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 spatial or temporal variation of the electron-to-proton mass ratio $\mu \equiv m_e/m_p$. We consider a nearly-degenerate pair of molecular vibrational levels, where each state is associated with a different electronic potential. The change in the splitting between such levels, with respect to a change in $\mu$, can be large both on an absolute scale and relative to the splitting. We demonstrate the existence of such pairs of levels in Cs$_2$. The narrow spectral lines achievable with ultracold Cs$_2$ in these long-lived levels make this system promising for future searches for small variations in $\mu$.

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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]. To date, most attention has focused on possible variation of the fine structure constant $\alpha$. However, variations in $\alpha$ are no more likely than in any other fundamental dimensionless parameter. In fact, it has been argued that within the context of grand unified theories, variation in the electron-to-proton mass ratio $\mu \equiv m_e/m_p$ should be larger than the variation in $\alpha$ by a factor of $\sim 30$ [2]. As a result, study of $\mu$ is a potentially more sensitive method to observe any variation of constants.

The most sensitive tests for variation in $\mu$ have come from examining molecular spectra from cosmologically distant sources, at redshifts corresponding to $\sim 10^{10}$ years ago [2]. 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 $\mu$. 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 $\mu$ with high sensitivity. We show that the energy of molecular vibrational levels can be highly sensitive to changes in $\mu$. In addition, pairs of closely-spaced levels can be used to enhance the sensitivity relative to the level splitting. We show spectroscopic data verifying such a near-degeneracy in the ground vibrionic levels of Cs$_2$. We argue that the splitting between pairs of levels in Cs$_2$ could be measured precisely 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 $\Omega$ with respect to a fractional change $\Delta \mu/\mu$: $\partial_{\mu}\Omega \equiv \delta \Omega / \partial (\ln \mu)$. (\(\hbar = c = 1\) throughout.) $\Omega$ can be measured with statistical uncertainty $\delta\Omega = \Gamma/S$, where $\Gamma$ 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 for any such measurement. However, the relative change of the splitting, $\partial_{\mu} \Omega / \Omega$, is also of importance, for two reasons. First, since ultimately $\Omega$ must be measured with respect to some reference clock (with fractional uncertainty $\delta \Omega_c / \Omega_c$), it is impossible to determine $\Omega$ to better than $\delta \Omega_{\min} = \Omega(\delta \Omega_c / \Omega_c)$. In addition, many systematic effects are proportional to $\Omega$ (e.g. Doppler shifts). Hence, $\partial_{\mu} \Omega / \Omega$ provides an important secondary figure of merit.

We analyze the shifts in molecular energy levels when $\mu$ changes, with the assumption that both $m_e$ and $\alpha$ remain constant. In this case, a change in $\mu$ corresponds to a variation of $m_p$; in addition, molecular electronic potentials are independent of $\mu$, since such potentials depend parametrically only on the Rydberg energy $Ry = m_e \alpha^2 / 2$. (The assumption of constant $\alpha$ and $m_e$ is equivalent to using a reference clock based on optical atomic transitions, which also depend parametrically only on $Ry$ and $\alpha$.) We approximate the vibrational energy levels $E_v$ via the WKB quantization condition:

$$\int_{R_i}^{R_o} \sqrt{2M(E_v - V(R))} dR = (v + \frac{1}{2})\pi,$$  \hspace{1cm} (1)

The change in the splitting between such levels, with respect to a change in $\mu$, can be large both on an absolute scale and relative to the splitting. We demonstrate the existence of such pairs of levels in Cs$_2$. The narrow spectral lines achievable with ultracold Cs$_2$ in these long-lived levels make this system promising for future searches for small variations in $\mu$. We show spectroscopic data verifying such a near-degeneracy in the ground vibrionic levels of Cs$_2$. We argue that the splitting between pairs of levels in Cs$_2$ could be measured precisely 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 $\Omega$ with respect to a fractional change $\Delta \mu/\mu$: $\partial_{\mu}\Omega \equiv \delta \Omega / \partial (\ln \mu)$. (\(\hbar = c = 1\) throughout.) $\Omega$ can be measured with statistical uncertainty $\delta\Omega = \Gamma/S$, where $\Gamma$ 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 for any such measurement. However, the relative change of the splitting, $\partial_{\mu} \Omega / \Omega$, is also of importance, for two reasons. First, since ultimately $\Omega$ must be measured with respect to some reference clock (with fractional uncertainty $\delta \Omega_c / \Omega_c$), it is impossible to determine $\Omega$ to better than $\delta \Omega_{\min} = \Omega(\delta \Omega_c / \Omega_c)$. In addition, many systematic effects are proportional to $\Omega$ (e.g. Doppler shifts). Hence, $\partial_{\mu} \Omega / \Omega$ provides an important secondary figure of merit.

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$$\int_{R_i}^{R_o} \sqrt{2M(E_v - V(R))} dR = (v + \frac{1}{2})\pi,$$  \hspace{1cm} (1)
where $R$ is the internuclear distance, $V(R)$ is the potential with minimum value 0, $R_{\mu}(R_{\nu})$ is the classical inner (outer) turning point of $V(R)$ at energy $E_{\mu}$, and $M \propto m_{\nu}$ is the reduced mass of the nuclei in the molecule. Varying Eq. (1) with respect to both $\mu$ and $v$, one obtains for the energy sensitivity $\partial_{\mu} E_{\nu}$:

$$\partial_{\mu} E_{\nu} \equiv \frac{\partial E_{\nu}}{\partial (\ln \mu)} = \frac{(v + \frac{1}{2})}{2 \rho(E_{\nu})}, \quad (2)$$

where $\rho(E_{\nu}) = (\partial E_{\nu}/\partial v)^{-1} \approx (E_{\nu} - E_{\nu - 1})^{-1}$ is the density of states at energy $E_{\nu}$ [4]. Near its minimum, a typical potential is harmonic, with $E_{\nu} = (v + \frac{1}{2})\omega$ and $\rho(E_{\nu}) = \omega^{-1}$ ($\omega$ is the classical oscillator frequency). Hence, for the harmonic part of the potential, $\partial_{\mu} E_{\nu} = (v + \frac{1}{2})\omega/2 = E_{\nu}/2$ has a $\sim v$-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 $\partial_{\mu} \Omega$.

For sufficiently large values of $v$, real molecular potentials are not harmonic. For highest values of $v$, $E_{\nu}$ approaches the dissociation limit $D$, and the density of states $\rho(E_{\nu})$ becomes large. Hence, the value of $\partial_{\mu} E_{\nu}$ again becomes small for the highest levels in any potential. Therefore, at some intermediate value of $v$, $\partial_{\mu} E_{\nu}$ is maximized. We verified this behavior both for a generic (Morse) potential with analytic expressions for $E_{\nu}$, and for the experimentally determined $X^{3}Sigma_{g}^{+}$ potential of Cs$_{2}$ (see below). In both cases, the maximum value of $\partial_{\mu} E_{\nu}$ is obtained for levels with $E_{\nu}^{(max)} \approx 3D/4$, and there the energy sensitivity is only slightly diminished from its expected value in the harmonic approximation: $\partial_{\mu} E_{\nu}^{(max)} \approx (2/3)E_{\nu}^{(max)}/2$. Note that a recent paper [4] discussed the prop for detecting variations in $\mu$ 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 $\partial_{\mu} E_{\nu}$ is small. The scheme discussed here uses the much larger energy sensitivity 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 $E_{1} = E^{(X)}_{v_{X}}$ can be quite near in energy to a lower vibrational level of $Y$ ($v_{Y} \ll v_{X}$), with energy $E_{2} = T_{Y} + E^{(Y)}_{v_{Y}}$. The energy difference between such a pair of levels is small ($\Omega = |E_{1} - E_{2}| \ll E^{(X)}_{v_{X}}$), but can retain a large sensitivity to changes in $\mu$, 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 $X^{3}Sigma_{g}^{+}$ ground state, and the shallower $a^{3}Sigma_{u}^{+}$ state, each of which dissociates to a pair of ground-state Cs atoms [5]. 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. [6] 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) [7], 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 $\Gamma$. Finally, it has been predicted that deeply-bound levels of the $a^{3}Sigma_{u}^{+}$ state—which lie near $E_{\nu}^{(max)}$ for the $X^{3}Sigma_{g}^{+}$ state—can be efficiently populated [9, 10].

We explicitly calculate $\partial_{\mu} E_{\nu}$ for all vibrational levels in the $X$ and $a$ states of Cs$_{2}$, using the fitted potentials described below and numerical solutions for $E_{\nu}$ with slightly different values of $M$. (Similar results were obtained very simply for all but the highest-$v$ levels of the $X$ state, using a Dunham expansion for $E_{\nu}$ [8, 10].) A plot of $\partial_{\mu} E_{\nu}$ versus binding energy ($E_{\nu}(v) \equiv E_{\nu} - D$) is shown for both potentials in Fig. [1]. The behavior throughout is as expected from Eq. [2]. Note that indeed, as expected from the previous discussion, $\partial_{\mu} E_{v_{X}}^{(a)} \ll \partial_{\mu} E_{v_{X}}^{(X)}$ for close-lying $X$ and $a$ state levels (such that $E_{v_{X}}^{(a)}(v_{a}) \approx E_{v_{X}}^{(X)}(v_{X})$). In addition, $\partial_{\mu} E_{v_{X}}^{(X)}$ increases monotonically with $|E_{\nu}|$, throughout the region of a state levels. Hence, a search for variation of $\mu$ will be most sensitive when using nearly-degenerate levels lying as close as possible to the $a$ state minimum.

**FIG. 1:** Energy sensitivity vs. binding energy, for the $X^{3}Sigma_{g}^{+}$ 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.
We experimentally determine the positions of deeply bound $a^3\Sigma_g^+$ levels, using two-color photoassociation (PA) spectroscopy \cite{11, 12}. A sample of ultracold ($T \sim 100$ μK) Cs atoms is cooled and confined in a dark SPOT magneto-optic trap. After applying a uniform magnetic field, the atoms are optically pumped into the $6s_{1/2}F = m_F = 4$ state. Next a CW laser (the PA laser) excites the atoms into a bound state \cite{14} of the Cs$_2$ (2)0$_g^+$ potential (dissociating to the $6s_{1/2} + 6p_{3/2}$ asymptote). This excited state decays to a manifold of $a^3\Sigma_u^+$ vibrational levels, which are ionized by a pulsed laser. A second CW (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 beam can shift the excited state off resonance with the PA laser and decrease the rate of molecule formation. We scan the probe laser frequency while monitoring the ion yield, and look for resonant dips in the signal. The difference between the frequencies of the resonant probe and PA lasers gives the difference between the excited state off resonance with the PA laser and deexcitation energy. The only plausible mechanism to explain this additional energy in this vibrational state is two-photon resonance \cite{8} followed by stimulated pumping to the desired level \cite{18, 19}. By launching the molecules (or pre-
Alternatively, an E1 transition can be driven between mixing of $M$ with transition amplitude $a$ the line from the ion. Ion signals are plotted vs. probe laser frequency (relative to bound level), for two adjacent vibrational levels tentatively assigned as $v_a = 38, 37$ (upper and lower panels, respectively). The label $\sigma^+$ refers to the polarization of the probe laser. Frequency scales are slightly offset (by $\sim 20$ MHz) to align the $F = 8, 9$ spectral lines, and hence to emphasize the similarity between the two $\sigma^+$ spectra. The dashed vertical lines are meant to guide the eye in comparing the relative line positions.

FIG. 2: Data indicating a degeneracy between the deeply bound $a^3\Sigma^+_u (v_a = 37)$ and $X^1\Sigma^+_g (\epsilon_X = 138)$ levels in Cs$_2$. To estimate the absolute sensitivity, we conservatively assume one measurement every 2 sec with $S = 100$ vs. $S \sim 1000$ every $\sim 1.3$ sec for the atomic fonts in [20], yielding $\delta \Omega \sim 5 \times 10^{-5}$ Hz in one day of integration. From Fig. [1] $\delta \Omega \sim 5 \times 10^{12}$ Hz for transitions of this type. Hence, $\delta (\Delta \mu / \mu) \sim 10^{-17}$ could be achieved in $\sim 1$ day. This requires only $\delta \Omega / \Omega \sim 10^{-14}$, i.e. over ten 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. Note: during preparation of this manuscript, we learned of two papers exploring similar ideas in other systems [21].

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