Λ-doublet spectra of diatomic radicals and their dependence on fundamental constants

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Λ-doublet spectra of light diatomic radicals have high sensitivity to the possible variations in the fine-structure constant α and electron-to-proton mass ratio β. For molecules OH and CH sensitivity is further enhanced because of the J-dependent decoupling of the electron spin from the molecular axis, where J is total angular momentum of the molecule. When Λ-splitting has different signs in two limiting coupling cases a and b, decoupling of the spin leads to the change in sign of the splitting and to the growth of the dimensionless sensitivity coefficients. For example, sensitivity coefficients for the Λ-doublet lines $J=\frac{9}{2}$ of the $\Pi_{1/2}$ state of OH molecule are on the order of 10^3.

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I. INTRODUCTION

At present an intensive search is going on for the possible space and time variations in fundamental constants (FCs). On a short time scale very tight bounds on such variations were obtained in laboratory experiments [1,2]. On the other hand astrophysical observations provide information on the variation in FC on the time scale of the order of 10^{10} years. Here results of Ref. [3] indicate variation in the level of five sigma, $\Delta\alpha/\alpha=(-0.57\pm0.11)\times10^{-5}$. At the same time, Ref. [4] reports no variation, $\Delta\alpha/\alpha=(-0.06\pm0.06)\times10^{-5}$, and Ref. [5] reports variation of the opposite sign, $\Delta\alpha/\alpha=(+0.54\pm0.25)\times10^{-5}$. An intermediate time scale $\sim2\times10^9$ years is tested by the Oklo phenomenon [6,7].

Recently there was much attention in this context to the microwave spectra of molecules. Generally these spectra are sensitive to possible variations in the electron to proton mass ratio $\beta=m_e/m_p$. When fine and hyperfine structures are involved, they also become sensitive to variations of the fine-structure constant α and nuclear g-factor $g_{\rm nuc}$. There were several proposals of microwave experiments with diatomic molecules. Rotational microwave spectra were used numerous times to study time variation in fundamental constants in astrophysics. However, all such lines have same dependence on FC, $\delta\omega_{\rm rot}/\omega_{\rm rot}=\delta\beta/\beta$, so one needs to use reference lines with different dependence on FC. In the microwave band there are several examples of such lines (see Table I).

First, the famous 21 cm hydrogen hyperfine line depends on all three FC, $\delta\omega_{\rm hf}/\omega_{\rm hf}=\delta\mathcal{F}/\mathcal{F}$, $\mathcal{F}=\alpha^2\beta g_{\rm nuc}$ (note that the 21 cm line of hydrogen was used to constrain variation in FC as early as 1956 [13]). Second, the 18 cm Λ-doublet line of OH molecule depends on α and β as follows: $\delta\omega_{\rm OH}/\omega_{\rm OH}=\delta\mathcal{F}/\mathcal{F}$, with $\mathcal{F}=\alpha^{-1.14}\beta^{2.57}$ [14–16]. Third, the 1.2 cm inversion line of ammonia depends only on β, $\delta\omega_{\rm inv}/\omega_{\rm inv}=4.46\delta\beta/\beta$ [17,18]. Finally, the fine-structure far-infrared 158 μm line of C II is sensitive only to α, $\delta\omega_{\rm fs}/\omega_{\rm fs}=2\delta\alpha/\alpha$. All these four reference lines were used in combination with some rotational lines to put strong limits on variation in FC [18–22].

If the hydrogen 21 cm line is used as a reference for 18 cm OH line, the combination of constants, which is constrained, has the form [20]

$$\mathcal{F}=\alpha^{3.14}\beta^{-1.57}g_{\rm nuc}. \tag{1}$$

The tightest limit on the variation in $\mathcal{F}$ was obtained from observations of the absorber at the redshift $z=0.765$ and the $z=0.685$ gravitational lens [20]:

$$\delta\mathcal{F}/\mathcal{F}=(0.44\pm0.36^{\rm stat}\pm1.0^{\rm syst})\times10^{-5}. \tag{2}$$

For OH molecule at least two more Λ-doublet lines were detected from interstellar medium in addition to the lowest 18 cm line, which was used in Ref. [20]. Sensitivity coefficients for these lines were found in Ref. [23]. They appeared to be rather different from those of the lowest Λ-doublet line. Therefore, it is possible to use different Λ-doublet lines of the OH molecule to place a limit on the variation in fundamental constants without using reference lines of other species. This can help to eliminate systematic effect from the different velocity distributions of different species in molecular clouds. Two lowest Λ-doublet lines of CH molecule (9 and 42 cm) were detected in the interstellar medium [11,24]. Recently Henkel and Menten suggested that these lines can be used for astrophysical search of the time variation in fundamental constants [25]. There are also several other light molecules with Λ doubling, where microwave spectra were observed in the interstellar medium. For example, the first extragalactic microwave rotational spectra of NO were observed in [26]. Therefore, we decided to study sensitivities of the Λ-doublet lines to the variation in the fundamental constants in a more systematic way.

Astrophysical studies of variation in fundamental constants require accurate knowledge of the laboratory frequencies. In the microwave band it is not so rare that the accuracy of the astrophysical observations is higher than the accuracy of the respective laboratory measurements. Therefore, some of the recommended "laboratory" frequencies are actually recalculated from astrophysical spectra (see, for example, [11,27]). This method is based on the assumption that different lines from the same distant object have the same redshifts. Thus, the redshift is first determined from one set of lines and then is used to find rest frame frequencies of the other set of observed lines. The logic in these works is opposite to the one used in the search of the variation in FC. In such a search one looks for the difference in the *apparent* redshifts of the lines from the same object and compare these

TABLE I. Quantum numbers and frequencies of microwave lines used for astrophysical studies of possible variation in FC. For Λ transitions of CH and OH molecules only one of the strongest hyperfine components is given. Ammonia inversion transition has rotational structure described by quantum numbers J and K, where K is projection of the angular momentum $\boldsymbol{J}$ on the molecular axis and smaller hyperfine structure described by the total angular momentum quantum number F and intermediate quantum number F_1. Here we present one of the 18 hyperfine components of the inversion line $(J,K)=(1,1)$.

Atom or molecule	λ (cm)	Quantum numbers	Frequency (MHz)	Ref.
H	21	$1s_{1/2}$, $F=0-1$	1420.405751767(1)	[8]
OH	18	$\Pi_{3/2}$, $J=\frac{3}{2}$, $F=2$	1667.358996(4)	[9]
CH	9.0	$\Pi_{1/2}$, $J=\frac{1}{2}$, $F=1$	3335.481(1)	[10]
CH	42	$\Pi_{3/2}$, $J=\frac{3}{2}$, $F=2$	701.677(10)	[11]
CH	4.1	$\Pi_{1/2}$, $J=\frac{3}{2}$, $F=2$	7348.419(1)	[10]
NH_3	1.2	$(J,K)=(1,1)$; $F,F_1=\frac{1}{2},1$	23694.4591(1)	[12]

differences to the sensitivities of respective lines to variation in the constants to get information on constant variation.

Recently the laboratory frequencies of all four hyperfine components of the 18 cm line of OH molecule were measured with a record precision ($<10^{-9}$) [9,28]. Also, the frequencies of all three components of the 9 cm Λ-doublet line $J=\frac{1}{2}$ in CH molecule were recently remeasured in Ref. [10] with the accuracy of 0.1 ppm or better (1 ppm$=10^{-6}$). This opens possibility to study variation in fundamental constants at the level below 1 ppm. Such studies can supplement the limits on β-variation based on the observations of the ammonia inversion line [18,21,29,30] because Λ-doublet lines are sensitive to variation in α and β, while ammonia line is sensitive only to β. Moreover, as we will show below, because of the decoupling of the electron spin from the molecular axis, the sensitivity coefficients here strongly depend on the rotational quantum numbers. Therefore, if more than one line is observed, it may be possible to obtain model independent limits on variation in both constants. Sensitivity to the third constant $g_{\rm nuc}$ is typically much weaker, except for some low-frequency lines where hyperfine contribution to transition frequency becomes significant. If such lines are observed, it is possible to make *full* experiment and constrain variation in *all three constants.*

Additional motivation to the present work comes from rapid progress in laboratory experiments with cold and ultracold molecules. New laboratory techniques can make it possible to use molecular Λ-doublet lines for laboratory tests on variation in FC. The most recent developments in this field are summarized in the review [31].

In this paper we estimate sensitivity coefficients of different Λ-doublet lines to variations in constants α, β, and $g_{\rm nuc}$. The analysis is basically the same for all light molecules in the $^2\Pi_{1/2}$ or $^2\Pi_{3/2}$ states. We include several of them here, for which there are sufficient data in the databases of microwave molecular spectra [32–34]. We use these data to find parameters of the effective spin-rotational Hamiltonian and to calculate sensitivity coefficients.

II. SENSITIVITY COEFFICIENTS

We restrict ourselves to the case of the diatomic radicals in doublet states $^2\Pi_{1/2}$ or $^2\Pi_{3/2}$. Let us define dimensionless sensitivity coefficients to the variation in FC so that

$$\frac{\delta\omega}{\omega}=K_\alpha\frac{\delta\alpha}{\alpha}+K_\beta\frac{\delta\beta}{\beta}+K_g\frac{\delta g_{\rm nuc}}{g_{\rm nuc}}. \tag{3}$$

Dimensionless sensitivity coefficients K_i are most relevant in astrophysics, where lines are Doppler broadened, so $\Gamma\approx\Gamma_D=\omega\times\Delta v/c$, where Δv is velocity variance and c is the speed of light. The redshift of a given line is defined as $z_i=\omega_{{\rm lab},i}/\omega_i-1$. Frequency shift [Eq. (3)] leads to the change in the apparent redshifts of individual lines. The difference in the redshifts of two lines is given by

$$\frac{z_i-z_j}{1+z}=-\Delta K_\alpha\frac{\delta\alpha}{\alpha}-\Delta K_\beta\frac{\delta\beta}{\beta}-\Delta K_g\frac{\delta g_{\rm nuc}}{g_{\rm nuc}}, \tag{4}$$

where z is the average redshift of both lines and $\Delta K_\alpha=K_{\alpha,i}-K_{\alpha,j}$, etc. We can rewrite Eq. (4) in terms of the variation in a single parameter $\mathcal{F}$:

$$\frac{z_i-z_j}{1+z}=-\frac{\delta\mathcal{F}}{\mathcal{F}},\quad \mathcal{F}\equiv\alpha^{\Delta K_\alpha}\beta^{\Delta K_\beta}g_{\rm nuc}^{\Delta K_g}. \tag{5}$$

The typical values of Δv for the extragalactic spectra is on the order of few km/s. This determines the accuracy of the redshift measurements on the order of $\delta z=10^{-5}-10^{-6}$, practically independent of the transition frequency. Therefore, the sensitivity of astrophysical spectra to variations in FC directly depend on ΔK_i.

In optical range sensitivity coefficients are typically on the order of $10^{-2}-10^{-3}$, while in microwave and far-infrared frequency regions they are typically on the order of unity. In fact, as we will see below, in some special cases sensitivity coefficients can be much greater that unity. This makes observations in microwave and far-infrared wavelength regions potentially more sensitive to variations in FC as compared to observations in optical region. Because of the lower sensitivity, systematic effects in optics may be significantly larger (for the most recent discussion of the systematic effects see [35] and references therein).

In Sec. II A we briefly recall the theory of Λ and Ω doublings in the pure coupling cases a and b and find respective sensitivity coefficients. After that we will calculate sensitivity coefficients for particular molecules using simplified vari-

ant of effective Hamiltonian from Ref. [36]. This Hamiltonian accounts for decoupling phenomena and for the hyperfine structure of Λ doublets. We fit free parameters of this Hamiltonian to match experimental frequencies. After that we use numerical differentiation to find sensitivity coefficients.

A. Λ doubling and Ω doubling

Consider electronic state with nonzero projection Λ of the orbital angular momentum on the molecular axis. The spin-orbit interaction couples electron spin $\boldsymbol{S}$ to the molecular axis, its projection being Σ. To a first approximation the spin-orbit interaction is reduced to the form $H_{so}=A\Lambda\Sigma$. Total electronic angular momentum $\boldsymbol{J}_e=\boldsymbol{L}+\boldsymbol{S}$ has projection Ω on the axis, $\Omega=\Lambda+\Sigma$. For a particular case of $\Lambda=1$ and $S=\frac{1}{2}$ we have two states $\Pi_{1/2}$ and $\Pi_{3/2}$ and the energy difference between them is $E(\Pi_{3/2})-E(\Pi_{1/2})=A$.

Rotational energy of the molecule is described by the Hamiltonian

$$H_{\rm rot}=B(\boldsymbol{J}-\boldsymbol{J}_e)^2 \tag{6a}$$

$$=B\boldsymbol{J}^2-2B(\boldsymbol{J}\cdot\boldsymbol{J}_e)+B\boldsymbol{J}_e^2, \tag{6b}$$

where B is rotational constant and $\boldsymbol{J}$ is the total angular momentum of the molecule. The first term in expression (6b) describes conventional rotational spectrum. The last term is constant for a given electronic state and can be added to the electronic energy.[1] The second term describes Ω doubling and is known as Coriolis interaction $H_{\rm Cor}$.

If we neglect Coriolis interaction, the eigenvectors of Hamiltonian (6) have definite projections M and Ω of the molecular angular momentum $\boldsymbol{J}$ on the laboratory axis and on the molecular axis, respectively. In this approximation the states $|J,M,\Lambda,\Sigma,\Omega\rangle$ and $|J,M,-\Lambda,-\Sigma,-\Omega\rangle$ are degenerate, $E_{J,\pm\Omega}=BJ(J+1)$. Coriolis interaction couples these states and removes degeneracy. New eigenstates are the states of definite parity $p=\pm1$ [37]:

$$|J,M,\Omega,p\rangle=(|J,M,\Omega\rangle+p(-1)^{J-S}|J,M,-\Omega\rangle)/\sqrt{2}. \tag{7}$$

Operator $H_{\rm Cor}$ can only change quantum number Ω by one, so the coupling of states $|\Omega\rangle$ and $|-\Omega\rangle$ takes place in the 2Ω order of the perturbation theory in $H_{\rm Cor}$.

Ω doubling for the state $\Pi_{1/2}$ happens already in the first order in Coriolis interaction but has additional smallness from the spin-orbit mixing. Operator $H_{\rm Cor}$ cannot directly mix degenerate states $|\Lambda=1,\Sigma=-\frac{1}{2},\Omega=\frac{1}{2}\rangle$ and $|\Lambda=-1,\Sigma=\frac{1}{2},\Omega=-\frac{1}{2}\rangle$ because it requires changing Λ by two. Therefore, we need to consider spin-orbit mixing between Π and Σ states:

$$\left|\Omega=\frac{1}{2}\right\rangle=\left|\Lambda=1,\Sigma=-\frac{1}{2},\Omega=\frac{1}{2}\right\rangle+\zeta\left|\Lambda=0,\Sigma=\frac{1}{2},\Omega=\frac{1}{2}\right\rangle, \tag{8}$$

where

$$\zeta\sim A/(E_\Pi-E_\Sigma), \tag{9}$$

and then

$$\left\langle\Omega=\frac{1}{2}\middle|H_{\rm Cor}\middle|\Omega=-\frac{1}{2}\right\rangle=2\zeta B\left(J+\frac{1}{2}\right)\langle\Lambda=1|L_x|\Lambda=0\rangle. \tag{10}$$

Note that ζ depends on the nondiagonal matrix element of spin-orbit interaction and Eq. (9) is only an order of magnitude estimate. It is important, though, that nondiagonal and diagonal matrix elements have similar dependence on FC. We conclude that Ω splitting for the $\Pi_{1/2}$ level must scale as $ABJ/(E_\Pi-E_\Sigma)$.

The Ω doubling for $\Pi_{3/2}$ state takes place in the third order in Coriolis interaction. Here $H_{\rm Cor}$ has to mix the states $\Pi_{3/2}$ with $\Pi_{1/2}$ and $\Pi_{-3/2}$ with $\Pi_{-1/2}$ before matrix element (10) can be used. Therefore, the splitting scales as $B^3J^3/[A(E_\Pi-E_\Sigma)]$.

The above consideration corresponds to the coupling case a when $|A|\gg B$. In the opposite limit the states $\Pi_{1/2}$ and $\Pi_{3/2}$ are strongly mixed by the Coriolis interaction and spin $\boldsymbol{S}$ decouples from the molecular axis (coupling case b). As a result, the quantum numbers Σ and Ω are not defined and we only have one quantum number $\Lambda=\pm1$. Now Λ splitting takes place in the second order in Coriolis interaction via intermediate Σ state. The scaling here is obviously of the form $B^2J^2/(E_\Pi-E_\Sigma)$. Note that in contrast to the previous case $|A|\gg B$, the splitting here is independent of A.

We can now use found scalings of the Λ and Ω doublings to determine the sensitivity coefficients [Eq. (3)]. For this we only need to know how parameters A and B depend on α and β. In atomic units these parameters obviously scale as $A\propto\alpha^2$ and $B\propto\beta$. We conclude that for the case a the Ω-doubling spectrum has following sensitivity coefficients:

$$\text{State } {}^2\Pi_{1/2}:\quad K_\alpha=2,\quad K_\beta=1, \tag{11a}$$

$$\text{State } {}^2\Pi_{3/2}:\quad K_\alpha=-2,\quad K_\beta=3. \tag{11b}$$

For the case b, when $\boldsymbol{S}$ is completely decoupled from the axis, the Λ-doubling spectrum has following sensitivity coefficients:

$$\text{State } \Pi:\quad K_\alpha=0,\quad K_\beta=2. \tag{11c}$$

When constant A is slightly larger than B, the spin $\boldsymbol{S}$ is coupled to the axis only for lower rotational levels. As rotational energy grows with J and becomes larger than the splitting between states $\Pi_{1/2}$ and $\Pi_{3/2}$, the spin decouples from the axis. Consequently, the Ω doubling is transformed into Λ doubling. Equations (11) show that this can cause significant changes in sensitivity coefficients. The spin-orbit constant A can be either positive (CH molecule) or negative (OH). The

[1]Note that this term contributes to the separation between states $\Pi_{1/2}$ and $\Pi_{3/2}$. This becomes particularly important for light molecules, where constant A is small.

sign of the Ω doubling depends on the sign of A, while Λ doubling does not depend on A at all. Therefore, decoupling of the spin can change the sign of the splitting. In Sec. II B we will see that this can lead to the dramatic enhancement of the sensitivity to the variation in FC.

B. Intermediate coupling

Λ doubling for the intermediate coupling was studied in detail in many papers, including [36,38,39] (see also the book [37]). Here we use effective Hamiltonian $H_{\rm eff}$ from Ref. [36] in the subspace of the levels $\Pi^{\pm}_{1/2}$ and $\Pi^{\pm}_{3/2}$, where upper sign corresponds to parity p in Eq. (7). Operator $H_{\rm eff}$ includes spin-rotational and hyperfine parts[2]:

$$H_{\rm eff} = H_{\rm sr} + H_{\rm hf}. \tag{12}$$

Neglecting third-order terms in Coriolis and spin-orbit interactions, we get the following simplified form of spin-rotational part:

$$\langle \Pi^{\pm}_{1/2}|H_{\rm sr}|\Pi^{\pm}_{1/2}\rangle = -\frac{1}{2}A + B\left(J+\frac{1}{2}\right)^2 \pm (S_1+S_2)(2J+1), \tag{13a}$$

$$\langle \Pi^{\pm}_{3/2}|H_{\rm sr}|\Pi^{\pm}_{3/2}\rangle = +\frac{1}{2}A + B\left(J+\frac{1}{2}\right)^2 - 2B, \tag{13b}$$

$$\langle \Pi^{\pm}_{3/2}|H_{\rm sr}|\Pi^{\pm}_{1/2}\rangle = \left[B \pm S_2\left(J+\frac{1}{2}\right)\right]\sqrt{\left(J-\frac{1}{2}\right)\left(J+\frac{3}{2}\right)}. \tag{13c}$$

Here in addition to parameters A and B we have two parameters, which appear in the second order of perturbation theory via intermediate state(s) $\Sigma_{1/2}$. Parameter S_1 corresponds to the cross term of the perturbation theory in spin-orbit and Coriolis interactions, while parameter S_2 is quadratic in Coriolis interaction. Because of this S_1 scales as $\alpha^2\beta$ and S_2 scales as β^2. The third-order parameters neglected in Eq. (13) consist of several terms each with different dependencies on parameters α and β [36]. For this reason we cannot use them to study sensitivity coefficients. Fortunately, all third-order terms are very small for the molecules considered here. They account only for the fine tuning of the spectrum and do not noticeably affect sensitivity coefficients for transitions with moderate quantum numbers J. It is easy to see that Hamiltonian $H_{\rm sr}$ describes limiting cases $|A| \gg B$ and $|A| \ll B$ considered in Sec. II A.

The hyperfine part of effective Hamiltonian is defined in the lowest order of perturbation theory and has the form

$$\langle \Pi^{\pm}_{1/2}|H_{\rm hf}|\Pi^{\pm}_{1/2}\rangle = C_F[2a - b - c \pm (2J+1)d], \tag{14a}$$

$$\langle \Pi^{\pm}_{3/2}|H_{\rm hf}|\Pi^{\pm}_{3/2}\rangle = 3C_F[2a + b + c], \tag{14b}$$

$$\langle \Pi^{\pm}_{3/2}|H_{\rm hf}|\Pi^{\pm}_{1/2}\rangle = -C_F\sqrt{(2J-1)(2J+3)}\,b, \tag{14c}$$

[2]Here we use notation $H_{\rm sr}$ to define part of the effective Hamiltonian, which describes rotational degrees of freedom and electron spin.

$$C_F \equiv \frac{F(F+1) - J(J+1) - I(I+1)}{8J(J+1)}.$$

Here we assume that only one nucleus has spin and include only magnetic dipole hyperfine interaction. In this approximation all four parameters of $H_{\rm hf}$ scale as $\alpha^2\beta g_{\rm nuc}$.

Effective Hamiltonian described by Eqs. (13) and (14) has eight parameters. We use NIST values [32] for the fine-structure splitting A, rotational constant B, and magnetic hyperfine constants a, b, c, and d. The remaining two parameters S_1 and S_2 are found by minimizing rms deviation between theoretical and experimental Λ-doubling spectra.

In order to find sensitivity coefficients K_α we calculate transition frequency for two values of $\alpha = \alpha_0 \pm \delta$ near its physical value $\alpha_0 = 1/137.035\,999\,679(94)$ and similarly for K_β and K_g. We use scaling rules discussed above to recalculate parameters of the effective Hamiltonian for different values of FC. Then we use numerical differentiation to find respective sensitivity coefficient.

We check the accuracy of our approach by adding three most important third-order parameters from Ref. [36] to Hamiltonian (13) and including them in fitting procedure. That leads to noticeable improvement of the theoretical frequencies for higher values of J. Each of our three third-order parameters actually include several terms, which scale as different combination of A and B (A^2B, AB^2, etc.) Each term, therefore, has different dependence on α and β. On the other hand, they have same dependence on the quantum numbers and cannot be independently determined from the fitting procedure. Because of that it is impossible to unambiguously determine dependence of these parameters on FC. Therefore, we calculate sensitivity coefficients assuming dominance of one term for each third-order parameter and look how the answer depends on these assumptions. We found that sensitivity coefficients changed by less than 1%. Therefore, we conclude that this simple model is sufficiently accurate for our purposes and currently there is no need to use more elaborate theory.

Hyperfine Hamiltonian (14) accounts only for one nuclear spin and does not include interaction with nuclear electric quadrupole moment. Generalization to two spins is straightforward, but in this paper we restrict consideration to molecules with one spin. For molecules with $I > \frac{1}{2}$ we must add quadrupole term to Eq. (14):

$$\langle \Pi^{\pm}_{\Omega}|\tilde{H}_{\rm hf}|\Pi^{\pm}_{\Omega}\rangle = \frac{C(C+1) - 4I(I+1)J(J+1)}{8I(2I-1)J(J+1)(2J+3)} \times (-1)^{2J}[3\Omega^2 - J(J+1)](eq_0Q_{\rm nuc}),$$

$$C \equiv F(F+1) - J(J+1) - I(I+1). \tag{15}$$

In this case there is additional hyperfine parameter $eq_0Q_{\rm nuc}$ which includes electronic matrix element eq_0 and nuclear quadrupole moment $Q_{\rm nuc}$. Matrix element eq_0 for light molecules can be calculated in nonrelativistic approximation and does not depend on FC. Dependence of $Q_{\rm nuc}$ on FC can be very complex (see discussion in [7]). Without

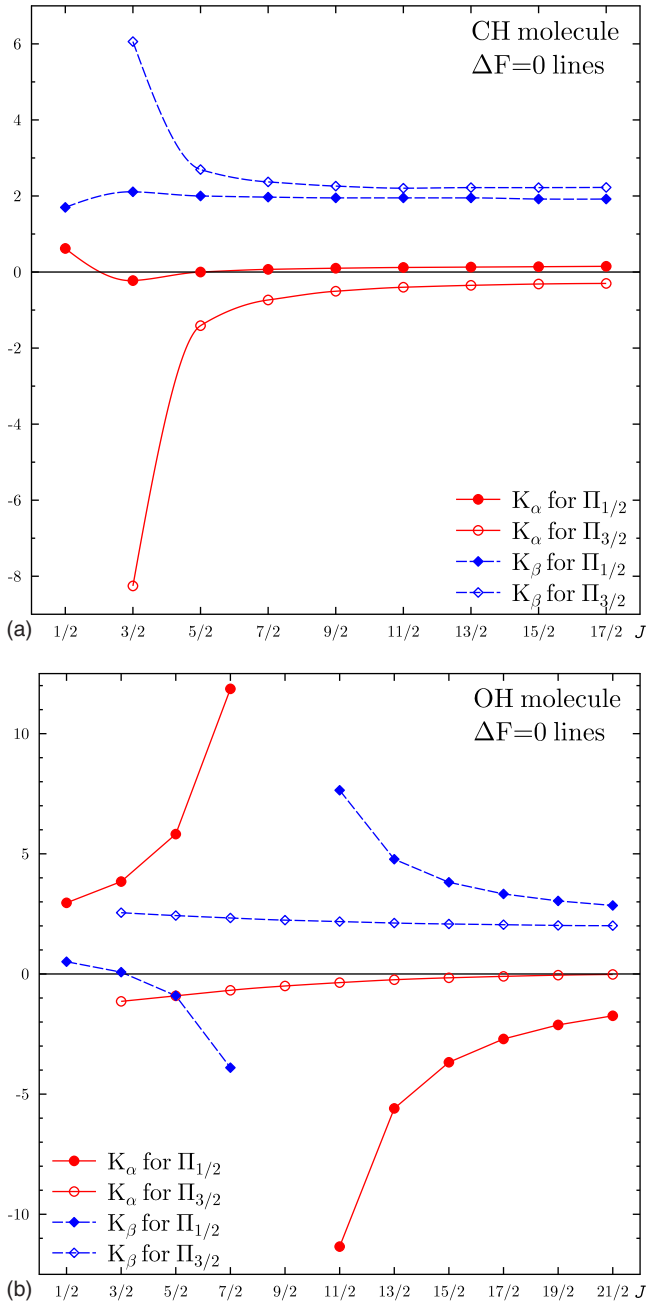

FIG. 1. (Color online) Sensitivity coefficients K_α and K_β for Λ-doublet lines with $\Delta F=0$ in CH and OH molecules. The difference between lines with $F=J+\frac{1}{2}$ and $F=J-\frac{1}{2}$ is too small to be seen. For the state $\Pi_{3/2}$ of OH molecule the values for $J=\frac{9}{2}$ are too large to be shown on the plot. They are listed in Table II.

going into nuclear theory, one can consider $Q_{\rm nuc}$ as independent fundamental parameter and introduce additional sensitivity coefficient K_Q. Below we will see that coefficients K_g and K_Q are usually very small except for the transitions with very low frequency.

III. RESULTS AND DISCUSSION

We applied the above method to ^{16}OH, ^{12}CH, ^{7}Li^{16}O, ^{14}N^{16}O, and ^{15}N^{16}O. Molecules CH and NO have ground state $^2\Pi_{1/2}$ $(A>0)$, while OH and LiO have ground state $^2\Pi_{3/2}$ $(A<0)$. The ratio $|A/B|$ changes from 2 for CH molecule to 7 for OH and to almost a hundred for LiO and NO. Therefore, LiO and NO definitely belong to the coupling case *a*. For OH molecule we can expect transition from case *a* for lower rotational states to case *b* for higher ones. Finally, for CH we expect intermediate coupling for lower rotational states and coupling case *b* for higher states.

Let us see how this scheme works in practice for the effective Hamiltonians (13) and (14). Figure 1 demonstrate J dependence of sensitivity coefficients for CH and OH molecules. Both of them have only one nuclear spin $I=\frac{1}{2}$. For a given quantum number J, each Λ-doublet transition has four hyperfine components: two strong transitions with $\Delta F=0$ and $F=J\pm\frac{1}{2}$ (for $J=\frac{1}{2}$ there is only one transition with $F=1$) and two weaker transitions with $\Delta F=\pm 1$. The hyperfine structure for OH and CH molecules is rather small and sensitivity coefficients for all hyperfine components are very close. Because of that Fig. 1 presents only averaged values for strong transitions with $\Delta F=0$.

We see that for large values of J the sensitivity coefficients for both molecules approach limit [Eq. (11c)] of the coupling case *b*. The opposite limits [Eqs. (11a) and (11b)] are not reached for either molecule even for smallest values of J. So, we conclude that coupling case *a* is not realized. It is interesting that in Fig. 1 the curves for the lower states are smooth, while for upper states there are singularities. For CH molecule this singularity takes place for the state $\Pi_{3/2}$ near the lowest possible value $J=3/2$. Singularity for OH molecule takes place for state $\Pi_{1/2}$ near $J=9/2$.

These singularities appear because Λ splitting turns to zero. As we saw above, the sign of the splitting for the coupling case *a* depends on the sign of the constant A. The same sign determines which state $\Pi_{1/2}$ or $\Pi_{3/2}$ lies higher. As a result, for the lower state the sign of the splitting is the same for both limiting cases, but decoupling of the electron spin S for the upper state leads to the change in sign of the splitting. Of course, these singularities are most interesting for our purposes as they lead to large sensitivity coefficients which strongly depend on the quantum numbers. Note that when the frequency of the transition is small, it becomes sensitive to the hyperfine part of the Hamiltonian and sensitivity coefficients for hyperfine components may differ significantly. Sensitivity coefficients of all hyperfine components of such Λ lines are given in Table II. We can see that near the singularities all sensitivity coefficients, including K_g, are enhanced.

Now let us consider sensitivity coefficients for the molecule ^{15}NO. Here we expect expressions for the coupling case *a* to be applicable. In fact, for the state $\Pi_{1/2}$ coefficients K_α and K_β agree with prediction (11a) within few percent and $K_g\ll 1$. However, for the state $\Pi_{3/2}$ Eq. (11b) works only for transitions with $\Delta F=0$, see Fig. 2. Indeed, Λ splitting for low values of J is smaller than the hyperfine structure. As a result, the frequencies of $\Delta F=\pm 1$ transitions strongly depend on the hyperfine parameters. For some values of J these frequencies can be very small because Λ splitting and hyperfine splitting cancel each other. This leads to enhancement of

TABLE II. Frequencies (in MHz) and sensitivity coefficients for hyperfine components $(J,F\rightarrow J,F')$ of Λ-doublet lines in CH and OH molecules. Recommended frequencies and their uncertainties are taken from Refs. [32–34].

Molecule	Level	J	F	F'	ω (MHz) Recom.	Uncert.	Theor.	Diff.	K_α	K_β	K_g
^{12}CH	$^2\Pi_{1/2}$	0.5	0	1	3263.795	0.003	3269.40	−5.61	0.59	1.71	−0.02
		0.5	1	1	3335.481	0.001	3340.77	−5.29	0.62	1.70	0.00
		0.5	1	0	3349.194	0.003	3354.11	−4.92	0.63	1.69	0.01
		1.5	1	2	7275.004	0.001	7262.25	12.75	−0.24	2.12	−0.01
		1.5	1	1	7325.203	0.001	7312.02	13.18	−0.23	2.11	0.00
		1.5	2	2	7348.419	0.001	7335.30	13.12	−0.22	2.11	0.00
		1.5	2	1	7398.618	0.001	7385.08	13.54	−0.20	2.10	0.01
^{12}CH	$^2\Pi_{3/2}$	1.5	2	2	701.68	0.01	682.96	18.72	−8.44	6.15	−0.01
		1.5	1	2	703.97	0.03	679.83	24.14	−8.66	6.32	−0.01
		1.5	2	1	722.30	0.03	702.98	19.52	−8.37	6.17	0.02
		1.5	1	1	724.79	0.01	699.85	24.94	−8.07	5.97	0.02
^{16}OH	$^2\Pi_{3/2}$	1.5	1	2	1612.2310	0.0002	1595.42	16.81	−1.27	2.61	−0.03
		1.5	1	1	1665.4018	0.0002	1648.93	16.47	−1.14	2.55	0.00
		1.5	2	2	1667.3590	0.0002	1650.66	16.70	−1.14	2.55	0.00
		1.5	2	1	1720.5300	0.0002	1704.17	16.36	−1.02	2.49	0.03
^{16}OH	$^2\Pi_{1/2}$	0.5	0	1	4660.2420	0.0030	4638.98	21.26	2.98	0.50	−0.02
		0.5	1	1	4750.6560	0.0030	4729.51	21.15	2.96	0.51	0.00
		0.5	1	0	4765.5620	0.0030	4744.50	21.06	2.96	0.51	0.01
		4.5	5	4	88.9504	0.0011	64.34	24.61	−921.58	459.86	−0.56
		4.5	5	5	117.1495	0.0011	92.35	24.80	−699.65	349.59	−0.19
		4.5	4	4	164.7960	0.0011	141.20	23.60	−496.67	248.77	0.16
		4.5	4	5	192.9957	0.0011	169.22	23.78	−424.05	212.68	0.28

sensitivity coefficients, similar to that discussed in Ref. [40]. Figure 2 shows that for ^{15}NO molecule such singularity takes place for $\Delta F=-1$ transition near $J=\frac{11}{2}$. For smaller values of J the hyperfine contribution to transition frequency dominates over Λ splitting. Sensitivity coefficients for this case are similar to those of the normal hyperfine transitions, i.e., $K_\alpha\approx 2$ and $K_\beta\approx K_g\approx 1$. For higher values of J they approach limit (11b). For $\Delta F=1$ transitions there is no singularity and sensitivities change smoothly between same limiting values. Finally, the hyperfine energy for the lines with $\Delta F=0$ is negligible and these lines are described by Eq. (11b) for all values of J.

The spectrum and sensitivity coefficients of the molecule ^{14}NO are similar to those of ^{15}NO. Because ^{14}N has nuclear spin $I=1$, the hyperfine structure of the Λ-doublet lines is more complex and consists of up to seven hyperfine components. Hyperfine Hamiltonian includes magnetic dipole part [Eq. (14)] and electric quadrupole part [Eq. (15)] and is described by five hyperfine parameters, which we take from Ref. [32]. As we said above, we are not discussing nuclear theory here and consider nuclear quadrupole moment as independent FC. Because of that Λ-doublet spectrum is now described by four sensitivity coefficients (see Table III).

Sensitivity coefficients K_α and K_β of the Λ-doublet lines of the state $\Pi_{1/2}$ again agree with Eq. (11a) within few percent. The lowest-frequency transitions for $J=\frac{1}{2}$ have sensitiv-

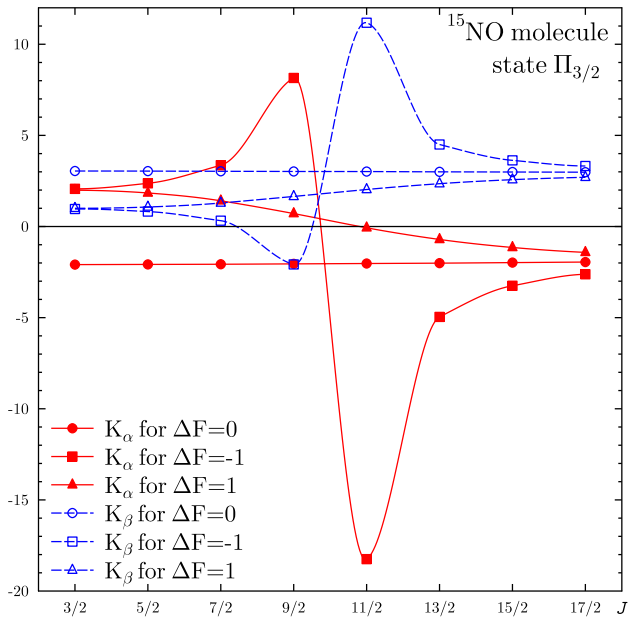

FIG. 2. (Color online) Sensitivity coefficients for Λ-doublet lines in $\Pi_{3/2}$ state of ^{15}NO molecule. The difference between two hyperfine components with $\Delta F=0$ is too small to be seen. Sensitivity coefficients for $\Pi_{1/2}$ state correspond to the coupling case *a* [see Eq. (11a)].

TABLE III. Frequencies (in MHz) and sensitivity coefficients for Λ-doublet lines in $^{14}N^{16}O$. Experimental frequencies and their uncertainties are taken from Refs. [32,33].

Level	J	F	F'	ω (MHz) Expt.	Uncert.	Theor.	Diff.	K_α	K_β	K_g	K_Q
$^2\Pi_{1/2}$	0.5	0.5	0.5	205.9510	0.0002	205.96	−0.01	1.95	1.03	−0.73	0.00
	0.5	0.5	1.5	225.9357	0.0002	225.93	0.00	1.95	1.02	−0.58	0.00
	0.5	1.5	0.5	411.2056	0.0002	411.19	0.01	1.97	1.01	0.13	0.00
	0.5	1.5	1.5	431.1905	0.0002	431.16	0.03	1.97	1.01	0.17	0.00
	1.5	0.5	0.5	560.8538	0.0002	561.22	−0.37	1.97	1.02	−0.27	0.00
	1.5	0.5	1.5	587.7467	0.0002	587.54	0.21	1.97	1.01	−0.21	0.09
	1.5	1.5	0.5	624.6494	0.0002	624.93	−0.28	1.97	1.02	−0.14	−0.09
	1.5	1.5	1.5	651.5425	0.0002	651.25	0.29	1.97	1.01	−0.09	0.00
	1.5	1.5	2.5	693.8282	0.0002	693.88	−0.05	1.98	1.01	−0.02	−0.04
	1.5	2.5	1.5	758.9106	0.0002	758.66	0.25	1.97	1.01	0.06	0.04
	1.5	2.5	2.5	801.1963	0.0002	801.29	−0.10	1.98	1.01	0.11	0.00
	2.5	3.5	3.5	1160.7768	0.0003	1160.95	−0.18	1.98	1.01	0.08	0.00
	3.5	4.5	4.5	1514.768	0.001	1514.97	−0.20	2.00	1.00	0.07	0.00
$^2\Pi_{3/2}$	1.5	0.5	0.5			0.81		−2.09	3.05	−0.11	0.00
	1.5	1.5	1.5	0.612	0.001	0.87	−0.25	−2.96	4.31	−0.06	0.00
	1.5	2.5	2.5	1.029	0.001	0.96	0.07	−1.94	2.83	0.05	0.00
	1.5	0.5	1.5			44.45		2.09	0.93	1.01	1.25
	1.5	1.5	0.5	46.464	0.003	46.12	0.34	1.92	1.00	0.96	1.19
	1.5	1.5	2.5	73.286	0.003	73.33	−0.05	2.10	0.96	1.02	−0.42
	1.5	2.5	1.5	74.931	0.003	75.15	−0.22	2.00	1.02	1.00	−0.41
	2.5	1.5	1.5			3.38		−2.08	3.04	−0.06	0.00
	2.5	2.5	2.5	3.121	0.001	3.54	−0.41	−2.36	3.44	−0.02	0.00
	2.5	3.5	3.5	3.923	0.001	3.75	0.17	−1.99	2.91	0.04	0.00
	2.5	1.5	2.5			27.37		2.64	0.70	1.14	−0.97
	2.5	2.5	1.5	34.39	0.03	34.28	0.11	1.68	1.17	0.90	−0.77
	2.5	2.5	3.5	40.172		40.07	0.10	2.46	0.76	1.08	0.46
	2.5	3.5	2.5	47.211	0.001	47.36	−0.14	1.77	1.11	0.92	0.39
	3.5	2.5	2.5			8.58		−2.07	3.03	−0.04	0.00
	3.5	3.5	3.5			8.88		−2.07	3.03	−0.01	0.00
	3.5	4.5	4.5			9.26		−2.07	3.03	0.03	0.00
	3.5	2.5	3.5			13.59		5.06	−0.39	1.73	−6.83
	3.5	3.5	2.5	31.550	0.004	31.05	0.50	1.03	1.51	0.73	−2.94
	3.5	3.5	4.5			21.54		3.90	−0.01	1.38	3.32
	3.5	4.5	3.5	39.221	0.002	39.67	−0.45	1.18	1.40	0.76	1.82
	4.5	3.5	3.5			17.25		−2.05	3.02	−0.03	0.00
	4.5	4.5	4.5			17.74		−2.05	3.02	−0.01	0.00
	4.5	5.5	5.5			18.33		−2.05	3.03	0.03	0.00
	4.5	3.5	4.5			0.96		−80.19	38.95	−19.07	157.32
	4.5	4.5	3.5	35.045	0.002	34.02	1.02	0.16	1.95	0.50	−4.33
	4.5	4.5	5.5			5.26		16.68	−6.81	4.16	23.52
	4.5	5.5	4.5	40.512	0.001	41.33	−0.81	0.34	1.81	0.55	3.05

ity coefficients K_g of the order of unity, but they rapidly decrease with frequency and with J. Coefficients K_Q for the state $\Pi_{1/2}$ are always small.

For the state $\Pi_{3/2}$ there are transitions of three types. The first type transitions correspond to $\Delta F=0$. The hyperfine energy difference here is small compared to Λ splitting. These transitions have sensitivity coefficients K_α and K_β close to prediction (11b) and small coefficients K_g and K_Q. The second type transitions correspond to $\Delta F=\pm 1$ and small values of J. Hyperfine energy for these transitions dominates over Λ

TABLE IV. Frequencies (in MHz) and sensitivity coefficients for Λ-doublet lines in $^{7}Li^{16}O$. Experimental frequencies and their uncertainties are taken from Ref. [32].

				ω (MHz)							
Level	J	F	F'	Expt.	Uncert.	Theor.	Diff.	K_α	K_β	K_g	K_Q
$^2\Pi_{3/2}$	1.5	1	1	11.28	0.01	11.18	0.10	−1.90	2.94	0.00	0.00
	1.5	2	2	11.28	0.01	11.18	0.10	−1.90	2.94	0.00	0.00
	1.5	3	3	11.28	0.01	11.19	0.09	−1.90	2.94	0.00	0.00
	1.5	0	1			9.82		−2.51	3.25	−0.14	0.63
	1.5	1	0			12.53		−1.46	2.74	0.11	−0.49
	1.5	1	2	8.55	0.10	8.41	0.14	−3.26	3.59	−0.33	0.72
	1.5	2	1	14.00	0.05	13.95	0.05	−1.07	2.55	0.20	−0.44
	1.5	2	3	6.95	0.05	6.87	0.08	−4.47	4.24	−0.61	−0.89
	1.5	3	2	15.60	0.02	15.50	0.10	−0.76	2.36	0.27	0.40
	2.5	1	1	45.02	0.03	44.80	0.22	−1.90	2.95	0.00	0.00
	2.5	2	2	45.02	0.03	44.80	0.22	−1.90	2.95	0.00	0.00
	2.5	3	3	45.02	0.03	44.81	0.21	−1.90	2.95	0.00	0.00
	2.5	4	4	45.02	0.03	44.83	0.19	−1.90	2.95	0.00	0.00
	2.5	1	2	44.04	0.03	43.82	0.22	−2.01	3.01	−0.02	−0.08
	2.5	2	1	45.97	0.03	45.78	0.19	−1.81	2.90	0.02	0.08
	2.5	2	3	43.60	0.03	43.37	0.23	−2.06	3.03	−0.03	−0.05
	2.5	3	2	46.43	0.03	46.24	0.19	−1.76	2.88	0.03	0.04
	2.5	3	4	43.17	0.03	42.97	0.20	−2.11	3.06	−0.04	0.08
	2.5	4	3	46.86	0.03	46.67	0.19	−1.71	2.86	0.04	−0.08
	3.5	3	3	112.237	0.002	112.28	−0.04	−1.91	2.96	0.00	0.00
	4.5	4	4	223.756	0.003	225.24	−1.48	−1.91	2.99	0.00	0.00
$^2\Pi_{1/2}$	0.5	1	1			2958.44		2.10	0.95	0.00	0.00
	0.5	2	2			2969.20		2.10	0.95	0.00	0.00
	0.5	1	2			2947.37		2.10	0.95	−0.01	0.00
	0.5	2	1			2980.27		2.10	0.95	0.01	0.00
	1.5	1	1			5971.29		2.10	0.96	0.00	0.00
	1.5	2	2			5975.59		2.10	0.96	0.00	0.00
	1.5	3	3			5982.05		2.10	0.96	0.00	0.00
	1.5	1	2			5969.71		2.10	0.96	0.00	0.00
	1.5	2	1			5977.18		2.10	0.96	0.00	0.00
	1.5	2	3			5973.38		2.10	0.96	0.00	0.00
	1.5	3	2			5984.26		2.10	0.96	0.00	0.00
	2.5	2	2			9078.46		2.11	0.97	0.00	0.00
	3.5	2	2	12321.51	0.03	12322.14	−0.63	2.13	0.99	0.00	0.00
	3.5	3	3	12325.82	0.03	12325.21	0.61	2.13	0.99	0.00	0.00
	3.5	2	3	12319.93	0.03	12321.60	−1.67	2.13	0.99	0.00	0.00
	3.5	3	2	12327.41	0.03	12325.75	1.66	2.13	0.99	0.00	0.00

splitting. The sensitivity coefficients here are close to those of pure hyperfine transitions, i.e., $K_\alpha=2$ and $K_\beta=1$. As long as hyperfine energy includes comparable magnetic dipole and electric quadrupole parts, coefficients K_g and K_Q are of the order of unity but may significantly differ from one transition to another. Note that all transitions of this type for ^{15}NO molecule have $K_g \approx 1$.

Transitions of the third type also correspond to $\Delta F = \pm 1$, but higher rotational quantum numbers $J=\frac{7}{2},\frac{9}{2}$. The hyperfine transition energy here is comparable to Λ splitting, and they can either double or almost cancel each other. Consequently, sensitivity coefficient are widely spread and can become very large for transitions with anomalously low frequency.

Note that low-frequency transitions for $J=\frac{9}{2}$ were not observed experimentally, and we use theoretical frequencies to calculate sensitivity coefficients. Because of significant cancellation of different contributions, the accuracy of these fre-

quencies can be low. When these frequencies are measured, respective sensitivity coefficients should be corrected:

$$K_{i,\mathrm{cor}} = K_i \frac{\omega_{\mathrm{theor}}}{\omega_{\mathrm{expt.}}}. \tag{16}$$

Sensitivity coefficients for LiO molecule are listed in Table IV. The hyperfine structure here is smaller than for NO molecule and sensitivity coefficients are closer to case *a* values [Eqs. (11a) and (11b)]. Significant deviations are found only for $J=\frac{3}{2}$, $\Delta F=\pm 1$ transitions of $\Pi_{3/2}$ state. Also, these are the only transitions, where coefficients K_g and K_Q are not negligible. For this molecule there are no transitions with anomalously small frequencies, and therefore, sensitivity coefficients are not enhanced.

IV. CONCLUSIONS

In this paper we calculated sensitivity coefficients to variation in fundamental constants for Λ-doublet spectra of several light diatomic molecules. We found several lines with anomalously high sensitivity. All these lines have relatively low frequencies and enhanced sensitivity is caused by the significant cancellations between contributions from different parts of the effective Hamiltonian (12).

In CH and OH molecules enhancement takes place when electron spin decouples from the molecular axis and Ω doubling is transformed into Λ doubling. For one of the two states $\Pi_{1/2}$ or $\Pi_{3/2}$ this transformation leads to the change in sign of the splitting between states with definite parity and enhanced sensitivity to FC variation.

Rotational constant B for ^{14}NO and ^{15}NO molecules is much smaller than for CH and NH molecules and electron spin is strongly coupled to the axis. Consequently, there is no enhancement caused by decoupling. On the other hand, the hyperfine structure of the Λ-doublet lines is comparable to Λ splitting in $\Pi_{3/2}$ state. For some transition lines with $\Delta F=\pm 1$ the hyperfine energy almost cancel Λ splitting leading to enhanced sensitivity.

For LiO molecule electron spin is strongly coupled to the axis and hyperfine structure is smaller than Λ splitting. As a result, there is no strong enhancement of the sensitivity to FC variation. However, even here sensitivity coefficients strongly depend on the quantum numbers.

Sensitivity coefficients for six Λ-doublet transitions of OH molecule were calculated before in Refs. [20,23]. For all these transitions our results are in good agreement with those calculations. In particular, from Table II we find sensitivity coefficients for the 18 cm ground-state Λ-doublet transitions with $J=\frac{3}{2}$ and $F'=F$ to be $K_\alpha=-1.14$, $K_\beta=2.55$, and $K_g=0$. In the paper [20] the 21 cm hydrogen line was used as a reference. It has $K_\alpha=2$, $K_\beta=1$, and $K_g=1$. Parameter $\mathcal{F}$ according to Eq. (5) is given by the expression

$$\mathcal{F} = \alpha^{\Delta K_\alpha}\beta^{\Delta K_\beta} g_{\mathrm{nuc}}^{\Delta K_g} = \alpha^{3.14}\beta^{-1.55} g_{\mathrm{nuc}}^{1}. \tag{17}$$

This result is sufficiently close to Eq. (1).

For astrophysical observations it is important to have accurate laboratory measurements so that frequency ratios for distant object can be compared to the respective local ratios. Sufficiently accurate frequency measurements were done only for 18 cm lines of OH [9,28] and for 9 cm lines of CH [10]. These lines can be used for new studies of the variation in FC without significant preliminary work. For other lines at present there are no sufficiently accurate laboratory frequencies. New laboratory measurements are necessary before these lines can be used for our purposes. In particular, the hyperfine components of the 42 cm CH line are most interesting as they have high sensitivity to both fundamental constants and were already observed in astrophysics for distant objects.

In principle it is possible to study time variation in FC without referring to the laboratory measurements. For this purpose it is possible to compare microwave spectra for molecular clouds from our galaxy with extragalactic spectra of the same species. In many cases the line widths for the galactic spectra are one to two orders of magnitude smaller than for objects at cosmological distances so they can serve as very good reference.

Let us briefly discuss the feasibility of the laboratory tests of time variation of FC using molecular Λ doublets. Present model independent laboratory limit on β variation is [1]

$$\frac{d\beta/dt}{\beta} = (3.8 \pm 5.6) \times 10^{-14}\ \mathrm{yr}^{-1}, \tag{18}$$

and the limit on α variation is three orders of magnitude stronger on the level 10^{-17} [2]. To improve constrained Eq. (18) one needs to measure frequency shifts $\delta\omega < K_\beta \omega \delta\beta/\beta$. For the 18 cm OH line this corresponds to the shift $\delta\omega \lesssim 4 \times 10^{-4}$ Hz. This is few orders of magnitude smaller than the accuracy of the best present measurements [9,28]. On the other hand, at present there is rapid progress in precision molecular spectroscopy caused by development of sources of ultracold molecules (see review [31] and references therein). Thus it is possible that molecular tests of FC variation using Λ-doublet lines can become competitive in the near future.

When comparing sensitivity of different laboratory experiments on time variation it is not sufficient to look for large dimensionless sensitivity coefficients [Eq. (3)]. In high-precision laboratory measurements the line widths are not dominated by the Doppler effect and are not proportional to the frequency. Because of that, instead of the dimensionless sensitivity coefficients K_i, which determine relative frequency shifts [Eq. (3)], one has to look for large absolute sensitivities $K_i\omega$, which determine absolute frequency shifts $\delta\omega$ and for narrow lines. In astrophysics, on the contrary, all lines are Doppler-broadened and dimensionless sensitivity coefficients K_i become crucial.

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