Indication of a Cosmological Variation of the Proton-Electron Mass Ratio Based on Laboratory Measurement and Reanalysis of H_2 Spectra

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Based on highly accurate laboratory measurements of Lyman bands of H_2 and an updated representation of the structure of the ground $X\,^1\Sigma_g^+$ and excited $B\,^1\Sigma_u^+$ and $C\,^1\Pi_u$ states, a new set of sensitivity coefficients K_i is derived for all lines in the H_2 spectrum, representing the dependence of their transition wavelengths on a possible variation of the proton-electron mass ratio $\mu = m_p/m_e$. Included are local perturbation effects between B and C levels and adiabatic corrections. The new wavelengths and K_i factors are used to compare with a recent set of highly accurate H_2 spectral lines observed in the Q 0347-383 and Q 0405-443 quasars, yielding a fractional change in the mass ratio of $\Delta\mu/\mu = (2.4 \pm 0.6) \times 10^{-5}$ for a weighted fit and $\Delta\mu/\mu = (2.0 \pm 0.6) \times 10^{-5}$ for an unweighted fit. This result indicates, at a 3.5σ confidence level, that μ could have decreased in the past 12 Gyr.

The issue of a possible variability of fundamental physical constants has been put on the agenda of contemporary physics with recent claims on evidence for a variation of the fine structure constant $\alpha = e^2/4\pi\epsilon_0\hbar c$, based on comparisons of laboratory data on atomic multiplet structures and the observations of the same features in the absorption spectra of quasars. Webb *et al.* [1] find a 4σ indication for a change in α for observations on quasars on the Northern Hemisphere. In contrast, other groups [2] recently reported an essential null result from observations on the Southern Hemisphere. Several authors have argued that the quantum chromodynamic scale Λ_{QCD} should vary faster than that of quantum electrodynamics and that, as a consequence, the proton-electron mass ratio $\mu = m_p/m_e$ is expected to vary more than α, if any change will occur [3]. This makes μ an important target for searching temporal variation of a constant *per se*. The spectrum of H_2, the most abundant molecule in the Universe, provides a direct operational handle to test a variation of the dimensionless constant μ, in the modern epoch equaling $1836.152\,672\,61(85)$ [4].

Each of the many rovibrational lines in the $C\,^1\Pi_u$-$X\,^1\Sigma_g^+(v',0)$ Werner and the $B\,^1\Sigma_u^+$-$X\,^1\Sigma_g^+(v',0)$ Lyman band systems depends in a different way on a possible change in μ. Sensitivity coefficients K_i can be defined for each spectral line at $\nu_i = c/\lambda_i$ [5]:

$$K_i := \frac{d\ln\lambda_i}{d\ln\mu} = \frac{\mu}{\lambda_i}\frac{d\lambda_i}{d\mu} = -\frac{\mu}{\nu_i}\frac{d\nu_i}{d\mu}. \qquad (1)$$

Then rest-frame laboratory wavelengths λ_i^0 are related to those in the quasar absorption system λ_i via

$$\lambda_i/\lambda_i^0 = (1 + z_{abs})(1 + K_i\Delta\mu/\mu), \qquad (2)$$

with z_{abs} the redshift of the absorbing cloud. This model

was applied to H_2 absorption systems at high z in the spectra of quasar sources by various groups [6], resulting in constraints on a relative variation of the proton-electron mass ratio $|\Delta\mu/\mu|$ within 10^{-5}–10^{-4}. Recently, a new set of high-quality observations of H_2 absorptions in quasar systems was obtained [7]. These data are used here in a refined analysis, assessing a possible variation of μ based on new extremely accurate H_2 laboratory spectroscopic measurements as well as an improved calculation of K_i coefficients. Accurate laboratory data, the lack of which had become evident [6,7], were partially provided with the extreme ultraviolet laser spectroscopic studies performed in Amsterdam [8]. However, the important lines in the longest wavelength range of the Lyman bands, the $B\,^1\Sigma_u^+$-$X\,^1\Sigma_g^+(v',0)$ bands for $v' = 0$–2, remained missing, due to the difficulty of producing narrow band laser radiation in the range $\lambda = 107$–111 nm and the fact that accurately calibrated I_2-saturation lines were not available. Now with the aid of the extended I_2 reference standard [9], the missing lines in the low v' Lyman bands were measured along the procedures described in Ref. [8]. A spectral recording of the $R(0)$ line in the B-X $(1,0)$ Lyman band is shown in Fig. 1. The results, listed in Table I, are at an accuracy of 5×10^{-8}.

In particular, because the L15 $R(2)$ line (L15 defined as the 15-0 Lyman band) was missing from the database of accurately known H_2 lines, the region near $\lambda = 94.5$ nm was reinvestigated. In contradiction to the previous study [8], we now succeeded in generating the direct sixth harmonic of a tunable laser system, leading to better accuracies. Five lines in the L14 and L15 bands were measured at an accuracy of 6×10^{-8} (listed in Table I).

In the procedure of deriving an updated set of K_i factors, some important deviations from the Born-Oppenheimer
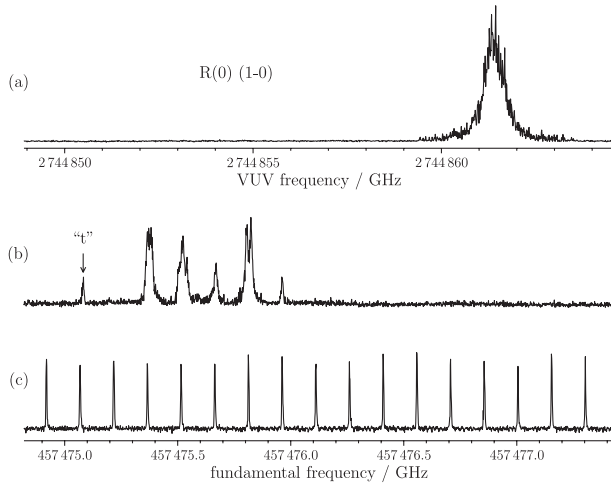
FIG. 1. (a) Recording of the $R(0)$ line in the B-X (1, 0) Lyman band with (b) the I_2 reference spectrum and (c) étalon markers for the calibration. The line marked is the t-hyperfine component of the $R(46)$ line in the B-X (5, 5) band of I_2 at $15\,259.726\,171$ cm^{-1} [9].

approximation (BOA) are included for the first time; the starting point, however, is the same semiempirical approach based on the BOA as in previous studies [5]. Energy levels are represented by a polynomial in v and J quantum numbers, the Dunham formula [10]:

$$E(v, J) = \sum_{k,l} Y_{kl}\left(v + \frac{1}{2}\right)^k [J(J+1) - \Lambda^2]^l, \quad (3)$$

with $\Lambda = 1$ for the $C\,^1\Pi_u$ state and $\Lambda = 0$ for the $B\,^1\Sigma_u^+$ and $X\,^1\Sigma_g^+$ states, and Y_{kl} the Dunham coefficients. Three kinds of contributions to the energy can be distinguished: the electronic energy of a molecular state, independent from the nuclear mass, and rotational and vibrational energies of quantum states having their characteristic, and different, first-order mass dependencies [10]:

$$Y_{kl} \propto \mu_n^{-l-k/2}, \quad (4)$$

where μ_n refers to the reduced nuclear mass in H_2.

TABLE I. Measured wavelengths of hitherto missing accurate lines in the $B\,^1\Sigma_u^+$-$X\,^1\Sigma_g^+$ Lyman bands. The line marked with (*) is calculated from a ground state combination difference.

Line	λ_0 (nm)	Line	λ_0 (nm)
L0 $P(1)$	111.006 251 (6)	L1 $R(3)$	109.672 534 (6)
L0 $R(0)$	110.812 733 (7)	L2 $R(2)$	107.922 542 (6)
L0 $R(1)$	110.863 326 (7)	L2 $R(3)$	108.171 124 (7)
L0 $P(2)$	111.249 600 (7)*	L2 $R(4)$	108.514 554 (6)
L1 $P(1)$	109.405 198 (6)	L14 $R(2)$	94.847 125 (6)
L1 $P(2)$	109.643 894 (6)	L15 $R(2)$	94.062 637 (6)
L1 $P(3)$	109.978 718 (7)	L15 $R(3)$	94.296 422 (6)
L1 $R(0)$	109.219 523 (6)	L15 $P(3)$	94.433 046 (6)
L1 $R(1)$	109.273 243 (6)	L15 $R(4)$	94.612 271 (6)
L1 $R(2)$	109.424 460 (6)		

The sensitivity coefficients K_i can be expressed in first order by the Y_{kl} of the ground and excited states; substituting μ by $\mu_n = m_e \mu / 2$ in Eq. (1) leads to:

$$K_i = -\frac{\mu_n}{\nu_i} \frac{d\nu_i}{d\mu_n} = \frac{1}{E_e - E_g}\left(-\mu_n \frac{dE_e}{d\mu_n} + \mu_n \frac{dE_g}{d\mu_n}\right). \quad (5)$$

The derivatives can be evaluated separately for the X ground state and the B or C excited state with Eq. (3), where we can substitute according to Eq. (4):

$$-\mu_n \frac{dY_{kl}}{d\mu_n} = \left(l + \frac{k}{2}\right) Y_{kl}. \quad (6)$$

For the $X\,^1\Sigma_g^+$ electronic ground state, the comprehensive level energies from an *ab initio* calculation [11] were used to derive a set of Dunham coefficients; these theoretical data of Wolniewicz are consistent with all reported spectroscopic data on H_2.

The set of accurate transition wavelengths, as listed in Table I and in Ref. [8], was converted into level energies for the $C\,^1\Pi_u$ and $B\,^1\Sigma_u^+$ states. Direct determination of Dunham coefficients Y_{kl} from these energies is prevented by strong mutual interaction between both excited states, showing as avoided crossings in the rotational structures in pairs of nearby-lying vibrational B and C levels.

For an analysis of this non-BOA effect in the spectrum of H_2, we treat the perturbations locally at the crossing points [12]. The interaction is diagonal in J and preserves parity and, hence, does not affect the $^1\Pi_u^-$ levels in the C state, for which reason these are treated separately. For each rotational quantum number J, a two-by-two matrix with a common interaction term for heterogeneous coupling ($\Delta\Lambda = 1$) per pair of interacting vibrational levels is diagonalized:

$$\begin{pmatrix} E_{v_B J}^B & H_{v_B, v_C}\sqrt{J(J+1)} \\ H_{v_B, v_C}\sqrt{J(J+1)} & E_{v_C J}^C \end{pmatrix} \Psi = E\Psi. \quad (7)$$

Resulting values for pairs of (v_B, v_C) are (in cm^{-1}) $H_{8,0} = 2.59$, $H_{10,1} = 6.20$, $H_{12,2} = 7.98$, $H_{14,3} = 9.29$, $H_{16,4} = 10.62$, and $H_{19,5} = 7.71$.

Dunham coefficients for the B state and the Π^+ levels of the C state are then determined from the deperturbed level energies $E_{v_B J}^B$ and $E_{v_C J}^C$, in combination with observed energies of those B vibrational levels that are relatively unperturbed. These sets of energies show a smooth dependence on v and J, resulting in Dunham expansions with 22 Y_{kl} parameters for the B state (for 100 levels with $v = 0$–19), 12 parameters for the C^+ state (25 levels with $v = 0$–5), and 10 parameters for the C^- state (21 levels with $v = 0$–5).

The mass dependence of energies of the perturbed states is determined by the mass dependence of the eigenenergies E in Eq. (7). For a normalized eigenstate $\Psi = c_1 \psi_{v_B J}^B + c_2 \psi_{v_C J}^C$, it is given in first order and, in approximation of mass-independent H, by the weighted sum of the B and C state mass dependences:

$$\frac{dE}{d\mu_n} = |c_1|^2 \frac{dE^B_{v_B J}}{d\mu_n} + |c_2|^2 \frac{dE^C_{v_C J}}{d\mu_n}. \qquad (8)$$

All eigenstates for which we find $|c_i|^2 > 0.001$, $i = 1, 2$, are treated in this way.

Another significant step beyond the BOA is made by including the adiabatic correction, a nuclear-mass dependent contribution to the electronic energy of each state, which is a slowly varying function of internuclear distance R on the order of 100 cm^{-1} in the three states of H_2, and scales with mass as $\propto 1/\mu_n$ [13]. Its effect is approximately that of the Bohr shift on the levels of an electron bound to an H_2^+ core, due to the finite mass of the latter. For a transition with an electronic energy difference ΔE_∞ for a core of infinite mass, the Bohr shift in the $e^- + H_2^+$ system equals $\Delta E_\infty - \Delta E = \Delta E/(2\mu + 1)$. Identifying ΔE with the difference of the empirical Y_{00} values of the (deperturbed) B or C state and the ground state, we obtain 25.0 and 27.2 cm^{-1}, respectively. The mass scaling of the Bohr shift leads to an extra term in the parentheses in Eq. (5) of $-\mu d/d\mu(\Delta E/(2\mu + 1)) \approx \Delta E/(2\mu + 2)$. This semiempirical treatment of the adiabatic correction leaves some uncertainty, particularly for the B state, where it is strongly R-dependent [13]. The resulting uncertainty is up to ± 0.0005 for the high-v levels.

Calculated sensitivity coefficients K_i can be found in Ref. [14]. In the present analysis, three important improvements are obtained: First, nonadiabatic interaction included for strongly perturbed excited states contributes considerably to K_i for a number of transitions, e.g., -0.00378 for L14R(1) and $+0.00380$ for W3P(3), $+0.00127$ for W3R(2), and -0.00483 for L12R(3). Second, energies of high-v levels of the B state could now be included in the determination of the Y_{kl} by using their deperturbed values, thus avoiding extrapolations as in Ref. [5]. Changes in K_i rise sharply from <0.0001 at $v \leq 7$ to -0.005 at B, $v = 14$. Finally, the improvement on K_i by inclusion of the Bohr shift amounts to about -0.0002.

The presented treatment shows the fundamental limitation of a semiempirical derivation of the mass dependence of energies of individual molecular quantum states, making a distinction between electronic, vibrational, and rotational contributions: The J dependence of energy not only reflects rotational energy but also J-dependent nonadiabatic interaction; the same holds for the v dependence. We conclude that remaining uncertainties of the improved K_i values are dominated by adiabatic and nonadiabatic effects beyond the BOA and that they are $>10^{-4}$ (absolute) throughout and may approach 10^{-3} for the higher B, v levels and for the C^+ levels.

Recently, an accurate set of H_2 lines was observed in two quasar absorption systems, Q 0405-443 and Q 0347-383, by Ivanchik *et al.* [7]. Data were obtained at the Ultraviolet and Visible Echelle Spectrograph mounted on the Very Large Telescope of the European Southern Observatory at a resolving power of $R = 53\,000$, at a signal-to-noise ratio of 30–70, and at accuracies of 2×10^{-7}–1×10^{-6}. A

curve-of-growth test was applied to the data to verify if H_2 lines were blended by part of the Ly-α forest, which led to discarding 6 lines out of 82 selected lines not fulfilling this criterion. Further tests related to the kinematics of hydrogen in the absorbing clouds (the possibility that various J states may be located in different environments) and to the calibration procedures on the spectrograph were performed to ensure that no artifacts underlie the data set [7]. The data were included in tests on variation of μ using two different data sets and a zero-order estimate of K_i coefficients, excluding the perturbative effects discussed here; results indicated a possible variation of μ but depended largely on the reference set used [7]. The set of 76 lines, 37 toward Q 0347-383 and 39 toward Q 0405-443, is included here in a refined analysis probing a variation of μ. In the comparative analysis, the zero-frame wavelengths λ_i^0 of Ref. [8] and of Table I are used, except for the two missing lines in the B-X (6, 0) Lyman band [R(2) and R(3)] and the R(3) line in the (0, 0) band, which are calculated from classical spectroscopic studies [15]. For the K_i coefficients, we used the presently derived values including the non-Born-Oppenheimer effects in the electronic structure [14]. All lines were included in a comprehensive analysis using reduced redshifts ζ_i [7]:

$$\zeta_i := \frac{z_i - z_{q,abs}}{1 + z_{q,abs}} = \frac{\Delta\mu}{\mu} K_i, \qquad (9)$$

where, like in Eq. (2), $z_{q,abs}$ are the absolute redshifts of the quasar absorption systems for transitions with $K_i = 0$.

From a combined error-weighted linear regression, with both $z_{q,abs}$ values as well as the fractional change of μ as fit parameters, we find the central result of the present study: $\Delta\mu/\mu = (2.44 \pm 0.59) \times 10^{-5}$. Figure 2 shows the ζ_i values for both quasars as a function of K_i together with the fit result. The fit also yields accurate values for the
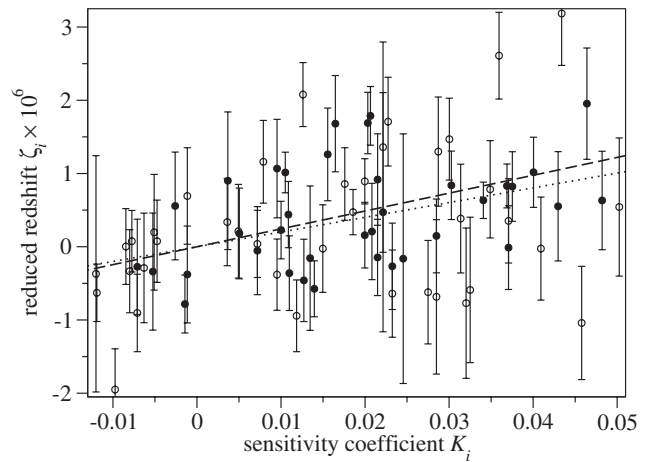

FIG. 2. Linear fit to reduced redshift of quasar absorption lines ζ as defined by Eq. (9). Solid circles: Q 0347-383, $z = 3.024\,897\,0$; open circles: Q 0405-443, $z = 2.594\,732\,5$. The error-weighted linear fit is shown by a dashed line, the unweighted fit by a dotted line.

redshift of both quasar systems: $z = 2.594\,733\,15(81)$ for Q 0405-443 and $z = 3.024\,899\,0(12)$ for Q 0347-383. Complete results of the fit and the residuals are given in Ref. [14]. The result for $\Delta\mu/\mu$ differs from previously published values based on the same quasar data [7] mainly by the addition of laboratory wavelengths for the $\nu = 0$ and 1 Lyman bands (2.3×10^{-5} vs 1.7×10^{-5}); additional change is due to improved K_i values of higher ν Lyman bands, which are systematically smaller by up to 0.005 than previously published. Similar changes apply to K_i values of some transitions to perturbed states.

Here we present some further details on the statistical analysis of the data and the robustness of the fitting procedures. First, from separate least-squares fits on data for the two quasars, yielding $(2.06 \pm 0.79) \times 10^{-5}$ for Q 0347-383 and $(2.78 \pm 0.88) \times 10^{-5}$ for Q 0405-443, it follows that the observed effect originates equally from comparison with both quasars. The χ^2 per degree of freedom in the weighted fit is 2.1 times larger than expected from the uncertainties on the data points. The observational errors may be slightly underestimated, as it is very difficult to estimate the uncertainty due to continuum fitting and blending. In such a situation, an unweighted fit is more appropriate, because the dispersion of the experimental points (Fig. 2) then characterizes the true statistical errors. The latter procedure yields $\Delta\mu/\mu = (1.98 \pm 0.58) \times 10^{-5}$, consistent with the above result. Another characteristic test of fit robustness is demonstrated by imposing a least-absolute value criterion [16] in the fit routine, yielding a value of $\Delta\mu/\mu = 2.15 \times 10^{-5}$. Furthermore, by consecutively discarding the data with the largest deviations, the outcome of the fit remains within the stated error margin; a fit without the nine data producing a large χ^2 yields $\Delta\mu/\mu = (1.98 \pm 0.43) \times 10^{-5}$, a result with a higher statistical significance; it also demonstrates that the nonzero result is not created by a few outlier data points.

The presently available set of laboratory data (Ref. [8] and the new data presented here) are so accurate that they can be considered exact for the purpose of comparison with observations from echelle-grating based spectrometers attached to the most modern telescopes. The level of uncertainty in the novel K_i coefficients, being few times 10^{-4} for low B, ν and all C^- levels and approaching 10^{-3} for the highest B, ν and the C^+ levels, may have an influence on the result for the variation of μ; it is estimated at 5%–10% and, hence, is insignificant for the present finding at the 3.5σ level. Further statistical analysis shows that there is no significant correlation between ζ_i and the J quantum number of the ground state, nor with λ_i^0, excluding temperature gradients in the absorbing cloud in the field of view of the quasars, and wavelength dependencies of the measured redshift as a source of the reported indication of a variable proton-electron mass ratio μ.

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[14] See EPAPS Document No. E-PRLTAO-96-057617 for the values of the sensitivity coefficients K_i and the results for the weighted and unweighted fits, comparing the laboratory wavelengths and the observed wavelengths in quasar spectral data. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.

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