Enhanced Sensitivity to the Time Variation of the Fine-Structure Constant and $m_p/m_e$ in Diatomic Molecules

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Sensitivity to temporal variation of the fundamental constants may be strongly enhanced in transitions between narrow close levels of different nature. This enhancement may be realized in a large number of molecules due to cancellation between the ground state fine-structure $\omega_f$ and vibrational interval $\omega_v$ [$\omega = \omega_f - n \omega_v = 0$, $\delta \omega \sim K(2\delta \alpha/\alpha + 0.5\delta \mu/\mu)$, $K \gg 1$, $\mu = m_p/m_e$]. The intervals between the levels are conveniently located in microwave frequency range and the level widths are very small. Required accuracy of the shift measurements is about 0.01–1 Hz. As examples, we consider molecules Cl$^+$, CuS, InC, SiBr, and HIF$^+$.

Introduction.—Theories unifying gravity with other interactions suggest temporal and spatial variations of the fundamental “constants” in the expanding Universe. The spatial variation can explain fine tuning of the gravitational potential which allows humans (and any life) to appear. We appeared in the space-time area of the Universe where the values of the fundamental constants are consistent with our existence. Another possible effect is dependence of the fundamental constants on the gravitational potential which leads to the violation of local position invariance. The strongest limits [1,2] are obtained from the measurements of dependence of atomic frequencies on the distance from the Sun (this distance varies due to the ellipticity of the Earth’s orbit).

There are hints for the variation of the fine-structure constant $\alpha = e^2/\hbar c$, strength constant of the strong interaction, and mass in Big Bang nucleosynthesis from quasar absorption spectra and Oklo natural nuclear reactor data (see, e.g., Refs. [3–9]). However, a majority of publications report only limits on possible variations (see, e.g., reviews in Refs. [10–12]).

A very promising method to search for the variation consists in the comparison of different atomic clocks (see recent measurements in Refs. [1,13–19]). An enhancement of the relative variation effects happens in transitions between very close atomic [20–24], molecular [25–28], and nuclear [29,30] energy levels.

In this Letter we would like to note that very close narrow levels of a different nature exist in diatomic molecules due to the cancellation between the fine-structure and vibrational intervals in the electronic ground state. The intervals between the levels are conveniently located in the microwave frequency range and the level widths are very small, typically $\sim 10^{-3}$ Hz. The relative enhancement of the variation effect $K$ can exceed 5 orders of magnitude.

Effects of the variation and selection of molecules.—The fine-structure interval $\omega_f$ rapidly increases with increase of nuclear charge $Z$:

$$\omega_f \sim Z^2 \alpha^2 E_H,$$

where $E_H = m_e e^4/\hbar$ is the atomic energy unit hartree ($E_H = 2$ Ry = 219475 cm$^{-1}$). On the contrary, the vibration energy quantum decreases with the atomic mass:

$$\omega_v \sim M_r^{-1/2} \mu^{-1/2} E_H,$$

where $\mu = m_p/m_e$, $m_p$ is the proton mass, $m_e$ is the electron mass, and the reduced mass for the molecular vibration is $M_r m_p$. Therefore, we obtain equation for the lines $Z = Z(M_r, n)$ where we have cancellation between the fine-structure and vibrational energy:

$$\omega = \omega_f - n \omega_v = 0, \quad n = 1, 2, \ldots$$

Using Eqs. (1)–(3) it is easy to find dependence of the transition frequency on the fundamental constants:

$$\frac{\delta \omega}{\omega} = \frac{1}{\omega} \left( 2 \frac{\delta \alpha}{\alpha} + \frac{n}{2} \frac{\delta \mu}{\mu} \right) \approx K \left( 2 \frac{\delta \alpha}{\alpha} + \frac{1}{2} \frac{\delta \mu}{\mu} \right).$$

where the enhancement factor $K = \omega/\omega_f$ determines the relative frequency shift for the given change of fundamental constants. Large values of factor $K$ hint at potentially favorable cases for making experiments, because it is usually preferable to have larger relative shifts. However, there is no strict rule that larger $K$ is always better. In some cases, such as very close levels, this factor may become irrelevant. Thus, it is also important to consider the absolute values of the shifts and compare them to the linewidths of the corresponding transitions. That will be done in the following sections.

Because the number of molecules is finite we cannot have $\omega = 0$ exactly. However, a large number of molecules have $\omega/\omega_f \ll 1$ and $|K| \gg 1$. Moreover, an additional
“fine tuning” may be achieved by selection of isotopes and rotational, Ω-doublet, and hyperfine components. Therefore, we have two large manifolds, the first one is built on the electron fine-structure excited state and the second one is built on the vibrational excited state. If these manifolds overlap one may select two or more transitions with different signs of $\omega$. In this case expected sign of the $|\omega|$ variation must be different (since the variation $\delta \omega$ has the same sign) and one can eliminate some systematic effects [31].

Note that $\omega$ is sensitive to the variation of two most important dimensionless parameters of the Standard Model. The first parameter, $\alpha$, determines the strength of the electroweak interactions. The second parameter, $\mu = m_p/m_e$, is related to the weak (mass) scale and strong interaction scale. Indeed, the electron mass is proportional to the vacuum expectation value of the Higgs field (the weak scale) which also determines masses of all fundamental particles. The proton mass is proportional to another fundamental parameter, the quantum chromodynamics scale $\Lambda_{QCD} (m_p = 3\Lambda_{QCD})$. 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 $\delta (\Lambda_{QCD}/m_e)/(\Lambda_{QCD}/m_p) = \delta \mu/\mu$.

In Table I we present the list of molecules from Ref. [32], where the ground state is split in two fine-structure levels and Eq. (3) is approximately fulfilled. The molecules Cl$^+$ and SiBr are particularly interesting. For both of them the frequency $\omega$ defined by (3) is of the order of 1 cm$^{-1}$ and comparable to the rotational constant $B$. That means that $\omega$ can be reduced further by the proper choice of isotopes, rotational quantum number $J$, and hyperfine components, so that we can expect $k \sim 10^3$–$10^5$. New dedicated measurements are needed to determined exact values of the transition frequencies and find the best transitions. However, it is easy to find necessary accuracy of the frequency shift measurements. According to Eq. (4) the expected frequency shift is

$$\delta \omega = 2 \omega_f \left( \frac{\delta \alpha}{\alpha} + \frac{1}{4} \frac{\delta \mu}{\mu} \right).$$

Assuming $\delta \alpha/\alpha \sim 10^{-15}$ and $\omega_f \sim 500$ cm$^{-1}$, we obtain $\delta \omega \sim 10^{-12}$ cm$^{-1} \sim 3 \times 10^2$ Hz. In order to obtain similar sensitivity comparing hyperfine transition frequencies for Cs and Rb one has to measure the shift $\sim 10^{-5}$ Hz.

Table I. Diatomic molecules with quasidegeneracy between the ground state vibrational and fine structures. All frequencies are in cm$^{-1}$. The data are taken from Ref. [32].

| Molecule | Electronic states | $\omega_f$ | $\omega_v$ |
|----------|------------------|------------|------------|
| Cl$^+$   | $^2\Pi_{3/2}$  | 645        | 645.6      |
| CuS      | $^2\Pi$          | 433.4      | 415        |
| IrC      | $^2\Delta_{1/2}$| 3200       | 1060       |
| SiBr     | $^2\Pi_{1/2}$   | 423.1      | 424.3      |

Molecular ion HfF$^+$.—The ion HfF$^+$ and other similar ions are considered by Cornell’s group in JILA for the experiment to search for the electric dipole moment (EDM) of the electron [33,34]. This experiment is supposed to trap the ions in the quadrupole radio frequency trap to achieve long coherence times. Similar experimental setup can be used to study possible time variation of fundamental constants. Recent calculation by Petrov et al. [35] suggests that the ground state of this ion is $^1\Sigma^+$ and the first excited state $^3\Delta_1$ lies only 1633 cm$^{-1}$ higher. Calculated vibrational frequencies for these two states are 790 and 746 cm$^{-1}$, respectively. For these parameters the vibrational level $n = 3$ of the ground state is only 10 cm$^{-1}$ apart from the $n = 1$ level of the state $^3\Delta_1$. Thus, instead of Eq. (3) we now have:

$$\omega = \omega_{el} + \frac{3}{2} \omega_v^{(1)} - \frac{7}{2} \omega_v^{(0)} = 0,$$

where superscripts 0 and 1 correspond to the ground and excited electronic states. Electronic transition $\omega_{el}$ is not a fine-structure transition and Eq. (1) is not applicable. Instead we can write:

$$\omega_{el} = \omega_{el,0} + qx,$$

where $\omega_{el,0}$ corresponds to the value of the fine-structure constant $\alpha = \alpha_0$ and $x = \alpha^2/\alpha_0^2 - 1$. The factor $q$ has been introduced in Refs. [20–22,36] and it appears due to the relativistic corrections to electronic energy. In order to calculate this factor for HfF$^+$ ion one needs to perform relativistic molecular calculation for several values of $\alpha$, which is far beyond the scope of this Letter. However, it is possible to make an order of magnitude estimate using atomic calculation for the Yb$^+$ ion [21]. According to [35] $^1\Sigma^+ - ^3\Delta_1$ transition to a first approximation corresponds to the 6s–5d transition in the hafnium ion. It is well known that valence $s$ and $d$ orbitals of heavy atoms have very different dependence on $\alpha$: while the binding energy of $s$ electrons grows with $\alpha$, the binding energy of $d$ electrons decreases [20–22,36]. For the same transition in the Yb$^+$ ion Ref. [21] gives $q_{sd} = 10000$ cm$^{-1}$. Using this value as an estimate, we can write by analogy with Eq. (4):

$$\frac{\delta \omega}{\omega} = \left( \frac{2q}{\omega} \frac{\delta \alpha}{\alpha} + \omega_{el} \frac{\delta \mu}{\mu} \right) \approx \left( 2000 \frac{\delta \alpha}{\alpha} + 80 \frac{\delta \mu}{\mu} \right).$$

Assuming $\delta \alpha/\alpha \sim 10^{-15}$ we obtain $\delta \omega \sim 0.6$ Hz.

Estimate of the natural linewidths of the quasidegenerate states.—As we mentioned above it is important to compare frequency shifts caused by time variation of constants to the linewidths of corresponding transitions. First let us estimate natural linewidth $\Gamma_\nu$ of the vibrational
level $n$:

$$
\Gamma_n = \frac{4\omega_0^3}{3hc^3}|\langle n|D|n-1\rangle|^2. \quad (10)
$$

To estimate the dipole matrix element we can write:

$$
\hat{D} = \frac{\partial D(R)}{\partial R} \bigg|_{R=R_0} (R-R_0) \sim \frac{D_0}{R_0} (R-R_0), \quad (11)
$$

where $D_0$ is the dipole moment of the molecule for equilibrium internuclear distance $R_0$. Using standard expression for the harmonic oscillator, $\langle n|x|n-1\rangle = (hn/2m\omega)^{1/2}$, we get:

$$
\Gamma_n = \frac{2\omega_0^2 D_0^2 n}{3c^3 M m_p R_0^6}. \quad (12)
$$

where $M, m_p$ is the reduced mass of the nuclei. For the homonuclear molecule Cl$_2^+$ $D_0 = 0$ and expression (12) turns to zero. For SiBr molecule it gives $\Gamma_1 \sim 10^{-2}$ Hz, where we assumed $D_0/R_0 \sim 0.1 e^2$.

Now let us estimate the width $\Gamma_f$ of the upper state of the fine-structure doublet $^2\Pi_{1/2,3/2}$. By analogy with (10) we can write:

$$
\Gamma_f = \frac{4\omega_0^3}{3hc^3}|\langle ^2\Pi_{3/2}|D_1|^2\Pi_{1/2}\rangle|^2. \quad (13)
$$

The dipole matrix element in this expression is written in the molecular rest frame and we have summed over final rotational states. This matrix element corresponds to the spin-flip and turns to zero in the nonrelativistic approximation. Spin-orbit interaction mixes $^2\Pi_{1/2}$ and $^2\Sigma_{1/2}$ states:

$$
| ^2\Pi_{1/2} \rangle \rightarrow | ^2\Pi_{1/2} \rangle + \xi | ^2\Sigma_{1/2} \rangle, \quad (14)
$$

and the matrix element in (13) becomes [37]:

$$
\langle ^2\Pi_{3/2}|D_1|^2\Pi_{1/2}\rangle = \xi \langle ^2\Pi|D_1|^2\Sigma \rangle \sim \frac{\alpha^2 Z^2 e^3}{10(E_{\Pi} - E_{\Sigma})}, \quad (15)
$$

where $E_{\Sigma}$ is the energy of the lowest $\Sigma$ state. Substituting (15) into (13) and using energies from Ref. [32] we get the following estimate for the molecules Cl$_2^+$ and SiBr:

$$
\Gamma_f \sim 10^{-2} \text{ Hz}. \quad (16)
$$

Here we took into account that unpaired electron in SiBr molecule is predominantly on Si (Z = 14) rather then on Br (Z = 35). Because of that the fine splitting in SiBr is smaller than that of Cl$_2^+$, where Z = 17 (see Table I).

We conclude that natural linewidths of the molecular levels considered here are of the order of $10^{-2}$ Hz. This can be compared, for example, to the natural linewidth 12 Hz of the level $^2D_{5/2}$ of Hg$^+$ ion, which was used in Ref. [1].

Conclusions.—We have demonstrated that for such molecules as Cl$_2^+$ and SiBr there are narrow levels of a different nature separated by the intervals $\leq 1 \text{ cm}^{-1}$. The linewidths are on the order of $10^{-2}$ Hz. This is comparable to the accuracy, which is necessary to reach the sensitivity $\delta \alpha/\alpha \sim 10^{-15}$ of the best modern laboratory tests. In the high precision frequency measurements the achieved accuracy is typically a few orders of magnitude higher than the linewidth. Therefore, molecular experiments proposed here look very promising.

Even higher sensitivity to the temporal variation of $\alpha$ can be found in HIF$^+$ and similar molecular ions, which are considered for the search of the electron EDM in JILA [33–35]. Transition amplitude between $^3\Delta_1$ and $^1\Sigma_0$ of HIF$^+$ ion is also suppressed. Corresponding width is larger than for Cl$_2^+$ and SiBr because of the larger value of Z and higher frequency $\omega_f$. In Ref. [35] the width of $^3\Delta_1$ state was estimated to be about 2 Hz. This width is also of the same order of magnitude as the expected frequency shift for $\delta \alpha/\alpha \sim 10^{-15}$. At present not much is known about these ions. More spectroscopic and theoretical data is needed to estimate the sensitivity to $\alpha$ variation reliably.

We hope that our present work will stimulate further studies in this direction. An additional advantage here is the possibility of measuring electron EDM and $\alpha$ variation using the same molecule and a similar experimental setup.

The idea of the molecular experiments proposed here is similar to that of the Cs$_2$ experiment, which is currently under way at Yale University [25,26,38]. The main difference is that the electron transition in Cs$_2$ goes between $^3\Sigma_+^0$ and $^1\Sigma_0^-$ and to a first approximation is independent on $\alpha$. On the other hand the sensitivity to $\mu$ is strongly enhanced because for Cs$_2$ the quantum number $n$ in Eq. (3) is $\sim 100$ [25]. Therefore, experiments on Cs$_2$ are primarily sensitive to the time variation of $\mu$, while this proposal allows to study time variation of $\alpha$. Another difference is that for the fine-structure doublets discussed here one can systematically satisfy Eq. (3) for many molecules with properly chosen Z and $M_r$. In the HIF$^+$ ion we have “accidental” quasidegeneracy of electronic levels $^1\Sigma_0^+$ and $^3\Delta_1$ with very different $\xi$ factors. Because of that the radio frequency transition (6) is even more sensitive to $\alpha$ variation than transitions (3). Thus, the experiments discussed here are complementary to the experiments of DeMille’s group at Yale.

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