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Ivanov, T.I.; Vieitez, M.O.; de Lange, C.A.; Ubachs, W.M.G.

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Frequency calibration of B $^1\Sigma_u^+$–X $^1\Sigma_g^+$ (6,0) Lyman transitions in H$_2$ for comparison with quasar data

T I Ivanov, M O Vieitez, C A de Lange and W Ubachs

Laser Centre, Vrije Universiteit, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands

E-mail: wimu@nat.vu.nl

Abstract

The Lyman and Werner spectroscopic transitions of molecular hydrogen, the most ubiquitous molecular spectral lines observed in the universe, provide a tool to probe a possible variation of the proton-to-electron mass ratio μ on a cosmological time scale. Such procedures require a database of zero-redshift, or laboratory-based wavelengths at the highest possible level of accuracy. Accurate transitions in the B $^1\Sigma_u^+$–X $^1\Sigma_g^+$ (6,0) Lyman band of H$_2$ are still missing in the set of laboratory data, due to previously encountered problems in generating the appropriate wavelengths using a narrow-band extreme ultraviolet laser source. Here frequency calibrations of the missing transitions are presented from a laser-based study at a $(5–8) \times 10^{-8}$ accuracy level.

1. Introduction

The issue of a possible variation of fundamental constants on a cosmological time scale has become a key query in modern physics. Besides detection of a variation of the fine structure constant α [1], the focus is now also on a possible variation of another dimensionless quantity, the proton-to-electron mass ratio $\mu = m_p/m_e$, in particular because it is hypothesized that the variation of μ should be larger than that of α [2]. Deductions on μ-variation relate to the absorption spectrum of the ubiquitous Lyman and Werner bands of the hydrogen molecule, the most abundant molecular species in the universe. Since the underlying concept was put forward by Thompson [3], and Varshalovich and Levshakov reported a first constraint on a variation of μ from H$_2$ spectroscopic comparisons over a range of redshifts [4], this subject has attracted much attention, especially after accurate laboratory frequencies of the prominent Lyman and Werner transitions have become available [5–7]. Ubachs and coworkers reported an indicative decrease of μ by 0.002% over a timespan of the past 12 Gyrs [8], based on a comparison between accurate laboratory data and 76 quasar H$_2$ spectral absorption features occurring in Q 0405–443 and Q 0347–383 at high redshifts. However in the database of accurately calibrated rest-frame frequencies a number of transitions were missing, in particular in the B $^1\Sigma_u^+$–X $^1\Sigma_g^+$ (6,0) Lyman band. In previous measurement campaigns difficulties were encountered in the narrow-band pulsed dye amplification system to generate wavelengths in the range 616–621 nm, the fundamental wavelengths required to generate the XUV-radiation at 102.5–103.5 nm for excitation of the B $^1\Sigma_u^+$ ($v' = 6$) state in H$_2$. The experimental difficulties have been resolved through the use of special solvent mixtures for the dyes used in the laser amplifier chain. This made it possible to measure accurate transition frequencies in the (6,0) band, which now complement the database of accurate laboratory frequencies of molecular hydrogen, which may be used in future comparisons with highly-redshifted H$_2$ transitions to extract information on possible variations of μ.

2. Experiment

The experimental setup is described in previous publications [5, 9, 10] and is only summarized briefly here. The tunable narrow bandwidth continuous wave output of a Spectra Physics 380 D Ring Dye Laser is used to seed a three-stage pulsed dye amplifier (PDA) producing nearly Fourier-transform limited laser pulses of 5 ns duration. The alignment procedures for the ring dye laser and the PDA are decoupled through the use of an optical fibre, allowing for a high spatial stability of

the seed beam. The ring laser was routinely operated in the range 616–621 nm by using Rhodamine B dye dissolved in glycol. As discussed in the comprehensive study by Philip *et al* [5], problems were encountered in the production of powerful laser pulses at wavelengths longer than 615 nm. This prohibited the production of corresponding wavelengths near 103 nm required for the excitation of B $^1\Sigma_u^+$ ($v' = 6$) levels in molecular hydrogen. Only three transitions originating from $J'' = 0$ and $J'' = 1$ could be observed previously at a low signal-to-noise ratio.

For the purpose of the present study we have carefully examined the operation of the PDA, while using several dyes and solvents. Optimum operation in the desired range was accomplished by using Sulforhodamine 101 dye in a solvent mixture of 60%–40% (volume) methanol and water. This way pulse energies of approximately 140 mJ could be obtained in the range 616–621 nm. The procedures to convert the Fourier-transform limited laser pulses from the PDA to UV pulses (using a KD*P crystal) and then to XUV pulses (via harmonic generation in a gas jet of xenon) are similar to those discussed previously [5, 9, 10].

The overlapping XUV and UV beams are crossed perpendicularly with a pulsed and skimmed beam of molecular hydrogen released from a pulsed nozzle (General Valve Series 9) with a stagnation pressure of approximately 2 bar. The nozzle is positioned 8 cm from the skimmer and 18 cm from the interaction region. The ions created by 1+1′ resonance enhanced multiphoton ionization (REMPI) are extracted by a pulsed electric field in a direction perpendicular to the plane formed by the laser and the molecular beams and detected with an electron multiplier. This time-of-flight (TOF) technique allows for mass identification of the ions and distinction against those arising from the background oil in the vacuum system. Moreover, the extraction field is switched on 0.2 μs after the laser pulse, ensuring field-free excitation. Absolute frequency calibration of the seeding light is derived by performing saturation spectroscopy of I_2 and recording the transmission fringes of an actively stabilized étalon (FSR $\approx$ 150 MHz). The integrated ion signal and the calibration signals are simultaneously read out by a computer. A typical spectrum recorded in this manner is shown in figure 1. The upper trace shows the spectrum of the B $^1\Sigma_u^+$ ($v' = 6$, $J' = 1$) $\leftarrow$ X$^1\Sigma_g^+$ ($v'' = 0$, $J'' = 0$) transition in H_2. The lower two traces represent the calibration spectra consisting of a Doppler-free absorption spectrum of molecular iodine (B–X system) and a transmission spectrum of the étalon.

Special attention is paid to Doppler shift effects as they contribute significantly to the experimental error budget. The velocity distribution in the molecular beam expansion can be monitored by varying the time delay of the gas pulse with respect to the laser pulse. By iterative comparison of the spectra arising from the early and late arrival parts of the molecular pulse, the angular position of the nozzle can be precisely adjusted: the position of near-zero Doppler shift is at the location where the transition frequency does not depend on the velocity in the beam. Also a separate experiment is done to determine and further minimize the residual Doppler shift. The measured spectra of the H_2 are compared to the
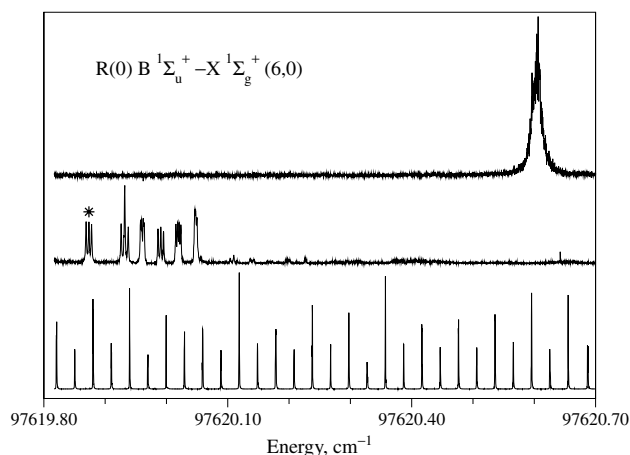
Figure 1. Spectrum of the B $^1\Sigma_u^+$($v' = 6$) $\leftarrow$ X $^1\Sigma_g^+$($v'' = 0$) R(0) Lyman transition in H_2 (upper trace). The line width of the measured transition is 450(25) MHz. The middle trace represents a simultaneously recorded Doppler-free calibration spectrum in molecular iodine; the R(101) (11−3) transition with the 't'-component at 16 269.978 92 cm^{-1} is marked with (∗). The lower trace represents a transmission spectrum of a frequency-stabilized étalon.

Table 1. Effects contributing to the error and their estimated values.

Source	σ^a (MHz)
Doppler uncertainty	100
AC Stark shift	30–50
Chirp shift	100–150
I_2 calibration	10
Étalon drift	2
Statistics	50
Resulting uncertainty^b	150–200

^{a} σ stands for standard deviation.
^{b} Calculated from the quadrature sum of all contributions.

spectra obtained for a seeded H_2 in Kr. Since the Kr is much heavier the velocity of the mixture is substantially lower. The observed transition frequency difference in the two cases was insignificant proving a Doppler-free alignment. Translated into frequency, we claim these two methods give a maximum uncertainty due to the Doppler effect of 100 MHz in the error budget estimation. The actual spectroscopic measurements are carried out by probing the slower molecules at the rear end of the pulse, thus allowing for a smaller residual Doppler shift. Under these conditions the linewidths are also the narrowest.

The largest contribution to the uncertainty budget arises from the effect of frequency chirp in the dye amplifiers, which may result in a net shift between the centre frequency of the XUV beam used for exciting the H_2 transitions, and the fundamental frequency in the CW seed beam (multiplied by a factor of 6 for harmonic conversion), which is, in fact, calibrated. This chirp phenomenon was quantitatively and experimentally addressed by Eikema *et al* [9] in a detailed study of a single spectral line. In the work of Philip *et al* [5] on a vast number of spectral lines in H_2 resulting uncertainties from the chirp effect were estimated, based on the general

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Table 2. Transition energies (in cm^{-1}) of the Lyman bands in H$_2$ for $v' = 6$ with uncertainties given in parentheses (1σ). For convenience of use in astrophysical comparisons the wavelengths of the spectral lines are also listed (in nm). The values in the last three columns represent previously reported results.

Line	This work (nm)	This work (cm^{-1})	[5]	[12][a]	[13][b]
P(1)	102.593 534(7)	97 472.029(6)	97 472.046(8)	97 472.12	97 472.13(10)
P(2)	102.810 598(7)	97 266.237(6)	–	97 266.27	97 266.28(10)
P(3)	103.119 284(8)	96 975.073(7)	–	96 975.14	96 975.18(10)
P(4)	103.518 295(9)	96 601.282(8)	–	96 601.42	96 601.32(10)
R(0)	102.437 386(6)	97 620.609(5)	97 620.600(8)	97 620.29	97 620.65(10)
R(1)	102.498 804(7)	97 562.114(6)	97 562.127(8)	97 562.25	97 562.21(10)
R(2)	102.652 844(7)	97 415.713(6)	–	97 415.90	97 415.75(10)
R(3)	102.898 676(7)	97 182.980(6)	–	97 183.32	97 183.09(10)
R(4)	103.235 111(8)	96 866.268(7)	–	96 865.97	96 866.28(10)

[a] Transitions of B $^1\Sigma_u^+$–X $^1\Sigma_g^+$ (6,0) Lyman band as reported by Abgrall *et al* in the atlas of [12].
[b] Calculated using combinations of level energies for the excited states as given in [13] (table VI) and ground-state level energies reported in [14]. The specified uncertainties are less than 0.1 cm^{-1}.

findings in [9] and included in the uncertainty budget. We have adopted this procedure as well, but we note that in cases where spectral measurements are performed at the short and long wavelength ends of the gain curve of a specific dye solution, the chirp-induced offsets may increase [11]. This is the case for the lines at the long wavelength side of the studied region, in particular for the R(4) and P(4) lines in (6,0) band. Whereas in [5] the chirp-induced shifts were estimated to be limited to 100 MHz, we conservatively estimate here an upper bound of 150 MHz in some cases. The comprehensive uncertainty budget is presented in table 1.

3. Results

The spectroscopic results for nine rotational transitions in the B $^1\Sigma_u^+$ ($v' = 6$) $\leftarrow$ X$^1\Sigma_g^+$ ($v'' = 0$) Lyman band in H$_2$ are summarized in table 2. These transitions were measured and calibrated to accuracies in the range 0.005–0.008 cm^{-1}. Three of them were previously calibrated by Philip *et al* [5], and in comparison the present values are lower by 0.007 on average, which represents a systematic shift at the level of 1σ in terms of the present uncertainties. The present results are also compared to the values given in the table of the Lyman band system of molecular hydrogen [12]. However, by making use of the B $^1\Sigma_u^+$ level energies determined from the comprehensive classical spectroscopy carried out in the Meudon Observatory [13], combined with the accurate level energies in the X $^1\Sigma_g^+$ ($v'' = 0$) ground state [14], an improved accuracy is established. The transition frequencies of the Lyman lines in the resulting classical database are considered to be accurate to within 0.1 cm^{-1}. The present results are on average shifted by -0.06 cm^{-1} from these values, which is within the estimated uncertainty of the Meudon data set.

In table 3, the combination differences R(J'') − P($J'' + 2$) for $J'' = 0, 1, 2$ of the B $^1\Sigma_u^+$ ($v' = 6$) $\leftarrow$ X$^1\Sigma_g^+$ ($v'' = 0$) Lyman transitions are compared with the corresponding S(J'') transitions in the X $^1\Sigma_g^+$ ground state of H$_2$. The values are consistent with the literature values of Jennings *et al* [14]. This result provides an independent validation of the calibration procedures followed in the present study.

Table 3. Comparison of the difference frequencies of R(J'') − P($J'' + 2$) for $J'' = 0, 1, 2$ of the Lyman transitions in H$_2$ for $v' = 6$ (see table 2) and the S(J'') transitions in the X $^1\Sigma_g^+$ ground state of H$_2$ (see [14] table I).

J''	R(J'') − P($J'' + 2$) (cm^{-1}) This work	S(J'') (cm^{-1}) [14]
0	354.372(8)	354.3733(2)
1	587.041(10)	587.0324(2)
2	814.431(10)	814.4246(3)

The presently obtained highly accurate transition frequencies were included in the database of zero-redshift Lyman transitions, thereby replacing some older and less accurate values. In particular, no previous laser-based calibrations were available for the R(2) and R(3) transitions, which were observed in quasar spectra at high redshift. The fit comparing the 76 high-redshift H$_2$ lines in the Q 0405–443 and Q 0347-383 quasar systems was reevaluated and produces a value for the variation of the proton-to-electron mass ratio of $\Delta\mu/\mu = (2.40 \pm 0.60) \times 10^{-5}$, fully consistent with the previously reported value [15].

4. Conclusions

We present new accurate frequency calibrations of nine rotational lines in the B–X (6,0) Lyman band in H$_2$ at accuracies in the range 0.005–0.008 cm^{-1}. These measurements fill an important gap in the recently published data set on the hydrogen Lyman and Werner bands for comparison with quasar data and for extracting possible variations of the proton-to-electron mass ratio on a cosmological time scale. It is particularly in this realm where the relevance of these measurements lies.

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