

# Enhanced Sensitivity to $m_p/m_e$ Variation from Microwave Transitions between Vibration-Inversion States of Ammonia

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**Abstract**—Ammonia microwave transitions between vibration-inversion states in the range 6300-7200  $\text{cm}^{-1}$  are predicted with enhanced sensitivity coefficients to the variation of the proton-electron mass ratio. These transitions may be addressed by optical pumping and Ramsey interrogation scheme with a molecular fountain setup. A molecular clock based on a sensitive transition may provide  $10^{-9}(\tau/1\text{ s})^{-1/2}$  level fractional stability and  $10^{-15}$  level fractional accuracy, and may enable probing proton-electron mass ratio fractional variation at the  $10^{-13}$  level or better in hours of averaging time.

**Keywords**—sensitivity to proton-electron mass ratio variation, ammonia rotation-vibration Hamiltonian, double resonance spectroscopy, molecular fountain, ammonia microwave clock.

## I. INTRODUCTION

Time variation of fundamental constants [1] is accurately addressed with clock comparisons [2,3]. In order to tighten the constraints, the well-known approach is to increase the averaging time, to decrease systematic uncertainties of the clocks and, finally, to use highly sensitive transitions. The transitions between near resonant energy levels enable access to enhanced sensitivity [4]. A molecular clock based on the  $^{12}\text{C}_2\text{H}_2$  transition at 10.363 GHz between excited rovibrational levels (sensitivity coefficient  $\sim 100$  at variation of proton-electron mass ratio  $\mu$ ) probed in a cell by Fourier-transform microwave spectroscopy may provide a fractional stability  $2.1 \times 10^{-10}(\tau/1\text{ s})^{-1/2}$  and a fractional accuracy of  $2.9 \times 10^{-11}$  [5].

One of the simplest hydride molecules, ammonia was exploited for building the first maser. Sub-Doppler spectroscopy of ammonia provided infrared frequency references at 1.5  $\mu\text{m}$  [6]. Slowing, cooling and trapping was demonstrated with ammonia [7] and a molecular fountain [8]. Ammonia spectroscopy interests the atmospheric physics and the astrophysics. Ammonia microwave transitions between the lowest degenerate vibration-inversion levels have an enhanced sensitivity to  $\mu$ -variation [9]. This work addresses theory for predicting transitions between higher near-degenerate ammonia energy levels, their sensitivity to  $\mu$ -variation, and the metrological performances of an ammonia clock based on a sensitive microwave transition.

## II. MOLECULAR PHYSICS AND SENSITIVITY TO VARIATIONS OF FUNDAMENTAL CONSTANTS

### A. Variability of fundamental constants

Variations of fundamental constants lead to a variation of the frequency  $f$  of an atomic or molecular transition:

$$\frac{\Delta f}{f} = Q_\alpha \frac{\Delta \alpha}{\alpha} + Q_\mu \frac{\Delta \mu}{\mu} + Q_q \frac{\Delta(\hat{m}/\Lambda)}{\hat{m}/\Lambda} \quad (1)$$

that is parametrized here in function of the variations of the fine structure constant  $\alpha$ , proton-electron mass ratio  $\mu$ , and ratio between the mean of quark masses  $\hat{m} = (m_u + m_d)/2$  and the QCD mass scale  $\Lambda$ , using the appropriate sensitivity coefficients  $Q_g = \partial \ln f / \partial \ln g$ ,  $g \in \{\alpha, \mu, \hat{m}/\Lambda\}$ . Here are addressed the molecular rovibrational frequencies that scale as  $f_{mol} \propto c R_\infty \mu^{Q_\mu^{mol}}$  in function of the Rydberg constant  $R_\infty$  and the speed of light in vacuum  $c$ . Fractional time variation of the frequency ratio between a molecular clock and the Cs standard  $X = f_{mol}/f_{Cs}$  is related to fractional time variations of the fundamental constants:

$$\frac{1}{X} \frac{dX}{dt} = (Q_\alpha^{mol} - Q_\alpha^{Cs}) \frac{1}{\alpha} \frac{d\alpha}{dt} + (Q_\mu^{mol} - Q_\mu^{Cs}) \frac{1}{\mu} \frac{d\mu}{dt} + (Q_q^{mol} - Q_q^{Cs}) \frac{1}{(\hat{m}/\Lambda)} \frac{d(\hat{m}/\Lambda)}{dt} \quad (2)$$

Atomic and nuclear physics calculations allow determination of the sensitivity coefficients for  $^{133}\text{Cs}$  [10]:  $Q_\alpha^{Cs} = 2.83$ ,  $Q_\mu^{Cs} = -1$ , and  $Q_q^{Cs} = 0.002$ . For hyperfine-free rotation-vibration molecular frequencies addressed here  $Q_\alpha^{mol} = 0$  and  $Q_q^{mol} = 0$ . Measurements against the Cs clock are interesting because they are sensitive mainly to variations of  $\alpha$  and  $\mu$ .

### B. Molecular theory and infrared spectroscopy of $\text{NH}_3$

The ground electronic state of ammonia is singlet with no electronic angular momentum. This molecule has four vibrational normal modes: the symmetric stretch and bend  $v_{1,2}$  are non-degenerate and the antisymmetric stretch and bend  $v_{3,4}$  are doubly degenerate. The vibrational states are labelled with the corresponding vibrational quantum number and display inversion doubling which is indicated with the  $s, a$  symmetry labels. Degenerate vibrational levels  $v_3^{l_3}, v_4^{l_4}$  are labelled in addition with vibrational angular momentum quantum numbers such as  $l_{3,4} = v_{3,4}, v_{3,4} - 2, \dots, -v_{3,4}$ . Vibrational angular momentum coupling is described with the effective quantum number  $l_{eff} = l_3 + l_4$ . Total rotational angular momentum is described with the quantum number  $J$ . Its projection on the molecule-fixed axis is described with the quantum number  $k = -J, -J + 1, \dots, J$  (absolute value  $K = |k|$ ). Finally, the energy levels are labelled with the  $\mathcal{D}_{3h}(M)$  group symmetry labels: *ortho* states  $A'_2, A''_2$ , *para* states  $E', E''$ .  $A'_1, A''_1$  states are suppressed by spin statistics. One-photon electric dipole transitions between rovibrational levels  $(v'_1, v'_2, (v'_3, v'_4)^{l'}, J', k') \leftarrow (v''_1, v''_2, (v''_3, v''_4)^{l'', J'', k''})$

obey to the following selection rules  $\Delta J = 0, \pm 1, J' + J'' \geq 1, A'_2 \leftrightarrow A''_2$ , and  $E' \leftrightarrow E''$ . In addition, molecular symmetry allows transitions  $\Delta(k-l) = 3n$  with  $n$  integer.

Theoretical modeling of ammonia spectra uses effective rotation-vibration-inversion effective Hamiltonians [11]. The *ab-initio* approach with the TROVE program aims to solve nuclear Schrödinger equation with a variational method [12].

Ammonia displays prominent vibrational bands in the 1.5  $\mu\text{m}$  region  $2\nu_3^0, \nu_1+\nu_3, \nu_1+2\nu_4^2, \nu_3+2\nu_4^2$  that were studied by high-resolution laser spectroscopy [13-17]. Extended line lists with positions, intensities, broadenings, and derived energy levels are available in the EXOMOL [18], HITRAN [19] and GEISA [20] databases. Empirical energy levels for ammonia are determined up to 7500  $\text{cm}^{-1}$  with the MARVEL (Measured Active Rotational-Vibrational Energy Levels) approach [21].

MARVEL  $^{14}\text{NH}_3$  rovibrational energy levels are adjusted here with a single-state model:

$$E_{rv}(J, K, l_{eff}) = E_{vib} + BJ(J+1) + (C - B)K^2 - D_{JJ}[J(J+1)]^2 - D_{JK}[J(J+1)]K^2 - D_{KK}K^4 - 2C\zeta l_{eff}K \quad (3)$$

that allows determination of effective parameters for the considered state: the vibrational energy  $E_{vib}$ , the rotational constants  $B, C$ , the centrifugal distortion constants  $D_{JJ}, D_{JK}, D_{KK}$  and the Coriolis coupling term  $\zeta$ .

The sensitivity of the rovibrational energy to the variation of the proton-electron mass ratio is calculated as:

$$\frac{dE_{rv}}{d\ln\mu} = \left(-\frac{1}{2}\right)E_{vib} + (-1)BJ(J+1) + (-1)(C - B)K^2 - (-2)D_{JJ}[J(J+1)]^2 - (-2)D_{JK}[J(J+1)]K^2 - (-2)D_{KK}K^4 - (-1)2C\zeta l_{eff}K \quad (4)$$

### C. Microwave transitions with enhanced sensitivity coefficients to $\mu$ -variation

Molecular theory predicts near-degeneracies between rovibrational levels that are due, as follows from equation (3), to the cancellation of vibrational energy gaps with differences of effective rotational intervals and contributions of centrifugal distortion and Coriolis coupling terms. Lowering the frequency of the transitions between energy levels with different sensitivities to  $\mu$ -variation increases significantly their sensitivity coefficient.

More than 3600 one-photon electric-dipole rovibrational transitions are predicted by *ab-initio* calculations with frequencies up to 30 GHz between  $^{14}\text{NH}_3$  energy levels that are located in the range 6300–7200  $\text{cm}^{-1}$  [18]. The involved vibrational energy levels are plotted in Fig. 1.A. The relevant MARVEL energy level values are adjusted with equation (3) in order to get effective values for the molecular parameters in each  $(\nu_1, \nu_2, (\nu_3, \nu_4)^{l_{eff}})$  vibrational state. Theoretical sensitivity coefficients to  $\mu$ -variation for these transitions may be predicted subsequently using equations (3,4). The resulting sensitivity coefficient is corrected with the ratio between the predicted frequency and the experimental frequency. These transitions may be accessed by optical pumping from the vibrational ground state and a selection is plotted in Fig. 1.B.

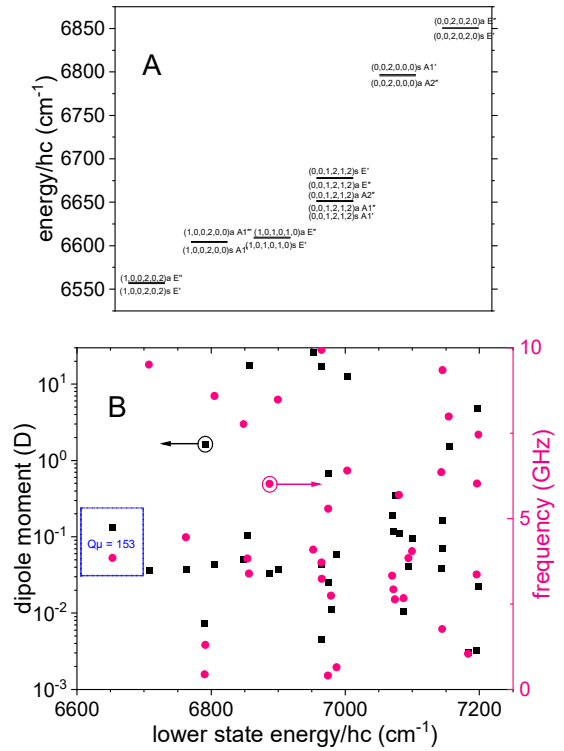


Fig. 1. A. Vibrational energy levels (indicated with the labels for vibration  $(\nu_1, \nu_2, \nu_3, \nu_4, l_3, l_4)$ , parity and group symmetry) that provide access microwave transitions with enhanced sensitivity coefficient to the variation of  $\mu$ . B. Dipole moment (left-axis, black squares) and frequency (right-axis, red circles) for a selection of such microwave transitions.

TABLE I. RADIATIVE LIFETIMES FOR SELECTED  $\text{NH}_3$  VIBRATIONAL LEVELS

| Vibrational level | total radiative lifetime (s) |
|-------------------|------------------------------|
| (2, 0, 0, 0)      | $7.54 \times 10^{-2}$        |
| (1, 0, 0, 2)      | $1.05 \times 10^{-1}$        |
| (1, 0, 1, 0)      | $7.47 \times 10^{-2}$        |
| (0, 0, 1, 2)      | $8.24 \times 10^{-2}$        |
| (0, 0, 2, 0)      | $1.10 \times 10^{-1}$        |

Transition dipole moments for the transitions of interest are derived here from the *ab-initio* calculations of transition frequencies and the Einstein A coefficients [18]. The values may be as high as some tens of Debye. The values for a selection of microwave rovibrational transitions between  $2\nu_3, \nu_1+\nu_3, \nu_1+2\nu_4, \nu_3+2\nu_4$  states is shown in Figure 1.B.

Finite radiative lifetimes of the energy levels limit the ultimate precision in high-resolution spectroscopy experiments. Total radiative lifetime for an energy level is calculated by summing of contributions of all relevant Einstein A coefficients. Contributions of all rotational levels pertaining to a given vibrational state are averaged with Boltzmann ponderations to get partial deexcitation lifetimes [22]. Total deexcitation lifetimes for the relevant energy levels of ammonia are indicated in Table 1.

### III. PROPOSED EXPERIMENTAL APPROACH AND METROLOGICAL PERFORMANCES

The transition predicted at  $f_{mol} = 3.85$  GHz ( $v_1, v_2, v_3, v_4, |l_3|, |l_4|; J, |k|$ ) $s/a = (1,0,0,2,0,2; 3,2)s \rightarrow (1,0,1,0,1,0; 2,2)a$  has a sensitivity coefficient to  $\mu$ -variation of  $Q_{\mu}^{mol} = 153$  and a transition dipole moment of 0.14 D. Access to this transition may be provided by optical pumping from the vibrational ground state using the transition: ( $v_1, v_2, v_3, v_4, |l_3|, |l_4|; J, |k|$ ) $s/a = (0,0,0,0,0,0; 1,1)s \rightarrow (1,0,1,0,1,0; 2,2)a$  that was measured at 198.94799 THz and has a 83 mD transition dipole moment [19]. The hyperfine structure is not taken into account in the following analysis.

In molecular clocks experiments, the statistical uncertainty of a frequency measurement at the limit of the quantum projection noise is  $\delta f_{mol} \cong 1/\sqrt{NT_c\tau}$ , in function of the interrogation time  $T_c$  of the experiment and the total acquisition time  $\tau$ . A number of  $N$  molecules are prepared in the excited vibrational state and probed at each interrogation. The ultimate coherence time  $T_c \sim 0.1$  s is dictated by spontaneous decays from the excited vibrational levels. Transition rates towards lower vibrational levels stimulated by the blackbody radiation (BBR) at  $T = 300$  K are negligible. BBR-driven excitation towards higher vibrational levels is assumed negligible.

The molecular fountain approach [8], demonstrated already for ammonia, is proposed here for developing a new microwave molecular clock. Ammonia molecules from a supersonic beam may be decelerated, cooled and trapped in the (0,0,0,0,0,0; 1,1) $a$  state using electric fields [8]. The molecular cloud is launched vertically with 1 m/s speed and  $\leq 10$  mK translational temperature and observed after free fall. During the ballistic flight,  $^{14}\text{NH}_3$  molecules are transferred to the (1,0,1,0,1,0; 2,2) $a$  state by optical pumping, cross two times a cylindrical microwave cavity where is performed Ramsey interrogation on the (1,0,0,2,0,2; 3,2) $s \rightarrow (1,0,1,0,1,0; 2,2)a$  transition with  $\pi/2$  pulses (projected parameters : quality factor 1000 on a TM011 mode, interaction zone with the  $^{14}\text{NH}_3$  cloud of radius 5 mm and length 2.8 cm), and, finally, addressed with a state-selective detection scheme. The Ramsey method is implemented with a total interrogation time of  $T_c = 0.1$  s. Adapting the wavelength of multiphoton ionization with an UV laser [23], may enable state-sensitive detection of  $^{14}\text{NH}_3$  at the level of  $N = 0.4$  molecule per shot on the (0,0,0,0,0,0; 1,1) $a$  state, as demonstrated in [8].

The projected linewidth of the Ramsey fringes is 5 Hz. The uncertainty of the frequency measurement is estimated at  $\delta f_{mol} = 5 (\tau/1s)^{-1/2}$  Hz. The fountain approach with the projected parameters enables constraining a  $\mu$ -variation of  $\delta \mu/\mu = \delta f_{mol}/(Q_{\mu}^{mol} \cdot f_{mol}) = 8.5 \times 10^{-12} (\tau/1s)^{-1/2}$ . A constraint of  $1 \times 10^{-13}$  is reached within an averaging time of two hours and  $5.5 \times 10^{-15}$  within one month.

Ultimately, the precision will be limited by systematic frequency shifts. They were estimated at  $10^{-15}$  fractionally or below for a microwave clock based on a hyperfine component of the inversion transition of  $^{14}\text{NH}_3$  ( $J = 1, K = 1$ ) $s \rightarrow (J = 1, K = 1)a$  in the vibrational ground state probed with the fountain approach [24]. Noteworthy, as the molecular cloud has a translational temperature at the  $\mu\text{K}$  level and a density at  $100 \text{ cm}^{-3}$  level, the collisional shift is negligible. The systematic Doppler shifts are estimated here with the

parameters of the ballistic motion of the molecular cloud. The fractional first-order Doppler shift is  $1.7 \times 10^{-14}$  with uncertainty  $< 2 \times 10^{-15}$  and the second-order Doppler shift is negligible. Moreover, the DC Stark shift and the Zeeman shift are evaluated here with the sensitivity coefficients from [24]. Efficient screening of the external fields (static DC electric field  $< 1 \text{ mV/cm}$  and static magnetic field  $< 0.1 \text{ mG}$ ) lead to a negligible Zeeman shift and to a DC Stark shift with fractional uncertainty of  $1.9 \times 10^{-15}$ . In addition, the microwave transition is well isolated and the nearby rovibrational transitions are detuned by at least 1 MHz. Pedestal of these transitions lead to negligible frequency pulling.

The cavity pulling fractional shift is evaluated here as  $\frac{\Delta f_{mol}^{CP}}{f_{mol}} \sim \left(\frac{Q_{cav}}{Q_{mol}}\right)^2 \times \frac{\Delta f_{cav}}{f_{mol}}$  [25] in function of the detuning of the cavity frequency  $\Delta f_{cav}$  against the molecular clock frequency  $f_{mol}$ . Using the quality factors for the molecular line  $Q_{mol} = 7.7 \times 10^8$ , the loaded cavity quality factor  $Q_{mol} = 1000$  and a mistuning of the cavity by 0.1 MHz, the cavity pulling shift is negligible ( $+0.2 \mu\text{Hz}$ ), thanks to the high-quality factor of the molecular line.

The shift of a molecular energy level  $E_i$  induced by coupling of the blackbody radiation to other energy levels  $E_f$  is evaluated with the perturbation theory as [26]:

$$\Delta E_i^{BBR} = \left(\frac{1}{12\epsilon_0}\right) \left(\sum_{f,\pm} P \int_0^\infty df \rho(f) \frac{\mu_{i \rightarrow f}^2}{E_i - E_f \pm hf}\right) \quad (5)$$

Here  $\rho(f) = \frac{8\pi hf^3}{c^3} \frac{1}{e^{hf/(k_B T)} - 1}$  is the spectral energy of the blackbody radiation at temperature  $T$  and  $\mu_{i \rightarrow f}$  are the transition moments for the electric dipole couplings towards all available states. Summing of these contributions is addressed with a principal value integral because of the discontinuities.

The shifts of the levels of interest  $A = (1,0,1,0,1,0; 2,2)a$ ;  $S = (1,0,0,2,0,2; 3,2)s$  are evaluated for BBR-driven couplings on dipole-allowed infrared and microwave transitions. The most important coupling is in the microwave range on the transition (1,0,1,0,1,0; 2,2) $a \leftrightarrow (1,0,1,0,1,0; 2,2)s$  with a transition dipole moment of 18.7 D. The contribution to the BBR shift is  $-0.17 \text{ Hz}$  at  $T = 300 \text{ K}$ . Another coupling at microwave frequency is on the transition (1,0,0,2,0,2; 3,2) $s \leftrightarrow (1,0,0,2,0,2; 3,2)a$  with a transition dipole moment of 7.9 D. The contribution to the BBR shift is  $-60 \text{ mHz}$  at  $T = 300 \text{ K}$ . Moreover, couplings to the levels pertaining to lower vibrational states may be estimated with effective vibrational transition dipole moments that are calculated here in the 0.1 – 1 D range using relevant data provided in [22]. The most important contribution to the BBR shift ( $+0.11 \text{ Hz}$  at  $T = 300 \text{ K}$ ) comes from the coupling between the vibrational states (1,0,1,0)  $\leftrightarrow$  (0,0,1,1). All these couplings yield a total BBR shift of the molecular clock transition of  $-84 \text{ mHz}$  at  $T = 300 \text{ K}$ . Temperature uncertainty of  $\Delta T = 0.1 \text{ K}$  translates into a remarkably low BBR shift uncertainty of  $2 \mu\text{Hz}$ , due to compensation of slopes of different contributions, that is a part of  $5 \times 10^{-16}$  of the molecular clock frequency. One should note that there are additional infrared BBR couplings of the levels of the transition of interest with higher vibrational states. They were not yet described by *ab-initio* calculations. These couplings

yield BBR shifts with an opposite sign comparing to that of the BBR shifts evaluated with lower vibrational states.

AC-Stark shift may arise from off-resonant couplings of the levels of interest to another levels during Ramsey interrogation with the microwave field. The nearest couplings are with levels  $A' = (1,0,1,0,1,0; 2,2)s$ ,  $S' = (1,0,0,2,0,2; 3,2)a$  that were addressed previously and are detuned by a few tens of GHz to the levels of interest. On-resonance Ramsey spectroscopy of the microwave transition with  $\pi/2$  pulses during a projected 20 ms cavity interrogation time has negligible AC-Stark shift.

#### IV. CONCLUSION

This contribution addresses the potential from a new molecular clock for testing time stability of fundamental constants. Microwave transitions of  $^{14}\text{NH}_3$  are predicted between nearby rovibrational levels in the range 6300-7200  $\text{cm}^{-1}$  and their sensitivity coefficient to the variation of  $\mu$  is calculated with a simple Hamiltonian model. The metrological performances are evaluated for an  $^{14}\text{NH}_3$  clock based on the Ramsey interrogation in a molecular fountain of a transition at 3.85 GHz with a sensitivity coefficient to  $\mu$ -variation of 153. The fractional stability of  $1.3 \times 10^{-9} (\tau/1\text{s})^{-1/2}$  and fractional accuracy of  $2.8 \times 10^{-15}$  of this clock enables probing fractional  $\mu$ -variation at  $10^{-13}$  level or better within hours of averaging time.

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