Enhanced Sensitivity to Variation of m_e/m_p in Molecular Spectra

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We propose new experiments with high sensitivity to a possible variation of the electron-to-proton mass ratio $\mu \equiv m_e/m_p$. We consider a nearly degenerate pair of molecular vibrational levels, each associated with a different electronic potential. With respect to a change in μ, the change in the splitting between such levels can be large both on an absolute scale and relative to the splitting. We demonstrate the existence of such pairs of states in Cs_2, where the narrow spectral lines achievable with ultracold molecules make the system promising for future searches for small variations in μ.

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The notion that the fundamental constants of nature may actually vary has recently generated intense interest [1,2]. Theoretical motivation comes from a variety of string-inspired models; these can include space-time with extra dimensions of variable geometry and/or light scalar fields whose variable amplitude couples to ordinary matter. Both effects can change the apparent values of constants. Such fields are potential candidates (dubbed "quintessence") to explain the observed dark energy that dominates the Universe. Sensitive probes for possible variation of fundamental constants are among the few ways to verify or constrain models such as these.

On quite general principles, measurements can only detect variation in *dimensionless* constants [2]. Most attention has focused on possible variation of the fine structure constant α. However, variations in α are no more likely than in any other fundamental parameter. In fact, it has been argued that in grand unified theories, variation in the electron-to-proton mass ratio $\mu \equiv m_e/m_p$ should be larger than that in α by a factor of ~ 30 [2]. Hence, study of μ is a potentially more sensitive method to observe any variation of constants.

The most sensitive tests for variation in μ have come from examining molecular spectra from cosmologically distant sources, at redshifts corresponding to $\sim 10^{10}$ years ago [3]. Comparisons of spectral lines in these objects to the same lines measured now in the laboratory yield stringent bounds at the level $\sim 10^{-15}$/year on the time variation of μ. However, systematic errors associated with these measurements can be significant and are difficult to eliminate due to the uncertainty in the structure, environment, and dynamics of the sources.

We propose a new type of laboratory experiment to search for variation of μ. We show that the energy of molecular vibrational levels can be highly sensitive to changes in μ; moreover, pairs of closely spaced levels can be used to enhance the sensitivity relative to the level splitting. We show data verifying such a near degeneracy in the ground vibronic levels of Cs_2. We argue that measurements in Cs_2 plausibly could be made precise enough to sense a fractional change $\Delta\mu/\mu \lesssim 10^{-17}$.

The sensitivity of our proposed measurement is governed by a few key parameters. Most important is the absolute change $\partial_\mu \Omega$ of the energy splitting Ω with respect to a fractional change $\Delta\mu/\mu$: $\partial_\mu \Omega \equiv \partial\Omega/\partial(\ln\mu)$ ($\hbar = c = 1$ throughout). Ω can be measured with statistical uncertainty $\delta\Omega = \Gamma/S$, where Γ is the linewidth of the transition and S is the signal to noise. Hence, $\Delta\mu/\mu$ can be detected with statistical uncertainty $\delta(\Delta\mu/\mu) = \delta\Omega/\partial_\mu\Omega = (\Gamma/\partial_\mu\Omega)S^{-1}$, and the ratio $\partial_\mu\Omega/\Gamma$ provides a primary figure of merit. However, the *relative* change of the splitting, $\partial_\mu\Omega/\Omega$, is also of importance, for two reasons. First, since Ω must be measured with respect to some reference clock (with fractional uncertainty $\delta\Omega_c/\Omega_c$), it is impossible to determine Ω to better than $\delta\Omega_{\min} = \Omega(\delta\Omega_c/\Omega_c)$. Second, many systematic effects are proportional to Ω (e.g., Doppler shifts). Hence, $\partial_\mu\Omega/\Omega$ provides an important secondary figure of merit.

To analyze the dependence of molecular energy levels on μ, without loss of generality we fix m_e, so a change in μ corresponds to variation of m_p. To isolate the dependence on μ, we assume a reference clock based on an optical atomic transition [4], with frequency Ω_c depending parametrically only on $\mathcal{R} = m_e\alpha^2/2$ and α. Good reference clock stability (such that $\delta\Omega_c/\Omega_c \ll \delta\Omega/\Omega$) is then equivalent to holding α and hence also $\mathcal{R}$ constant in our analysis. Under this assumption, molecular electronic potentials are also fixed: these also depend parametrically only on $\mathcal{R}$ and α, and they are independent of μ.

We approximate the vibrational energy levels E_v via the WKB quantization condition:

$$\int_{R_i}^{R_o} \sqrt{2M[E_v - V(R)]}\,dR = (v + \tfrac{1}{2})\pi, \qquad (1)$$

where R is the interatomic separation, $V(R)$ is the potential with minimum value 0, $R_i(R_o)$ is the classical inner (outer) turning point of $V(R)$ at energy E_v, and $M \propto m_p$ is the reduced mass of the nuclei in the molecule. Varying Eq. (1) with respect to both μ and v, one obtains for the *energy sensitivity* $\partial_\mu E_v$:

$$\partial_\mu E_v \equiv \frac{\partial E_v}{\partial(\ln\mu)} = \frac{(v+\frac{1}{2})}{2\rho(E_v)}, \qquad (2)$$

where $\rho(E_v) = (\partial E_v/\partial v)^{-1} \approx (E_v - E_{v-1})^{-1}$ is the density of states at energy E_v [5]. Near its minimum, a typical potential is harmonic, with $E_v = (v+\frac{1}{2})\omega$ and $\rho(E_v) = \omega^{-1}$ (ω is the classical oscillator frequency). Hence, for the harmonic part of the potential, $\partial_\mu E_v = (v+\frac{1}{2})\omega/2 = E_v/2$ has a $\approx v$-fold enhancement for the v^{th} vibrational level. (This can also be derived from $\omega \propto M^{-1/2}$.) This constitutes a general mechanism for amplifying the *absolute* size of $\partial_\mu\Omega$.

Real molecular potentials are not harmonic. For the highest values of v, E_v approaches the dissociation limit D, and $\rho(E_v)$ becomes large. Hence, the value of $\partial_\mu E_v$ again becomes small for the highest levels in any potential; at some intermediate value of v, $\partial_\mu E_v$ is maximized. We verified this behavior both for a generic (Morse) potential and for the empirically known $X\,^1\Sigma_g^+$ potential of Cs_2 (see below). In both cases, the maximum value of $\partial_\mu E_v$ is obtained for levels with $E_v^{(\max)} \cong 3D/4$, and there $\partial_\mu E_v$ is only slightly diminished from its expected value in the harmonic approximation: $\partial_\mu E_v^{(\max)} \cong (2/3)(E_v^{(\max)}/2)$. A recent Letter [5] proposed detecting variations in μ using Feschbach resonances in the scattering between ultracold atoms. However, such resonances arise from the presence of vibrational states (associated with potentials for other internal states of the atoms) that are very near D, where $\partial_\mu E_v$ is small. Our method uses the much larger value of $\partial_\mu E_v$ for states of intermediate vibrational excitation.

The same mechanism can be used, in some cases, to provide transitions with extremely large *relative* shifts $\partial_\mu\Omega/\Omega$. Consider a situation in which two molecular electronic potentials X and Y overlap, but the minimum of potential Y (at energy T_Y) is at higher energy than that of X (at 0). In this case, an excited level of X with vibrational number $v_X \gg 1$ and energy $E_1 = E_{v_X}^{(X)}$ can be quite near in energy to a lower vibrational level of Y ($v_Y \ll v_X$), with energy $E_2 = T_Y + E_{v_Y}^{(Y)}$. The energy difference between such a pair of levels is small ($\Omega = |E_1 - E_2| \ll E_{v_X}^{(X)}$), but can retain a large sensitivity to changes in μ, since $\partial_\mu\Omega = \partial_\mu E_{v_X}^{(X)} - \partial_\mu E_{v_Y}^{(Y)} \approx \partial_\mu E_{v_X}^{(X)}$.

The molecule Cs_2 is an attractive system for implementing this scheme. Cs_2 has two low-lying, overlapping potentials: the deep $X\,^1\Sigma_g^+$ ground state and the shallower $a\,^3\Sigma_u^+$ state, each of which dissociates to a pair of ground-state Cs atoms [6]. The vibrational splittings of these two potentials are incommensurate, and the large mass of Cs yields a high density of states; hence near degeneracies appeared likely. In fact, Ref. [7] reported evidence for such in the high-J levels of the $v_X = 137$ state. Furthermore, all rovibrational levels of both potentials have extremely long radiative lifetimes ($\gg$1 s) [8], and production of *ultracold* Cs_2 molecules (which can be measured over long coherence times) has become routine [8,9]; hence the system can yield spectral lines with narrow width Γ. Finally, it has been predicted that deeply bound levels of the $a\,^3\Sigma_u^+$ state—which lie near $E_v^{(\max)}$ for the $X\,^1\Sigma_g^+$ state—can be efficiently populated [10,11].

We calculate $\partial_\mu E_v$ for all vibrational levels in the X and a states of Cs_2, using the fitted potentials described below and numerical solutions for E_v with slightly different values of M. A plot of $\partial_\mu E_v$ versus binding energy [$E_b(v) \equiv E_v - D$] is shown for both potentials in Fig. 1. The behavior throughout is as expected from Eq. (2). As expected from the previous discussion, $\partial_\mu E_{v_a}^{(a)} \ll \partial_\mu E_{v_X}^{(X)}$ for close-lying X and a state levels [such that $E_b^{(a)}(v_a) \cong E_b^{(X)}(v_X)$]. Since $\partial_\mu E_{v_X}^{(X)}$ increases monotonically with $|E_b|$, throughout the region of a state levels, a search for variation of μ will be most sensitive when using nearly degenerate levels lying as close as possible to the a state minimum.

We experimentally locate deeply bound $a\,^3\Sigma_u^+$ levels, using two-color photoassociation (PA) spectroscopy [12,13]. A sample of ultracold ($T \approx 100\ \mu$K) Cs atoms is optically pumped into the $6s_{1/2}F = m_F = 4$ state. A PA laser excites the atoms into a bound state [14] of the Cs_2 $(2)0_g^-$ potential (dissociating to the $6s_{1/2} + 6p_{3/2}$ asymp-

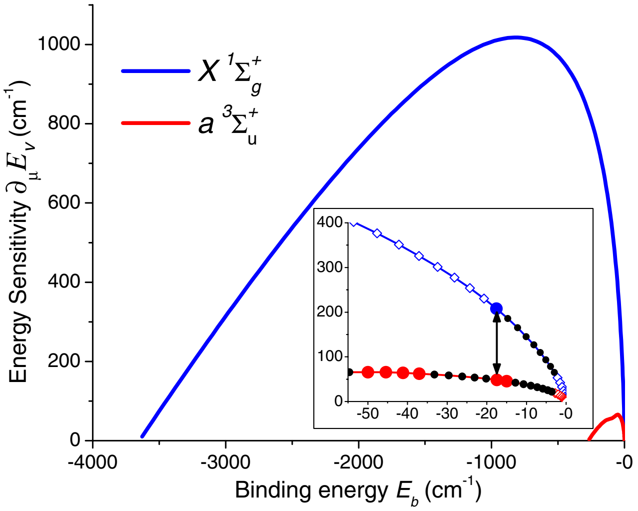

FIG. 1 (color online). Energy sensitivity vs binding energy, for the $X\,^1\Sigma_g^+$ and $a\,^3\Sigma_u^+$ states of Cs_2. Inset: a zoom into the region discussed here. Colored circles are levels observed in this work; open diamonds are levels from previous data; small black dots are predictions from our fitted potentials. The arrow indicates the degeneracy described in the text.

tote). This state decays to a manifold of $a\,^3\Sigma_u^+$ vibrational levels, which are ionized by a pulsed laser. A probe laser is applied to search for resonances between the desired $a\,^3\Sigma_u^+$ levels and the $(2)0_g^-$ level excited by the PA laser. On such a resonance, the probe can shift the excited state off resonance with the PA laser and decrease the rate of molecule formation. We scan the probe laser frequency and look for resonant dips in the ion signal. The frequencies of the resonant probe and PA lasers yield E_b for the $a\,^3\Sigma_u^+$ level. We give E_b relative to the hyperfine (HF) barycenter, located 8.04 GHz below the $6s_{1/2}F = 4 + 6s_{1/2}F = 4$ asymptote. Use of PA levels in the pure long-range well of the $(2)0_g^-$ state enables access to deeply bound $a\,^3\Sigma_u^+$ levels, because of favorable Franck-Condon factors [10,11].

Each ground-state vibrational level has considerable substructure. We write a and X states in the basis $|(S, I)f, \ell, \mathcal{F}\rangle$, where I is the total spin of the pair of Cs nuclei; S is the total electron spin; $\mathbf{f} \equiv \mathbf{S} + \mathbf{I}$; ℓ is the rotational angular momentum; and $\boldsymbol{\mathcal{F}} \equiv \mathbf{f} + \boldsymbol{\ell}$. For the $a\,^3\Sigma_u^+$ states of interest, $S = 1$ and the HF interaction dominates the sublevel structure, splitting levels with different f according to $E_{\mathrm{HF}} = \frac{A}{4}[f(f+1) - S(S+1) - I(I+1)]$, where $A \cong 2.3$ GHz is the Cs $6s_{1/2}$ HF constant. For each value of f, there is a manifold of closely spaced states: those with different ℓ are split by the rotational energy $B_v\ell(\ell+1)$ ($B_v \approx 0.1$ GHz), and states with different (same) $\mathcal{F}$ are split (mixed) by a 2nd-order spin-orbit (SO2) interaction of comparable strength [15]. For most states we consider, the eigenstate is well approximated by a basis state. However, levels of the $X\,^1\Sigma_g^+$ state ($S = 0$) can mix with nearby $a\,^3\Sigma_u^+$ levels via HF interactions.

Pairs of the spin-polarized Cs atoms have $f = m_f = 8$, and only pairs with $\ell = 0$ (s-wave scattering state) are excited by the PA laser; hence initially $\mathcal{F} = m_{\mathcal{F}} = 8$. The Hund's case (c) $(2)0_g^-$ state has resolved levels of definite J', where $\boldsymbol{J}' = \boldsymbol{\ell}' + \mathbf{S}' + \mathbf{L}'$, $L' = 1$ is the electron orbital angular momentum, and $S' = 1$. The PA laser is tuned to excite $J' = 2$ levels, which are a mixture of $\ell' = 0, 2, 4$ [16]. The PA laser has σ^+ polarization, so electric dipole ($E1$) selection rules ensure $\mathcal{F}' = m'_{\mathcal{F}} = 9$. Since $\boldsymbol{\mathcal{F}}' = \mathbf{J}' + \mathbf{I}'$ and $\mathcal{F}' = 9$, only $I' = 7$ is excited. From $E1$ selection rules for the probe transition, only $a\,^3\Sigma_u^+$ states with $I = 7$, $\ell = 0, 2, 4$, and $\mathcal{F} = m_{\mathcal{F}} = 10$ ($\mathcal{F} = 8, 9, 10$; $m_{\mathcal{F}} = 8$) are seen with polarization σ^- (σ^+).

We observe multiple sublevels for several $a\,^3\Sigma_u^+$ vibrational levels with $|E_b(v)| \cong 400$–1500 GHz. The level positions and line strengths qualitatively agree with predictions based on the $a\,^3\Sigma_u^+$ long-range potential [13], which yielded approximate values for $E_b(v)$ and B_v. These predictions guided an initial assignment of quantum numbers to the observed states. As expected, sublevels for each v are clustered according to their f value, and for each f we typically observe several sublevels with different values of ℓ and $\mathcal{F}$. We perform a fit of the a state potential to both our data and that of [13], taking into account HF-induced mixing between the a and X states and also the SO2 interaction. For the X state, we adjusted the long-range part of the potential given in [17] to make it consistent with the exchange and dispersion terms obtained from fitting a state levels. The quality of the fit to this data suggests a good understanding of the level assignments and interaction strengths: the r.m.s. deviation was $\cong 90$ MHz for HF-, rotational-, or SO2-induced sublevel splittings, and $\cong 200$ MHz for absolute binding energies, versus typical experimental uncertainties of $\cong 30$ MHz and $\cong 400$ MHz, respectively. Details of the data and the fit will be given elsewhere. For now, we focus on a specific feature in the data.

Figure 2 shows data corresponding to levels in the $f = 7$ manifold of states for two adjacent vibrational levels of the $a\,^3\Sigma_u^+$ state, with $|E_b(v)| \cong 523$ and 449 GHz, tentatively assigned from our fits as $v_a = 37$ and 38, respectively. Since only a single $\mathcal{F} = 10$ level in the $f = 7$ manifold satisfies all selection rules, we expect only a single line with σ^- probe polarization. This is indeed observed for the $v_a = 38$ state, and we hence assign this level as $|(1, 7)7, 4, 10\rangle$. In the same spectral region, using a σ^+ probe, we observe two nearby lines of comparable strength that we assign to states $|(1, 7)7, 4, 8\rangle$ and $|(1, 7)7, 4, 9\rangle$. In the $v_a = 37$ level, and again with a σ^+ probe, we observe a very similar spectrum: two lines of similar strength, with a similar splitting, and separated by nearly the same amount from sublevels with $f = 6, 8$ in the same vibrational level. However, in this $v_a = 37$ level, with the σ^- probe we observe *two* lines in the $f = 7$ manifold, each of similar strength but roughly 2 times weaker than the single analogous line in the $v_a = 38$ level. The only plausible mechanism to explain this additional line is that the single accessible $a\,^3\Sigma_u^+$ level $|(1, 7)7, 4, 10\rangle$ has mixed strongly with a nearby $X\,^1\Sigma_g^+$ level *only in this vibrational state*, due to the combined HF and SO2 interactions. Based on our fits, we assign this perturbing level as the $X\,^1\Sigma_g^+(v_X = 138)$ state $|(0, 6)6, 6, 10\rangle$.

The near degeneracy between the $v_a = 37$ and $v_X = 138$ levels provides the best presently known example of a system with all the favorable properties discussed above. A sensitive search for variation of μ could be accomplished by measuring the small energy splitting between any of several sublevels in the $v_a = 37/v_X = 138$ manifold. Ultracold Cs_2 molecules can be produced in any of the $a\,^3\Sigma_u^+$ levels observed here, either by PA or via Feshbach resonance [9] followed by stimulated pumping to the desired level [18,19]. By launching the molecules (or precursor atoms) in a manner like that used for atomic fountain clocks, a linewidth $\Gamma \approx 1$ Hz could be achieved [20]. A microwave field could drive transitions between sublevels of the $a\,^3\Sigma_u^+(v_a = 37)$ and $X\,^1\Sigma_g^+(v_X = 138)$ states (even though these transitions are nominally forbidden). The strong HF mixing reduces the value of $\partial_\mu E_v$ for

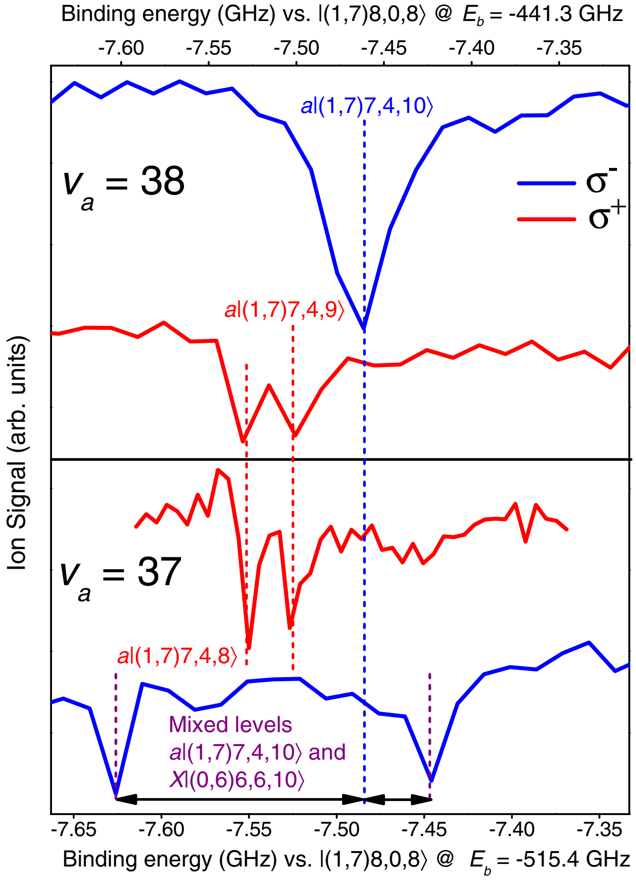

FIG. 2 (color online). Data indicating a degeneracy between the deeply bound $a\,^3\Sigma_u^+(v_a = 37)$ and $X\,^1\Sigma_g^+(v_X = 138)$ levels in Cs_2s. Ion signals are plotted vs probe laser frequency (relative to the line from the $a|(1,7)8,0,8\rangle$ state in the same vibrational level), for two adjacent vibrational levels tentatively assigned as $v_a = 38, 37$ (upper and lower panels, respectively). The label $\sigma^\pm$ refers to the polarization of the probe laser. Frequency scales are slightly offset (by ≅ 20 MHz) to align the $\mathcal{F} = 8, 9$ spectral lines, and hence to emphasize the similarity between the two σ^+ spectra. The dashed vertical lines are meant to guide the eye in comparing the relative line positions.

the directly observed $X|(0,6)6,6,10\rangle$ sublevel; however, from our data and fits we can accurately predict the position of other nearby, unobserved X state sublevels for use in the proposed experiment. For example, a magnetic dipole transition can be driven between the observed level $a|(1,7)6,4,10\rangle$ and $X|(0,6)6,4,10\rangle$, at $\Omega \cong 6.3$ GHz, with transition amplitude $\mathcal{A} \approx 0.1\mu_B$ induced by HF mixing of a and X (μ_B is the Bohr magneton). Alternatively, an $E1$ transition can be driven between the observed level $a|(1,7)8,2,10\rangle$ and $X|(0,7)7,3,10\rangle$ at $\Omega \cong 9.8$ GHz, with $\mathcal{A} \approx 1.5 \times 10^{-4} ea_0 \approx 0.04\mu_B$ induced by spin-orbit effects (e is the electron charge and a_0 is the Bohr radius).

To estimate the absolute sensitivity, we make a plausible assumption of one measurement every 2 sec with $S = 100$ (versus $S \cong 1000$ every 1.3 sec for the atomic fountains in [20]); this yields $\delta\Omega \approx 5 \times 10^{-5}$ Hz in 1 day of integration. From Fig. 1, $\partial_\mu \Omega \cong 5 \times 10^{12}$ Hz for transitions of this type. Hence, $\delta(\Delta\mu/\mu) \approx 10^{-17}$ could be achieved in ≈1 day. This requires only $\delta\Omega/\Omega \approx 10^{-14}$, i.e., over 10 times less accuracy than the best atomic clocks (see, e.g., [20]). Our fits also predict near degeneracies at energies where $\partial_\mu E_v$ is considerably larger, but these await further data for confirmation.

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Note added.—Recently, we learned of two groups exploring similar ideas in other systems [21].

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