Limit on the Cosmological Variation of m_p/m_e from the Inversion Spectrum of Ammonia

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We obtain the limit on the space-time variation of the ratio of the proton mass to the electron mass, $\mu = m_p/m_e$, based on comparison of quasar absorption spectra of NH_3 with CO, HCO^+ and HCN rotational spectra. For the inversion transition in NH_3 ($\lambda \approx 1.25\ \mathrm{cm}^{-1}$) the relative frequency shift is significantly enhanced: $\delta\omega/\omega = -4.46\delta\mu/\mu$. This enhancement allows one to increase sensitivity to the variation of μ using NH_3 spectra for high redshift objects. We use published data on microwave spectra of the object $B0218 + 357$ to place the limit $\delta\mu/\mu = (0.6 \pm 1.9) \times 10^{-6}$ at redshift $z = 0.6847$; this limit is several times better than the limits obtained by different methods and may be significantly improved. Assuming linear time dependence we obtain $\dot{\mu}/\mu = (-1 \pm 3) \times 10^{-16}\ \mathrm{yr}^{-1}$.

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Introduction.—The possible time variation of the fundamental constants has been discussed for a long time. The interest in this discussion has grown considerably after the recent discovery of the acceleration of the expansion of the Universe. The latter is usually regarded as evidence for the existence of dark energy. Cosmological evolution of dark energy may cause variations in fundamental constants, such as the fine-structure constant α and the proton to electron mass ratio, $\mu \equiv m_p/m_e$.

The electron mass is one of the parameters of the standard model. It is proportional to the vacuum expectation value of the Higgs field (the weak scale). The proton mass is proportional to another fundamental parameter, the quantum chromodynamics scale Λ_{QCD} ($m_p \approx 3\Lambda_{\mathrm{QCD}}$). The proportionality coefficients cancel out in the relative variation. Therefore, we are speaking about the relative variation of a very important dimensionless fundamental parameter of the standard model, the ratio of the strong to weak scale, defined as $\delta(\Lambda_{\mathrm{QCD}}/m_e)/(\Lambda_{\mathrm{QCD}}/m_e) = \delta\mu/\mu$.

It is known that μ defines the scales of electronic, vibrational, and rotational intervals in molecular spectra, $E_{\mathrm{el}}:E_{\mathrm{vib}}:E_{\mathrm{rot}} \sim 1:\mu^{-1/2}:\mu^{-1}$. Similarly, the ratio of electronic and hyperfine intervals in atoms and molecules also depends on μ, $E_{\mathrm{el}}:E_{\mathrm{hfs}} \sim 1:\alpha^2 g_p \mu^{-1}$, where g_p is the proton g factor. These scalings are used to look for the time variation of μ by comparing electronic, vibrational, rotational, and hyperfine spectra of atoms and molecules [1,2]. In the most recent astrophysical studies [3] a nonzero effect was reported for two quasars at 3.5σ level:

$$\delta\mu/\mu = (20 \pm 6) \times 10^{-6}, \tag{1}$$

at a time scale of approximately 12 Gyr. Assuming linear variation with time this result translates into $\dot{\mu}/\mu = (-17 \pm 5) \times 10^{-16}\ \mathrm{yr}^{-1}$. A different method, comparison of the hyperfine transition in atomic hydrogen with optical transitions in ions, was used in Refs. [4,5]. This method allows one to study variation of the parameter $x = \alpha^2 g_p/\mu$. Analysis of 9 quasar spectra with redshifts $0.23 \le z \le 2.35$ gave

$$\delta x/x = (6.3 \pm 9.9) \times 10^{-6}, \tag{2}$$

$$\dot{x}/x = (-6 \pm 12) \times 10^{-16}\ \mathrm{yr}^{-1}, \tag{3}$$

which is consistent with zero variation of μ. In Refs. [6–8] the 18 cm λ-doublet lines in an OH molecule were studied from objects at the redshifts $z \approx 0.247$, $z \approx 0.6847$, and $z \approx 0.765$ and no time variation of the parameter $g_p(\alpha^2\mu)^\nu$ was seen, where $\nu \lesssim 2$.

Reference [9] suggested to use a decelerated molecular beam of ND_3 to search for the variation of μ in laboratory experiments. The ND_3 molecule has a pyramidal shape and the inversion frequency depends on the exponentially small tunneling of three deuteriums through the potential barrier [10]. Because of that, it is very sensitive to any changes of the parameters of the system, particularly to the reduced mass for this vibrational mode. The authors of [9] found that $\delta\omega/\omega = 5.6\delta\mu/\mu$ (note that Ref. [9] contains a misprint in the sign of the effect). Slightly smaller enhancement should also exist in NH_3.

In this Letter we use the enhanced sensitivity of the inversion spectrum of NH_3 to variation of μ to place a new limit on the time variation of μ at the cosmological time scale. We use high-resolution ammonia spectra for the gravitational lens $B0218 + 357$, published by Henkel *et al.* [11]. The redshifts for ammonia lines are compared to the redshifts for the rotational lines of other molecules measured in Refs. [11–13]. The ammonia lines have an order of magnitude stronger dependence on μ than the usual vibrational lines; this enhancement allows us to place the best limit on the variation of μ.

Inversion spectrum of NH_3The inversion spectrum of NH_3 has been studied for a very long time [10] and is considered a classic example of the tunneling phenomenon. The inversion vibrational mode is described by a double well potential with the first two vibrational levels lying below the barrier. Because of the tunneling, these two levels are split in inversion doublets. The lower doublet corresponds to the wavelength $\lambda \approx 1.25$ cm and is used in ammonia masers. Molecular rotation leads to the centrifugal distortion of the potential curve. Because of that, the inversion splitting depends on the rotational angular momentum J and its projection on the molecular symmetry axis K:

$$\omega_{\text{inv}}(J,K) = \omega_{\text{inv}}^{0} - c_1[J(J+1) - K^2] + c_2 K^2, \tag{4}$$

where we omitted terms with higher powers of J and K. Numerically, $\omega_{\text{inv}}^{0} \approx 23.787$ GHz, $c_1 \approx 151.3$ MHz, and $c_2 \approx 59.7$ MHz.

In addition to the rotational structure (4) the inversion spectrum includes much smaller hyperfine structure. For the main nitrogen isotope ^{14}N, the hyperfine structure is dominated by the electric quadrupole interaction ($\sim$1 MHz) [14]. Because of the dipole selection rule $\Delta K = 0$ the levels with $J = K$ are metastable, and in laboratory experiments the width of the corresponding inversion lines is usually determined by collisional broadening. In astrophysics, the hyperfine structure for spectra with high redshifts is not resolved and we will not discuss it here.

For our purposes it is important to know how the parameters in (4) depend on fundamental constants. One can measure only dimensionless ratios of frequencies which do not depend on the units used. It is convenient to consider all parameters in atomic units. The energy unit Hartree is $E_H = m_e e^4/\hbar^2 = e^2/a_B$, where a_B is the Bohr radius ($E_H = 2$ Ry $= 219\,475$ cm^{-1}). In these units all electron energies (E_e/E_H) and electrostatic potentials ($U(r)/E_H$) have no dependence on the fundamental constants (here we neglect small relativistic corrections which give a weak α dependence), the vibrational intervals $\sim\mu^{-1/2}$ and the rotational intervals $\sim\mu^{-1}$. The inversion frequency $\omega_{\text{inv}}^{0}/E_H$ and constants $c_{1,2}/E_H$ are also functions of μ only (see below). Note that the coefficients c_i depend on μ through the reduced mass of the inversion mode and because they are inversely proportional to the molecular moments of inertia. That implies a different scaling of ω_{inv}^{0} and c_i with μ. The magnetic hyperfine structure of NH$_3$ is due to the interaction of nuclear magnetic moments and proportional to $\alpha^2 g_p^2 \mu^{-2}$.

We see that different frequencies in the inversion spectrum scale differently with μ and α. In principle, this allows one to study time variation of μ and α by comparing different lines of the inversion spectrum. On the other hand, it may be preferable to use independent references (see below).

Inversion Hamiltonian.—The inversion spectrum (4) can be approximately described by the following Hamiltonian:

$$H_{\text{inv}} = -\frac{1}{2M_1}\partial_x^2 + U(x) + \frac{1}{I_1(x)}[J(J+1) - K^2] + \frac{1}{I_2(x)}K^2, \tag{5}$$

where x is the distance from N to the H plane, I_1, I_2 are moments of inertia perpendicular and parallel to the molecular axis, correspondingly, and M_1 is the reduced mass for the inversion mode. If we assume that the length d of the N–H bond does not change during inversion, then $M_1 = 2.54 m_p$ and

$$I_1(x) \approx \tfrac{3}{2} m_p d^2 [1 + 0.2(x/d)^2], \tag{6}$$

$$I_2(x) \approx 3 m_p d^2 [1 - (x/d)^2]. \tag{7}$$

The dependence of $I_{1,2}$ on x generates a correction to the potential energy of the form $C(J,K)x^2/\mu$. This changes the vibrational frequency and the effective height of the potential barrier, therefore changing the inversion frequency ω_{inv} given by Eq. (4).

Following [15] we can write the potential $U(x)$ in (5) in the following form:

$$U(x) = \tfrac{1}{2} k x^2 + b \exp(-c x^2). \tag{8}$$

Fitting vibrational frequencies for NH$_3$ and ND$_3$ gives $k \approx 0.7598$ a.u., $b \approx 0.05684$ a.u., and $c \approx 1.3696$ a.u. Numerical integration of the Schrödinger equation with potential (8) gives the following result:

$$\frac{\delta\omega_{\text{inv}}}{\omega_{\text{inv}}} \approx -4.46 \frac{\delta\mu}{\mu}. \tag{9}$$

It is instructive to reproduce this result from an analytical calculation. In the semiclassical approximation the inversion frequency is estimated as [16]

$$\omega_{\text{inv}} = \frac{\omega_v}{\pi}\exp(-S) \tag{10a}$$

$$= \frac{\omega_v}{\pi}\exp\left(-\frac{1}{\hbar}\int_{-a}^{a}\sqrt{2M_1(U(x) - E)}\,dx\right), \tag{10b}$$

where ω_v is the vibrational frequency of the inversion mode, S is the action in units of $\hbar$, $x = \pm a$ are classical turning points for the energy E. For the lowest vibrational state $E = U_{\min} + \frac{1}{2}\omega_v$. Using the experimental values $\omega_v = 950$ cm^{-1} and $\omega_{\text{inv}} = 0.8$ cm^{-1}, we get $S \approx 5.9$.

Expression (10b) allows one to calculate the dependence of ω_{inv}^{0} on the mass ratio μ. Let us present S in the following form: $S = A\mu^{1/2}\int_{-a}^{a}\sqrt{(U(x) - E)/E_H}\,d(x/a_B)$, where A is a numerical constant. We see that the dependence of ω_{inv}^{0} on μ appears from the factor $\mu^{1/2}$ in S and from the vibrational frequency ω_v and $E - U_{\min} = \frac{1}{2}\omega_v$ which are proportional to $\mu^{-1/2}$. Below we assume that all energies are measured in atomic units and omit the atomic energy unit E_H. Then we obtain

$$\frac{d\omega_{\rm inv}^0}{d\mu} = -\omega_{\rm inv}^0\left(\frac{1}{2\mu} + \frac{dS}{d\mu}\right) \tag{11a}$$

$$= -\omega_{\rm inv}^0\left(\frac{1}{2\mu} + \frac{\partial S}{\partial \mu} + \frac{\partial S}{\partial E}\frac{\partial E}{\partial \mu}\right), \tag{11b}$$

where we took into account that $\partial S/\partial a = 0$ because the integrand in (10b) turns to zero at $x = \pm a$.

It is easy to see that $\partial S/\partial \mu = S/2\mu$. The value of the third term in Eq. (11b) depends on the form of the potential barrier:

$$\frac{\partial S}{\partial E} = -\frac{q}{4}\frac{S}{U_{\rm max} - E}, \tag{12}$$

where for the square barrier $q = 1$, and for the triangular barrier $q = 3$. For a more realistic barrier shape $q \approx 2$. Using parametrization (8) to determine $U_{\rm max}$ we get

$$\frac{\delta\omega_{\rm inv}^0}{\omega_{\rm inv}^0} \approx -\frac{\delta\mu}{2\mu}\left(1 + S + \frac{S}{2}\frac{\omega_v}{U_{\rm max} - E}\right) = -4.4\frac{\delta\mu}{\mu}. \tag{13}$$

We see that the inversion frequency of NH_3 is an order of magnitude more sensitive to the change of μ than typical vibrational frequencies. The reason for this is clear from Eq. (13): it is the large value of the action S for the tunneling process.

Let us also find the dependence of the constants $c_{1,2}$ on μ in Eq. (4). According to Eqs. (5)–(7) both constants must have the same dependence on μ. Below we focus on the constant c_2, which is linked to the last term in the Hamiltonian (5). It follows from Eq. (7) that this term generates a correction to the potential:

$$\delta U(x) = \frac{K^2}{3m_p d^4}x^2. \tag{14}$$

This correction does not change the height of the barrier, but changes the energy $E = U_{\rm min} + \frac{1}{2}\omega_v$ in (10b) by raising the potential minimum and increasing the vibrational frequency:

$$U_{\rm min} \to U_{\rm min} + \frac{K^2}{3m_p d^4}x_0^2, \tag{15}$$

$$\omega_v \to \omega_v\left(1 + \frac{K^2}{3m_p d^4 k}\right). \tag{16}$$

With the help of Eq. (12) with $q = 2$ we can find the constant c_2:

$$c_2 = \frac{\omega_{\rm inv}^0}{3m_p d^4 k}\left(1 + \frac{kx_0^2 + \omega_v}{U_{\rm max} - E}S\right). \tag{17}$$

We can differentiate Eq. (17) to estimate how c_2 depends on μ. This leads to $\delta c_2/c_2 = -5.0\delta\mu/\mu$, while the numerical solution with the Hamiltonian (5) gives

$$\frac{\delta c_{1,2}}{c_{1,2}} = -5.1\frac{\delta\mu}{\mu}. \tag{18}$$

It is clear that NH_3 is not the only molecule with enhanced sensitivity to variation of μ. Similar enhancement should take place for all tunneling transitions in molecular spectra. For example, the inversion frequency for a ND_3 molecule is 15 times smaller than for NH_3, and Eq. (10a) leads to $S \approx 8.4$, compared to $S \approx 5.9$ for NH_3. According to Eq. (13) that leads to a slightly higher sensitivity of the inversion frequency to μ (see also [9]):

$$ND_3: \begin{cases} \frac{\delta\omega_{\rm inv}}{\omega_{\rm inv}} \approx -5.7\frac{\delta\mu}{\mu} \\ \frac{\delta c_2}{c_2} \approx -6.2\frac{\delta\mu}{\mu}. \end{cases} \tag{19}$$

Redshifts for molecular lines in the microwave spectra of $B0218 + 357$In the previous section we saw that the inversion frequency $\omega_{\rm inv}^0$ and the rotational intervals $\omega_{\rm inv}(J_1, K_1) - \omega_{\rm inv}(J_2, K_2)$ have different dependencies on the constant μ. In principle, this allows one to study the time variation of μ by comparing different intervals in the inversion spectrum of ammonia. For example, if we compare the rotational interval to the inversion frequency, then Eqs. (9) and (18) give

$$\frac{\delta\{[\omega_{\rm inv}(J_1, K_1) - \omega_{\rm inv}(J_2, K_2)]/\omega_{\rm inv}^0\}}{[\omega_{\rm inv}(J_1, K_1) - \omega_{\rm inv}(J_2, K_2)]/\omega_{\rm inv}^0} = -0.6\frac{\delta\mu}{\mu}. \tag{20}$$

The relative effects are substantially larger if we compare the inversion transitions with the transitions between the quadrupole and magnetic hyperfine components. However, in practice this method will not work because of the smallness of the hyperfine structure compared to typical linewidths in astrophysics.

It is more promising to compare the inversion spectrum of NH_3 with rotational spectra of other molecules, where

$$\frac{\delta\omega_{\rm rot}}{\omega_{\rm rot}} = -\frac{\delta\mu}{\mu}. \tag{21}$$

In astrophysics any frequency shift is related to a corresponding apparent redshift:

$$\frac{\delta\omega}{\omega} = -\frac{\delta z}{1 + z}. \tag{22}$$

According to Eqs. (9) and (21), for a given astrophysical object with $z = z_0$ variation of μ will lead to a change of the apparent redshifts of all rotational lines $\delta z_{\rm rot} = (1 + z_0)\delta\mu/\mu$ and corresponding shifts of all inversion lines of ammonia $\delta z_{\rm inv} = 4.46(1 + z_0)\delta\mu/\mu$. Therefore, comparing the apparent redshift for NH_3 with the apparent redshifts for rotational lines we can find $\delta\mu/\mu$:

$$\frac{\delta\mu}{\mu} = 0.289\frac{z_{\rm inv} - z_{\rm rot}}{1 + z_0}. \tag{23}$$

In Table I we list the redshifts for microwave lines in the spectrum of the object $B0218 + 357$. Three inversion lines $(J, K) = (1, 1)$, $(2, 2)$, and $(3, 3)$ are reported in Ref. [11]. Each of them consists of a narrow redshifted and a wide blueshifted component. The splitting between the redshifted and blueshifted components, which is about

TABLE I. Redshifts for molecular rotational lines, ammonia inversion lines, and hydrogen hyperfine line in the spectrum of $B0218 + 357$.

	Rotational lines		
CO $J = 1 \rightarrow 2$	Redshifted	0.684 70	[12]
	Blueshifted	0.684 63	[12]
CO, HCO^+, HCN	Average	0.684 66(1)	[17]
	Inversion lines of NH_3		
NH_3 $(J, K) = (1, 1)$	Redshifted	0.684 679 (3)	[11]
	Blueshifted	0.684 649 (15)	[11]
$= (2, 2)$	Redshifted	0.684 677 (3)	[11]
	Blueshifted	0.684 650 (17)	[11]
$= (3, 3)$	Redshifted	0.684 673 (3)	[11]
	Blueshifted	0.684 627 (33)	[11]
	Average redshifted	0.684 676 (3)	
	Average blueshifted	0.684 647 (11)	
H	$\lambda = 21$ cm average	0.684 66(4)	[18]

5 km/s, is ascribed to the complicated structure of the molecular cloud [11]. Using average redshifts of these inversion components [0.684 676 (3) and 0.684 647 (11)] from Table I we can calculate the average deviation of the inversion redshift in respect to the average molecular redshift [0.684 66(1)]:

$$\Delta z_{\mathrm{av}}^{\mathrm{unweighted}} = (0.2 \pm 0.9) \times 10^{-5}, \tag{24}$$

$$\Delta z_{\mathrm{av}}^{\mathrm{weighted}} = (0.6 \pm 0.9) \times 10^{-5}. \tag{25}$$

Equation (23) gives the following estimate for variation of μ:

$$\frac{\delta\mu}{\mu} = 10^{-6} \times \begin{cases} 0.3 \pm 1.6 & \text{(unweighted)}, \\ 1.1 \pm 1.5 & \text{(weighted)}. \end{cases} \tag{26}$$

As a final result we present a conservative limit with larger error bars to cover the total interval between the minimal and maximal values for both estimates:

$$\frac{\delta\mu}{\mu} = (0.6 \pm 1.9) \times 10^{-6}. \tag{27}$$

We can also compare averaged redshift for ammonia with that of hydrogen to get a restriction on the variation of the parameter $y = \alpha^2 g_p \mu^{3.46}$:

$$\frac{\delta y}{y} = \frac{z_{\mathrm{inv}} - z_{\mathrm{hfs}}}{1 + z_0} = (1 \pm 17) \times 10^{-6}. \tag{28}$$

The estimates (26)–(28) can be further improved by dedicated analysis of the molecular spectra published in Refs. [11–13]. As mentioned in [12], the majority of molecular lines from $B0218 + 357$ have two velocity components. The same applies to the hydrogenic 21 cm line [19]. Instead of taking an average, as we have done in (26)–(28), all redshifted and all blueshifted components should be analyzed independently. That may allow one to reduce the error bars significantly.

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