New measurement of the $1S - 3S$ transition frequency of hydrogen: contribution to the proton charge radius puzzle

Hélène Fleurgaey, Sandrine Galtier, Simon Thomas, Marie Bonnau, Lucile Julien, François Biraben, and François Nez

Laboratoire Kastler Brossel, UPMC-Sorbonne Universités, CNRS, ENS-PSL Research University, Collège de France, 4 place Jussieu, Case 74, 75252 Paris Cedex 05, France

Michel Abgrall and Jocelyne Guéna

LNE-SYRTE, Observatoire de Paris, PSL Research University, CNRS, Sorbonne Universités, UPMC University Paris 06, 61 avenue de l’Observatoire, 75014 Paris, France

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We present a new measurement of the $1S - 3S$ two-photon transition frequency of hydrogen, realized with a continuous-wave excitation laser at 205 nm on a room-temperature atomic beam, with a relative uncertainty of $9 \times 10^{-15}$. The proton charge radius deduced from this measurement, $r_p = 0.877(13)$ fm, is in very good agreement with the current CODATA-recommended value. This result contributes to the ongoing search to solve the proton charge radius puzzle, which arose from a discrepancy between the CODATA value and a more precise determination of $r_p$ from muonic hydrogen spectroscopy.

Hydrogen is a cornerstone of atomic physics, as it plays a key role in the determination of the Rydberg constant and in testing fundamental theories such as the quantum electrodynamics (QED) theory. Since it is the simplest atom, the energy levels of hydrogen are described theoretically with a good accuracy, and can be written as the sum of two terms. The first term is directly linked to QED and relativistic contributions, as well as the finite nuclear size effect characterized by the proton rms charge radius $r_p$. Hydrogen spectroscopy provides an access to differences of energy levels, with even better precision. For instance, the $1S - 2S$ transition frequency has been measured with a relative uncertainty of $4.2 \times 10^{-15}$ [1]. By making an appropriate linear combination of this frequency with that of another transition such as the $2S - nS/D$ transitions [2], one obtains experimental values of the Rydberg constant and the ground-state Lamb shift, from which the proton radius can be derived assuming that the QED calculations are exact. The global adjustment of fundamental constants realized by the CODATA [3] partly relies on such a scheme, while also including electron-proton scattering experimental results [4].

In 2010, the spectroscopy of muonic hydrogen [5, 6] yielded a value of $r_p$, an order of magnitude more precise, but about 4% smaller, than the CODATA-recommended value. This discrepancy has become known as the proton radius puzzle [7]. A recent measurement of the hydrogen $2S - 4P$ transition frequency in Garching [8] has brought a new dimension to this conundrum, as it disagrees with other spectroscopic measurements in electronic hydrogen.

In this Letter, we present a new measurement of the $1S - 3S$ two-photon hydrogen transition frequency, realized with a continuous-wave (cw) 205 nm excitation laser and detected through the Balmer-α $3S - 2P$ fluorescence. For the first time, the uncertainty on this transition frequency (2.6 kHz) is significantly smaller than the proton radius discrepancy, which corresponds to a difference of 7 kHz in terms of the $1S - 3S$ transition frequency. This result improves previous measurements in Paris [9] as well as in Garching [10]. At this unprecedented level of precision, it will allow comparison with future results from the Garching experiment, which measures the same transition with an entirely different setup using a picosecond laser excitation.

As we study a two-photon transition, the first-order Doppler effect is canceled through a counter-propagating scheme. The main systematic effect in our experiment is the second-order Doppler (SOD) effect, which is on the order of 140 kHz and depends on the atomic velocity distribution of our room-temperature effusive atomic beam. To estimate this distribution, we follow a method detailed in Refs. [9, 11]. A transverse magnetic field $B$ is applied in the interaction region, so that an atom moving with velocity $v$ experiences a motional electric field $E = v \times B$. The Stark shift due to this electric field has a quadratic velocity dependence, like the SOD shift. In the mean time, the Zeeman effect lifts the degeneracy of the $m_F$ hyperfine sublevels. The $1S_{1/2} - 3S_{1/2}$ transition splits into three components, in accordance with the two-photon selection rules ($\Delta m_F = 0$). The $m_F = 0$ component is much shifted by the Zeeman effect and is used to calibrate the magnetic field. The two other components are, in first approximation, not shifted by the Zeem-
man effect. For a magnetic field of about 18 mT, a level crossing occurs between the $3S_{1/2}(F = 1, m_F = -1)$ and $3P_{1/2}(F = 1, m_F = 0)$ levels. The motional Stark shift is then large for the $m_F = -1$ component and could compensate the SOD shift for this particular sub-transition. But the $m_F = \pm 1$ components of the transition are not resolved, since both the SOD and Stark shifts are of order of magnitude smaller than the natural width of the transition (1 MHz). Thus, the SOD shift is only partly compensated. We record the transition signal for different values of the magnetic field around the level crossing, and for no applied magnetic field. By analyzing the signals with a theoretical lineshape which takes into account both the SOD and Stark effects, we are able to estimate the velocity distribution of our atomic beam.

The results presented in this Letter were obtained from data recorded in two separate sessions, in 2013 [12] and 2016-2017 [13]. The following description of the experimental setup emphasizes the modifications which took place between the two recording sessions. Figure 1 presents a simplified view of this setup.

Our 205 nm cw excitation laser has been well described in Ref. [14]. It is produced by sum frequency generation (SFG), in a $\beta$-baryum borate (BBO) crystal, of a homemade tunable titanium:sapphire (Ti:Sa) laser at 894 nm and a 266 nm radiation resulting from the frequency doubling of a 532 nm laser (Verdi V6 and MBD266, Coherent). This source delivers daily between 15 mW (in 2013) and 10 mW (in 2017), depending on the BBO crystal quality and the SFG efficiency.

The frequency stability of the Ti:Sa and Verdi lasers is ensured by a sequential locking procedure. Each laser is first stabilized to its own auxiliary Fabry-Perot (FPA) cavity, using a Pound-Drever-Hall scheme, to reduce its spectral width. To prevent more long-term frequency drifts, the length of each FPA cavity is controlled to maintain the lasers at resonance with a third, reference Fabry-Perot (FPR) cavity. The FPR length is itself locked to our standard laser, a 778 nm laser diode stabilized on a two-photon hyperfine transition of $^{85}$Rb [15]. A double-pass acousto-optic modulator (AOM) placed between the Ti:Sa laser and the frequency stabilization setup allows to scan the excitation frequency while keeping all lasers stabilized.

The Ti:Sa and Verdi laser frequencies are measured by comparison with our MenloSystems femtosecond frequency comb, whose 780 nm output is spectrally broadened in a photonic crystal fiber (PCF). The repetition rate and offset frequency of the frequency comb are referenced to the LNE-SYRTE Cs fountain primary frequency standards thanks to a 3-km-long optical fiber link [16]. In 2013, it was hard to optimize both 532 nm and 894 nm beatnotes at the same time because their frequencies were at both ends of the spectrum that could be obtained from the PCF. In particular, the 532 nm beatnote was problematic; it was weak because there was not enough power at this wavelength, and it was also rather broad. After several breakdowns of the frequency comb, and an unsuccessful attempt to improve the quality of this beatnote through the addition of an electro-optic modulator in the fs comb cavity to allow optical locking of a comb mode to a stable 1.5 µm signal, we opted in 2016 for an entirely different solution, which requires the use of an additional laser acting as a transfer laser. This cw Nd:YAG laser (Prometheus from Innolight) has two outputs: one at 532 nm, which is used to make a beatnote with our Verdi laser; the other at 1064 nm, whose frequency is measured through a beatnote with a new 1064 nm output of the frequency comb.

The frequency-stabilized 205 nm laser beam is injected into a power build-up cavity, whose axis is collinear with an effusive beam of H atoms formed by the dissociation of H$_2$ molecules in a radio-frequency discharge. The cavity mirrors have a 25 cm radius of curvature and are placed in a quasi-concentric configuration, yielding a waist of about 44 µm. The Balmer-$\alpha$ fluorescence photons are collected through a 656 nm interference filter and detected by a photomultiplier placed above the center of

![FIG. 1. Simplified view of the experimental setup. Frequency stabilization relies on several Fabry-Perot cavities and a Rb-stabilized standard laser. Since 2016, instead of making a beatnote directly with the frequency comb, the frequency of the Verdi laser is measured via a Nd:YAG transfer laser (more details in text). SHG: second harmonic generation, SFG: sum frequency generation, AOM: acousto-optic modulator, PM: photomultiplier.](image)
the cavity. The entire build-up cavity is inside a vacuum chamber, pumped by an oil diffusion pump. The pressure in the cavity is monitored by an ionisation gauge placed on the side of the vacuum chamber, which only provides a relative measurement of the actual atomic flux. The length of the build-up cavity is kept at resonance with the excitation laser by means of a lock-in amplifier. This stabilization loop is very sensitive to vibrations. In 2015, to improve the signal used for locking, we replaced the UV photodiode monitoring the transmitted light with a photodiode placed on the side of a quartz tube containing a fluorescein solution.

Helmholtz coils, placed around the vacuum chamber, create the vertical magnetic field used for velocity distribution determination. The current circulating in the coils is calibrated by monitoring the position of the $1S-3S(F=1, m_F=0)$ sub-transition, which undergoes a Zeeman shift of about 10 MHz/mT for a magnetic field around 18 mT. During recordings, we reverse the magnetic field direction from one day to the next to avoid bias due to a possible stray electric field.

To observe the transition, we scan the frequency of the AOM placed in the Ti:Sa stabilization loop, following a predefined back-and-forth 31-point sequence to avoid drifts. For each AOM frequency point, we record the number of fluorescence photons collected by the photomultiplier during one second, as well as the various beatnote frequencies. A “signal” is obtained by averaging ten such scans. Figure 2 shows an average of 47 signals, corresponding to an integration time of 4 hours, recorded in 2016 without any applied magnetic field. We observe a rather large background which is mainly due to UV-induced fluorescence.

The first recording session in 2013, lasting 29 days, yielded more than 900 signals recorded for a given pressure and 7 magnetic field values. Subsequently, after improving the frequency measurement setup, a second recording session was undertaken during 59 days (1700 signals) in 2016-2017. This time, the magnetic field procedure was applied for 2 different pressure values, in order to characterize a possible pressure dependence of the velocity distribution. For analysis, we separated the 2016 data in three sets: two sets at low pressure (LP1, LP2) recorded before and after the high-pressure set (HP).

The analysis relies on a theoretical line profile which includes the SOD and motional Stark shifts. The calculation of this profile has been described elsewhere [9]. Using the density matrix formalism, it involves summing the fluorescence of the $3S(F=1, m_F=0, \pm 1)$ sub-levels and that of the $3P$ levels to which they can be coupled by the motional Stark effect. The $m_F=0$ component only contributes to the signal for a null applied magnetic field. The profile is then integrated over a given atomic velocity distribution. Our velocity distribution model, \[ f(v, \sigma, v_0) \propto v^3 e^{-v^2/(2\sigma^2)} P(v/\sigma) e^{-v_0/v}, \] is based on the Maxwellian-type distribution of an effusive beam [17] and includes a correction which describes a depletion of slow atoms due to interactions within the nozzle [18]. It is multiplied by an exponential-decay term to modelize a possible additional depletion of the slow atoms in the effusive beam. This distribution is fully described by the two parameters $\sigma$ and $v_0$ [19]. Moreover, the profile is convoluted with a Lorentzian function to take into account broadening effects, mainly due to transit time and pressure.

The four data sets were analyzed independently to determine the velocity distribution parameters, through a chi-square minimization process. Each signal is fitted by theoretical profiles calculated for a grid of $(\sigma, v_0)$ parameters, to determine its center frequency. The other fit parameters are the amplitude, background offset and Lorentzian broadening width. For a given data set, the mean frequency and the chi-square $\chi^2$ are computed. The optimal velocity distribution parameters are given by the minimum of the $\chi^2(\sigma, v_0)$ surface fitted by a polynomial function. The results of this minimization for the various data sets are given in the first two columns of Table I. Eventually, the signals are fitted again using the theoretical profile calculated for the optimal velocity distribution. The average of this set gives the optimal frequency (third column of the table). The obtained frequencies are already corrected from the SOD and motional Stark shifts.

To take into account the light shift, we apply to each signal a frequency correction based on a parameter indicating the intra-cavity power. Two such parameters have
been used: the voltage of the photodiode recording the transmitted UV power (for the 2013 recordings) and the square root of the two-photon absorption signal height (for 2016-2017). As the signal height depends on pressure, the correction coefficient was determined separately for each pressure value. This coefficient is defined as the slope of a linear extrapolation of the frequency with respect to the chosen parameter. The light-shift-corrected average frequencies are given in the last column of Table I.

Collisions between atoms can also induce frequency shifts, depending linearly on the pressure. Unfortunately, the pressure gauge was replaced between the two recording sessions, so that we cannot merge the two sessions for the collisional shift analysis. To determine this pressure shift for the 2013 data set, measurements were carried out several times during that recording session, for two or three pressure values in the same day, with no applied magnetic field. At the time, the velocity distribution was measured for only one pressure value and our velocity distribution model could allow for pressure dependence of the parameter \( v_0 \), so that we did not know which parameters should be used to analyse the other pressure points [19]. The analysis of the 2016 data gave us insight on this question. In fact, the velocity distribution does not seem to depend significantly on pressure, at least within experimental uncertainties (see Table I). To check this assumption, we have fitted a number of signals using the various optimal distributions. The resulting change in the center frequency was at most of about 3 kHz. Hence, when analyzing the 2013 recordings, we use the same velocity distribution for all pressure values. The slope of a linear fit gives the collisional shift coefficient. To take into account the uncertainty on the velocity distribution determination, an uncertainty of 3 kHz divided by the maximal pressure difference is added in quadrature to that of the obtained coefficient. This entails a correction of \(+3.6(2.0)\) kHz on the frequency quoted in the last column of Table I. For the 2016 session, since the velocity distribution was determined for each pressure value, we simply extrapolate the light-shift corrected frequencies of the three data sets to zero pressure.

At this point, we add a correction of \(+0.6(2)\) kHz to take into account the frequency shift resulting from the cross-damping effect, following our theoretical estimation of this shift [20].

All the frequency measurements were done with respect to the 100 MHz reference signal from LNE-SYRTE. This reference was obtained from a hydrogen maser, whose frequency was continuously measured by the LNE-SYRTE atomic fountains realizing the frequency of the SI second to a few \( 10^{-16} \) [21, 22]. Using a simple linear frequency drift of the order of \( 10^{-16} \) per day to model the H-maser behavior over each period, we estimate the average fractional shift of the reference signal with respect to the SI to be \(-205(2) \times 10^{-15}\) in 2013, and \(-357(2) \times 10^{-15}\) in 2016-2017. This yields an absolute correction to the \( 1S - 3S \) transition frequency of \(-599(6)\) Hz for the 2013 measurement and \(-1043(6)\) Hz for the 2016-2017 measurement.

The centroid value of the transition is calculated by adding a hyperfine correction of \(+341 949.077(3)\) kHz derived from experimental values of the \( 1S \) and \( 2S \) hyperfine splittings [23]. Eventually, we obtain for the two recording sessions,

\[
\nu_{1S-3S}^{2013} = 2 922 743 278 671.6(2.8) \text{ kHz},
\]

\[
\nu_{1S-3S}^{2017} = 2 922 743 278 671.0(4.9) \text{ kHz}.
\]

We estimate a correlation coefficient of 0.186. The weighted average of our two measurements is then \( \nu_{1S-3S} = 2 922 743 278 671.5(2.6) \text{ kHz} \). Combining this result with the \( 1S - 2S \) transition frequency [1], one can derive values of the Rydberg constant, \( R_{\infty} = \)
and the proton charge radius, \( r_p = 0.877(13) \text{ fm} \). The latter is shown in Fig. 3 along with other determinations of the proton radius from hydrogen spectroscopy. The present result is in very good agreement with the CODATA-2014 recommended value (0.8751(61) fm \cite{3}), and disagrees with the value deduced from muonic spectroscopy \cite{6} by 2.8\( \sigma \), thus reinforcing the proton radius puzzle.

In the near future, we plan to cool the hydrogen beam down to the temperature of liquid nitrogen, in order to reduce the second-order Doppler shift and improve the accuracy of our measurement.

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