in combination with differential vacuum pumping [7] opens the possibility to produce eXtreme UltraViolet (XUV) radiation below the lithiumfluoride transparency cutoff ($\lambda < 105$ nm). Notwithstanding the low power levels these narrowband

XUV laser sources, based on nonlinear up-conversion of pulsed dye-laser radiation, have in recent years been applied in high-resolution atomic [8–10] and molecular spectroscopy [11–13].

In the present study of H_2 emphasis is put on the possibility to accurately calibrate absolute transition frequencies in the XUV by using a reference spectrum in the visible wavelength range, in this case the I_2 absorption standard [14, 15]. An absolute accuracy of 0.02 cm^{-1} is obtained after eliminating the largest error-source: the nonlinearity of the wavelength scan.

Accurate calibration of H_2 spectral lines is of astrophysical importance. H_2 absorptions in the range 90–100 nm may act as a radiative shield preventing photodissociation of the important CO molecule in the interior of interstellar clouds [16]. The Prasad-Tarafdar [17] cosmic-ray-induced XUV-radiation model relies on accidental coincidences between H_2 and CO resonances. In both cases accurate frequency calibration of the H_2 (and CO) transitions is of importance. The Lyman $B^1\Sigma_u^+ - X^1\Sigma_g^+$ band system of H_2 has been the subject of many previous investigations [18–21, 23] and recently an atlas of the XUV spectrum of H_2 has been completed [22]. Although the present XUV laser experiment is too time consuming to record the entire XUV spectrum of H_2, the absolute transition frequencies of a small number of lines may provide a tool to verify the calibration in other, more extensive studies. Also the lines presently investigated may be used as future reference lines in the XUV wavelength domain.

1 Experimental

A schematic of the experimental setup is shown in Fig. 1. The performance of the XUV laser source has been described before [24] and here only relevant details are given. A dye laser (Quanta Ray, PDL 3) is pumped by an injection-seeded frequency-doubled Nd:YAG laser (Quanta Ray, GCR 4) to generate tunable radiation in the 580–600 nm range. This light is frequency doubled in
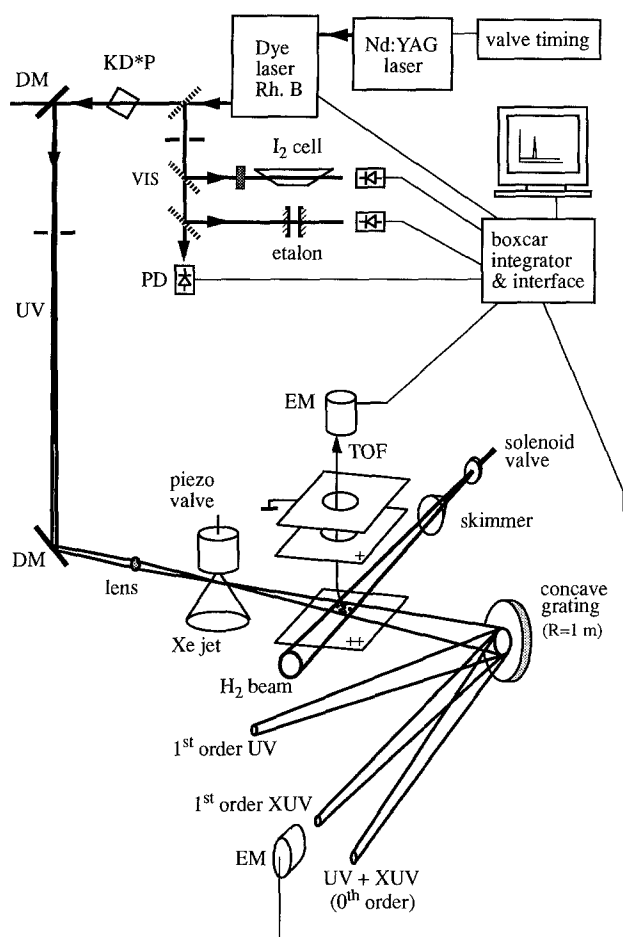
Fig. 1. Schematic of the experimental setup used for XUV spectroscopy. DM: Dichroic Mirror; EM: Electron Multiplier; TOF: Time Of Flight; PD: PhotoDiode

Fig. 2. The $B^1\Sigma_u^+$ $(v=11)-X^1\Sigma_g^+$ $(v=0)$ $R(0)$ resonance line of H_2 at 97.2 nm recorded by 1 XUV + 1 UV photoionization. Also shown is a part of the I_2 absorption spectrum and an etalon spectrum. The lines used for calibration purposes are labeled according to the iodine atlas [14]

a KD*P crystal to produce ultraviolet light. The UV radiation is separated from the fundamental light by two dichroic mirrors and focused into a first vacuum chamber with a 15 cm lens. Here the tunable XUV radiation is generated by frequency tripling in a dense xenon jet, produced by a home-built piezo-electrically driven valve, delivering dense gas pulses of about 100 μs. The spatially and temporally overlapping XUV and UV beams then enter a differentially pumped detection-chamber via a small hole where they interact with a pulsed and skimmed molecular beam in a crossed-beam configuration. In this setup H_2 resonance lines with a width below the Doppler width of 0.9 cm^{-1} can be measured.

H_2 molecules are resonantly excited by the XUV radiation and subsequently ionized by the ultraviolet photons (1 XUV + 1 UV ionization process). Ions are accelerated with an extraction field of 25 V/cm into a field-free Time-Of-Flight (TOF) region and detected on an electronmultiplier. After mass-selection in the TOF-drift tube signal at mass 2 is selected by a boxcar integrator for the recording of the resonances. At resonance also H^+ fragment ions are observed, which are neglected. During a laser scan the UV intensity is held constant using a home-built autotracker system. Up to 40 mJ
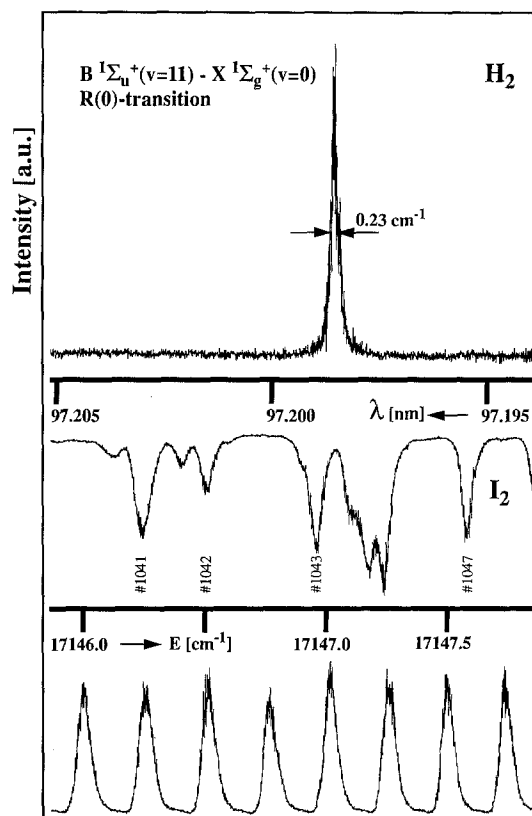
ultraviolet light could be produced but then severe broadening of the H_2 lines was observed. These effects were avoided by reducing the UV power to ≈ 6 mJ/pulse. With a fraction of the fundamental light of the dye laser an iodine absorption spectrum, an etalon spectrum (free spectral range = 0.25 cm^{-1}) and an output power spectrum of the dye laser are simultaneously recorded (Fig. 2). The I_2 spectrum is used for absolute calibration [14] of the frequency scale. As the frequency of the XUV radiation corresponds to the sixth harmonic of the fundamental, the I_2 frequencies are multiplied by six. The recalibration of the I_2 absorption standard is accounted for [15]. The etalon spectrum is used to compensate for nonlinearities in the wavelength-scan. A vacuum monochromator with a concave grating of 1 m radius was installed behind the photoionization-zone (Fig. 1) to separate the XUV from the UV light. The XUV intensity was recorded by detection of the first-order diffracted beam on an electronmultiplier. The output power of the dye laser is also recorded to correct for power fluctuations. Data handling is performed on a Sun4 workstation.

2 Results

In Fig. 2 simultaneous recordings of the $B^1\Sigma_u^+ - X^1\Sigma_g^+$ (11,0) $R(0)$ H_2 resonance line, the corresponding I_2 ab-

sorption spectrum and an etalon spectrum are presented. Each data point in the spectra is an average of 10 laser shots. Similar spectra were also recorded for other P and R lines of the $B-X(10,0)$ and $(11,0)$ Lyman bands. An advantage of the present setup is that a rotationally cooled H_2 beam is used, so that there is no ambiguity in the assignment of absorption lines. The H_2 resonances were fitted with a Voigt profile, whereas the iodine lines were fitted with a Gaussian lineshape. In this fitting procedure also the separations between the H_2 and I_2 line centers were determined. The linewidth of the measured H_2 transitions was 0.23(2) cm^{-1} (FWHM), mainly determined by the linewidth of the dye laser (0.065 cm^{-1}). In previous experiments [24] a linewidth of 0.30 cm^{-1} was obtained at this wavelength. The present lower value of the XUV laser bandwidth is obtained by filtering out the central part of the UV beam with an iris diaphragm, thus selecting the light with superior transverse coherence. By increasing the distance between the H_2 nozzle and the skimmer up to 12 cm, Doppler broadening is reduced to a minimum. A residual Doppler broadening due to the divergence of the molecular and the XUV beam of 0.02 cm^{-1} is estimated for a pure H_2 beam.

Line positions of the H_2 resonances are obtained from interpolation between the I_2 absorption lines. The $R(0)$ line of the $B-X(10,0)$ band could not be calibrated by this procedure, because the corresponding I_2 absorption spectrum is so dense that the single lines listed in the atlas were not resolved by the pulsed dye laser. The stepper motor for the wavelength control of the dye laser was modified with a gearing wheel in order to decrease the step size, such that at the sixth harmonic ≈ 40 data points were taken over the 0.23 cm^{-1} width of the XUV resonances. From an inspection of the etalon markers it is deduced that oscillations with an amplitude of ± 0.015 cm^{-1} occur on the frequency scale in the visible. This nonlinearity in the scan could give rise to systematic errors in the determination of H_2 resonance frequencies of up to 0.1 cm^{-1}. However, the etalon markers were used to linearize the frequency scale. For this purpose for each recording of a single rotational line large frequency scans were required, including at least 7 etalon fringes. With the small step size needed to cover the H_2 resonances, time consuming recordings of 45 min per scan were taken. Each line was recorded at least 5 times for statistical averaging. In this way the H_2 transition frequencies were determined relative to the I_2 standard with a statistical error of 0.015 cm^{-1} in the XUV. This error contains the inaccuracy in the determination of line centres of H_2 as well as I_2 resonances. The absolute accuracy (one standard deviation) of the I_2-frequency standard is 0.001 cm^{-1} in the visible [15] and therefore gives an additional but independent error on the XUV frequency scale of 0.006 cm^{-1}. Combining the unrelated errors, an uncertainty of 0.02 cm^{-1} results for the absolute transition frequencies of the H_2 resonances.

Systematic errors may play a role as well. First the H_2 molecular beam density was lowered to yield a density on the order of 10^{-6} Torr in the interaction zone. From the recorded XUV intensity it follows that under these conditions the absorption at resonance is below the detection

Table 1. Measured transitions of the Lyman band system of H_2. Δ_1: difference between the present value and that of [23]; Δ_2: the same for [19]. [r] self-reversed line in emission spectrum; [c] calculated value, not observed; [*] more than one assignment; [b] blended; [e] overlapped by strong emission lines of the source

Transition	Energy [cm^{-1}]	Δ_1 [cm^{-1}]	Δ_2 [cm^{-1}]
$B(10)-X(0)$, $P(1)$	101 746.48(2)	-0.10[r]	$+0.33$
$B(10)-X(0)$, $R(1)$	101 825.29(2)	-0.16[c]	[e]
$B(10)-X(0)$, $R(2)$	101 668.28(2)	-0.16[c]	$+0.40$
$B(11)-X(0)$, $P(1)$	102 738.55(2)	-0.23[r*]	$+0.34$
$B(11)-X(0)$, $R(0)$	102 882.16(2)	-0.09[c]	-0.16
$B(11)-X(0)$, $R(1)$	102 813.77(2)	-0.09[c]	-0.76[b]
$B(11)-X(0)$, $R(2)$	102 652.83(2)	-0.11[c]	-0.14

limit (5%). Strong XUV absorption would give rise to a net Doppler shift towards higher frequencies, but this effect is circumvented in the conditions of low molecular beam densities. Non-perfect perpendicular alignment of the XUV beam and the molecular beam can also cause a Doppler shift. This shift Δv is given by: $\Delta v = v_0 (v/c) \sin \theta$, where v_0 is the transition frequency; v is the velocity of the molecular beam; c is the velocity of light in vacuum; θ is the angle between the molecular- and the XUV-beam. By seeding H_2 in a krypton beam (approximately 20% H_2 seeded in Kr) the velocity of the H_2 molecular beam could be reduced from 1800(300) m/s to 480(100) m/s. The measured shift in the absolute transition frequency of the seeded and the pure beam is in the order of 0.01 cm^{-1} (to shorter wavelengths) in good agreement with a measured misalignment (i.e., deviation from perpendicular alignment) of 1.5(3) degrees of the two beams. From this we estimate a Doppler shift of about 0.005 cm^{-1} (to the blue) for the low-velocity seeded beam. The values for the H_2 transition frequencies, listed in Table 1, were corrected for this effect.

3 Discussion and conclusion

Seven rotational transitions in the Lyman band system of molecular hydrogen have been measured in high resolution in the wavelength range from 97–98 nm using coherent tunable XUV radiation. This XUV light was produced by third-harmonic generation in xenon gas of the frequency doubled output of a pulsed dye laser. The advantage of the frequency-tripling method for the production of XUV light compared to the more efficient sumfrequency-mixing techniques [6] is the on-line calibration possibility of the XUV radiation. In sumfrequency-mixing schemes always absolute calibration of two dye lasers is required. Although the tripling is less efficient the H_2 transitions could be satured easily with the XUV radiation produced.

Comparison of the present data with classical absorption measurements [19] as well as with more recent measurements which were performed by emission spectroscopy [23] are given in Table 1. The differences with the absorption measurements [19] are larger than 0.15 cm^{-1}

which is the absolute error stated for these classical experiments. In the recent emission study only the $B-X(10,0)$ $P(1)$ line was observed as a single, but self-reversed line. Its frequency agrees within 0.1 cm^{-1} with the present value.

In view of the limited amount of data points per band no attempt was made to derive new values for the molecular constants. On the present level of accuracy the rotational structure of the $B\,^1\Sigma_u^+$ state is known to be perturbed by non-adiabatic coupling to the $C\,^1\Pi_u$, $B'\,^1\Sigma_u^+$ and $D\,^1\Pi_u$ states. From the transition frequencies of the $P(1)$ lines of both vibrational bands accurate values for the band origins could be extracted, that may be useful for comparison in future with ab initio or RKR calculations. Using accurately known values for the rotational and centrifugal constants of the ground state of H_2 [25] the following values resulted: $\nu_0(v=10) = 101\,864.97(2)$ cm^{-1} and $\nu_0(v=11) = 102\,857.04(2)$ cm^{-1}.

Because of the high absolute accuracy of the measured transition frequencies these lines can in future be used for calibration purpose in the XUV-domain.

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