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 of 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 of 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 of the possible space and time variations of fundamental constants (FC). On a short time scale very stringent bounds on such variations were obtained in laboratory experiments. On the other hand astrophysical observations provide information on the variation of FC on the timescale of the order of 10 Gyr.[1] Here some results indicate variation on the level of few sigma, while other observations are consistent with no variation.

Recently there was much attention in this context to the microwave spectra of molecules. Generally these spectra are sensitive to possible variations of 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 of 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. 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 of FC as early as 1956 [2]). Second, the 18 cm Λ-doublet line of OH molecule depends on α and β as follows: $\delta\omega_{\rm OH}/\omega_{\rm OH} = \delta\mathcal{F}/\mathcal{F}$, $\mathcal{F} = \alpha^{-1.14}\beta^{2.57}$ [3, 4, 5]. Third, the 1.2 cm inversion line of ammonia depends only on β, $\delta\omega_{\rm inv}/\omega_{\rm inv} = 4.46\,\delta\beta/\beta$ [6, 7]. 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 of FC [7, 8, 9, 10, 11].

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 [9]:

$$\mathcal{F} = \alpha^{3.14}\beta^{-1.57}g_{\rm nuc}\,. \qquad (1)$$

The most stringent limit on the variation of $\mathcal{F}$ was obtained from observations of the $z = 0.765$ absorber and the $z = 0.685$ gravitational lens, Ref. [9]:

$$\delta\mathcal{F}/\mathcal{F} = \left(0.44 \pm 0.36^{\rm stat} \pm 1.0^{\rm syst}\right) \times 10^{-5}\,. \qquad (2)$$

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. [9]. Sensitivity coefficient for these lines were found in Ref. [12]. 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 of fundamental constants without using reference lines of other species. This can help to eliminate systematic effect from the different velocity distributions of species in molecular clouds. Two lowest Λ-doublet lines of CH molecule were detected in the interstellar medium [13, 14]. Recently Christian Henkel and Karl Menten suggested that these lines can be used for astrophysical search of the time-variation of fundamental constants [15]. There are also several other light molecules with Λ-doubling, who's microwave spectra were observed in the interstellar medium. For example, first extragalactic microwave rotational spectra of NO were observed in [16]. Therefore, we decided to study sensitivities of the Λ-doublet lines to the variation of the fundamental constants in a more systematic way.

Astrophysical studies of variation of 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, [17]). 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

[1] An intermediate timescale ~ 2 Gyr is tested by the Oklo phenomenon [1].

is used to find rest frame frequencies of the other set of observed lines. The logic here is opposite to the one used in the search of the variation of FC. In such a search one looks for the difference in the apparent redshifts of the lines from the same object and compare these differences to the sensitivities of respective lines to variation of the constants. Obviously, such method can work only with true laboratory frequencies.

Recently the laboratory frequencies of all four hyperfine components of the 18 cm line of OH molecule were measured with a record precision ($< 10^{-9}$) [18, 19]. Also, the frequencies of all three components of the lowest Λ-doublet line in CH molecule were recently remeasured in Ref. [20] with the accuracy of 0.1 ppm, or better ($1\,\text{ppm} = 10^{-6}$). This opens possibility to study variation of 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 [7, 10, 21] because Λ-doublet lines are sensitive to variation of 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 of 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 of all three constants.

In this paper we estimate sensitivity coefficients of different Λ-doublet lines to variations of the 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 is sufficient data in the databases of microwave molecular spectra [22, 23, 24]. We use this 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 of FC so that:

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

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 (3) leads to the change in the apparent redshifts of individual lines. The difference in the redshifts of two lines is given by:

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

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 of a single parameter $\mathcal{F}$:

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

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 $\delta z = 10^{-5} \div 10^{-6}$, practically independent on the waveband. Therefore, the sensitivity of astrophysical spectra to variations of FC directly depend on ΔK_i.

In optical waveband sensitivity coefficients are typically on the order of $10^{-2} \div 10^{-3}$, while in microwave and far infrared wavebands 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 wavebands potentially more sensitive to variations of FC, as compared to observations in optical waveband, where because of the lower sensitivity, systematic effects may be significantly larger (for the most recent discussion of the systematic effects see [25] and references therein).

In Sec. II A we briefly recall the theory of Λ- and Ω-doubling 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 variant of effective Hamiltonian from Ref. [26]. 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:

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

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

TABLE I: Frequencies (in MHz) and sensitivity coefficients for Λ-doublet lines ($J, F \to J, F'$) in ^{16}OH. Recommended frequencies and their uncertainties are taken from Ref. [23].

Level	J	F	F'	ω (MHz)				K_α	K_β
				Recom.	Uncert.	Theory	Diff.		
$^2\Pi_{3/2}$	1.5	1	2	1612.2310	0.0002	1595.42	16.81	−1.27	2.61
	1.5	1	1	1665.4018	0.0002	1648.93	16.47	−1.14	2.55
	1.5	2	2	1667.3590	0.0002	1650.66	16.70	−1.14	2.55
	1.5	2	1	1720.5300	0.0002	1704.17	16.36	−1.02	2.49
	2.5	2	2	6030.7485	0.0002	5982.27	48.48	−0.91	2.43
	3.5	3	3	13434.6374	0.0002	13361.09	73.55	−0.68	2.33
	4.5	4	4	23817.6150	0.0020	23764.85	52.77	−0.50	2.24
	5.5	5	5	36983.4700	0.0200	37048.19	−64.72	−0.36	2.18
$^2\Pi_{1/2}$	0.5	0	1	4660.2420	0.0030	4638.98	21.26	2.98	0.50
	0.5	1	1	4750.6560	0.0030	4729.51	21.15	2.96	0.51
	0.5	1	0	4765.5620	0.0030	4744.50	21.06	2.96	0.51
	1.5	1	1	7761.7470	0.0050	7739.66	22.09	3.85	0.07
	2.5	2	2	8135.8700	0.0050	8136.02	−0.15	5.83	−0.91
	3.5	3	3	5473.0450	0.0050	5500.04	−26.99	11.91	−3.92
	4.5	5	4	88.9504	0.0011	64.34	24.61	−921.58	459.86
	4.5	5	5	117.1495	0.0011	92.35	24.80	−699.65	349.59
	4.5	4	4	164.7960	0.0011	141.20	23.60	−496.67	248.77
	4.5	4	5	192.9957	0.0011	169.22	23.78	−424.05	212.68
	5.5	6	6	8534.8600	0.0200	8590.13	−55.27	−11.38	7.66

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.[2] 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 $p = \pm 1$:

$$|J, M, \Omega, p\rangle = \left(|J, M, \Omega\rangle + p\chi|J, M, -\Omega\rangle\right)/\sqrt{2}\,, \qquad (7)$$

where χ is a phase factor. 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-orbital mixing. Operator $H_{\rm Cor}$ can not 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-orbital mixing between Π and Σ states:

$$|\Omega = \tfrac{1}{2}\rangle = |\Lambda = 1, \Sigma = -\tfrac{1}{2}, \Omega = \tfrac{1}{2}\rangle + \zeta|\Lambda = 0, \Sigma = \tfrac{1}{2}, \Omega = \tfrac{1}{2}\rangle, \qquad (8)$$

where $\zeta \sim A/(E_\Pi - E_\Sigma)$, and then

$$\langle\Omega = \tfrac{1}{2}|H_{\rm Cor}|\Omega = -\tfrac{1}{2}\rangle = 2\zeta B(J + \tfrac{1}{2})\langle\Lambda = 1|L_x|\Lambda = 0\rangle. \qquad (9)$$

We conclude that Ω-splitting for the $\Pi_{1/2}$ level must scale as $ABJ/(E_\Pi - E_\Sigma)$.

Ω-doubling for $\Pi_{3/2}$ state takes place in the third order in Coriolis interaction. Here $H_{\rm Cor}$ has to mix first states $\Pi_{3/2}$ with $\Pi_{1/2}$ and $\Pi_{-3/2}$ with $\Pi_{-1/2}$ before matrix element (9) can be used. Therefore, the splitting scales as $B^3J^3/[A(E_\Pi - E_\Sigma)]$ (note, that we use parameter A to estimate Σ - Π mixing ζ and it also determines splitting between $\Pi_{3/2}$ and $\Pi_{1/2}$).

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 $\Lambda = \pm 1$. 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 on A.

We can now use found scalings of the Λ- and Ω-doublings to determine sensitivity coefficients (3). For this we only need to know how parameters A and B

[2] 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.

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:

$$\text{State } {}^2\Pi_{1/2}: \quad K_\alpha = \ \ 2\,, \quad K_\beta = 1\,, \tag{10a}$$

$$\text{State } {}^2\Pi_{3/2}: \quad K_\alpha = -2\,, \quad K_\beta = 3\,. \tag{10b}$$

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

$$\text{State } \Pi: \quad K_\alpha = 0\,, \quad K_\beta = 2\,. \tag{10c}$$

When constant A is only 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 (10) show that this can cause significant changes in sensitivity coefficients. The spin-orbit constant A can be both positive (CH molecule) and negative (OH). The 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 of FC.

B. Intermediate coupling

Λ-doubling for the intermediate coupling was studied in detail in [26] with the help of effective Hamiltonian $H_{\rm eff}$ 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:

$$H_{\rm eff} = H_{\rm sr} + H_{\rm hf}\,. \tag{11}$$

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

$$\langle\Pi^{\pm}_{1/2}|H_{\rm sr}|\Pi^{\pm}_{1/2}\rangle = -\tfrac{1}{2}A + B(J+\tfrac{1}{2})^2 \pm (S_1+S_2)(2J+1)\,, \tag{12a}$$

$$\langle\Pi^{\pm}_{3/2}|H_{\rm sr}|\Pi^{\pm}_{3/2}\rangle = +\tfrac{1}{2}A + B(J+\tfrac{1}{2})^2 - 2B\,, \tag{12b}$$

$$\langle\Pi^{\pm}_{3/2}|H_{\rm sr}|\Pi^{\pm}_{1/2}\rangle = \left[B \pm S_2(J+\tfrac{1}{2})\right] \times \sqrt{(J-\tfrac{1}{2})(J+\tfrac{3}{2})}\,, \tag{12c}$$

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 (12) consist of several terms each with different dependencies on parameters α and β [26]. For this reason we can not 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:

$$\langle\Pi^{\pm}_{1/2}|H_{\rm sr}|\Pi^{\pm}_{1/2}\rangle = C_F\,[2a - b - c \pm (2J+1)d]\,, \tag{13a}$$

$$\langle\Pi^{\pm}_{3/2}|H_{\rm hf}|\Pi^{\pm}_{3/2}\rangle = 3C_F\,[2a + b + c]\,, \tag{13b}$$

$$\langle\Pi^{\pm}_{3/2}|H_{\rm sr}|\Pi^{\pm}_{1/2}\rangle = -C_F\sqrt{(2J-1)(2J+3)}\,b\,, \tag{13c}$$

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

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. (12,13) has 8 parameters. We use NIST values [22] for the fine structure splitting A, rotational constant B, and magnetic hyperfine constants a, b, c, d. 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 $\alpha_0 = 1/137.035999679(94)$ and similarly for K_β and $K_{\rm nuc}$. 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. [26] to Hamiltonian (12) 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 can not 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 have not found any noticeable changes for the sensitivity coefficients. Therefore, we conclude that this simple model is sufficiently accurate for our purposes and currently there

TABLE II: Frequencies and sensitivity coefficients for Λ-doublet lines in ^{12}CH. Recommended frequencies and their uncertainties are taken from Ref. [24].

Level	J	F	F'	ω (MHz)				K_α	K_β
				Recom.	Uncert.	Theory	Diff.		
$^2\Pi_{1/2}$	0.5	0	1	3263.795	0.003	3269.40	−5.61	0.59	1.71
	0.5	1	1	3335.481	0.001	3340.77	−5.29	0.62	1.70
	0.5	1	0	3349.194	0.003	3354.11	−4.92	0.63	1.69
	1.5	1	1	7325.203	0.001	7312.02	13.18	−0.23	2.11
	2.5	2	2	14756.670	0.003	14739.25	17.42	0.00	2.00
	3.5	3	3	24420.628	0.005	24432.60	−11.97	0.07	1.97
$^2\Pi_{3/2}$	1.5	1	2	701.677	0.007	682.96	18.72	−8.66	6.32
	1.5	2	2	703.971	0.031	679.83	24.14	−8.44	6.15
	1.5	1	1	722.491	0.031	702.98	19.51	−8.07	5.97
	1.5	2	1	724.789	0.007	699.85	24.94	−8.37	6.17
	2.5	3	3	4847.761	0.006	4822.08	25.68	−1.42	2.70
	3.5	4	4	11264.978	0.010	11274.97	−9.99	−0.74	2.37

TABLE III: Frequencies (in MHz) and sensitivity coefficients for Λ-doublet lines in ^{7}Li^{16}O. Experimental frequencies and their uncertainties are taken from Ref. [22].

Level	J	F	F'	ω (MHz)				K_α	K_β	$K_{\rm nuc}$
				Exper.	Uncert.	Theory	Diff.			
$^2\Pi_{3/2}$	1.5	2	3	6.95	0.05	6.88	0.07	−4.47	4.22	−0.61
	1.5	1	2	8.55	0.10	8.29	0.26	−3.26	3.57	−0.33
	1.5	3	3	11.28	0.01	11.13	0.15	−1.90	2.93	0.00
	1.5	2	2	11.28	0.01	11.13	0.15	−1.90	2.93	0.00
	1.5	1	1	11.28	0.01	11.13	0.16	−1.90	2.93	0.00
	1.5	2	1	14.00	0.05	13.96	0.04	−1.08	2.53	0.20
	1.5	3	2	15.60	0.02	15.38	0.22	−0.76	2.35	0.27
	1.5	0	1			9.71		−2.54	3.27	−0.15
	1.5	1	0			12.54		−1.46	2.73	0.11
	2.5	2	2	45.02	0.03	44.59	0.43	−1.91	2.94	0.00
	3.5	3	3	112.237	0.002	111.74	0.50	−1.91	2.96	0.00
$^2\Pi_{1/2}$	0.5	2	2			2969.23		2.10	0.95	0.00
	1.5	1	1			5971.35		2.10	0.96	0.00
	2.5	2	2			9078.50		2.11	0.97	0.00
	3.5	3	3	12325.82	0.03	12325.19	0.63	2.13	0.99	0.00

is no need to use more elaborate theory.

As mentioned above, we account for only one nuclear spin and neglect quadrupole hyperfine structure. These simplifications reduce the number of parameters and are not important for molecules ^{12}CH and ^{16}OH. Some caution is necessary when this simplification is used for molecules with the spin $I > 1/2$ (i.e. ^{7}Li^{16}O and ^{14}N^{16}O). Largest corrections can be expected for the low-frequency transitions, where hyperfine energy is not small compared to the transition energy. Even for these transitions corrections should not be large, if one uses experimental frequencies to define sensitivity coefficients (3).

We applied the above method to ^{16}OH, ^{12}CH, ^{7}Li^{16}O, ^{14}N^{16}O, and ^{15}N^{16}O. Results of the calculations are presented in Tables I – V. 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 belong to the coupling case a, while for CH and OH molecules we can expect transition from case a for lower rotational states to case b for higher ones. Because of that sensitivity coefficients for CH and OH molecules significantly deviate from predictions (10) in the transition region, but approach limit (10c) for large J's. On the other hand, the hyperfine structure in LiO and NO is comparable to Ω-doubling in $\Pi_{3/2}$ state. This also causes deviations from Eq. (10b) for low-frequency transitions in LiO and NO. In particular, some transitions become sensitive to variations of $g_{\rm nuc}$. Moreover, for some low-frequency transitions we see strong enhancement of the sensitivity to variation of FC.

Let us check that our calculations reproduce the form of the parameter $\mathcal{F}$, as given by Eq. (1). From Table I we find sensitivity coefficients for the ground state Λ-doublet transitions with $J = \frac{3}{2}$ and $F' = F$ to be: $K_\alpha = -1.14$ and $K_\beta = 2.55$. Hyperfine contribution for the transition frequencies are small here and $K_{\rm nuc} \approx 0$. The

TABLE IV: Frequencies (in MHz) and sensitivity coefficients for Λ-doublet lines in $^{14}N^{16}O$. Experimental frequencies and their uncertainties are taken from Refs. [22, 23].

Level	J	F	F'	ω (MHz)				K_α	K_β	$K_{\rm nuc}$
				Exper.	Uncert.	Theory	Diff.			
$^2\Pi_{1/2}$	0.5	0.5	0.5	205.9510	0.0002	205.97	−0.02	1.95	1.03	−0.73
	0.5	0.5	1.5	225.9357	0.0002	225.94	0.00	1.95	1.02	−0.58
	0.5	1.5	0.5	411.2056	0.0002	411.20	0.01	1.97	1.01	0.13
	0.5	1.5	1.5	431.1905	0.0002	431.17	0.02	1.97	1.01	0.17
	1.5	2.5	2.5	801.1963	0.0002	801.30	−0.11	1.98	1.01	0.11
	2.5	3.5	3.5	1160.7768	0.0003	1160.96	−0.19	1.98	1.01	0.08
	3.5	4.5	4.5	1514.768	0.001	1514.97	−0.20	2.00	1.00	0.07
$^2\Pi_{3/2}$	1.5	1.5	1.5	0.612	0.001	0.86	−0.25	−2.95	4.29	−0.06
	1.5	2.5	2.5	1.029	0.001	0.95	0.08	−1.94	2.82	0.05
	1.5	2.5	1.5	74.931	0.003	75.46	−0.53	2.00	1.01	1.00
	1.5	1.5	2.5	73.286	0.003	73.64	−0.36	2.10	0.96	1.02
	1.5	0.5	0.5			0.81		−2.09	3.05	−0.11
	1.5	1.5	0.5	46.464	0.003	45.57	0.90	1.92	1.00	0.96
	1.5	0.5	1.5			43.90		2.11	0.94	1.02
	2.5	2.5	2.5	3.121	0.001	3.52	−0.40	−2.35	3.43	−0.02
	2.5	3.5	3.5	3.923	0.001	3.74	0.18	−1.98	2.90	0.04
	2.5	1.5	1.5			3.37		−2.08	3.04	−0.06
	2.5	1.5	2.5			27.64		2.61	0.69	1.13
	2.5	2.5	1.5	34.39	0.03	34.53	−0.14	1.68	1.17	0.90
	2.5	2.5	3.5	40.172		39.89	0.28	2.46	0.76	1.08
	2.5	3.5	2.5	47.211	0.001	47.16	0.05	1.77	1.11	0.92
	3.5	2.5	2.5			8.54		−2.07	3.03	−0.05
	3.5	3.5	2.5	31.550	0.004	31.94	−0.39	1.04	1.51	0.73
	3.5	2.5	3.5			14.55		4.72	−0.36	1.61
	3.5	3.5	3.5			8.84		−2.07	3.03	−0.01
	3.5	4.5	3.5	39.221	0.002	38.93	0.29	1.18	1.39	0.76
	3.5	3.5	4.5			20.85		4.02	−0.01	1.43
	3.5	4.5	4.5			9.23		−2.07	3.03	0.03
	4.5	3.5	3.5			17.18		−2.05	3.02	−0.03
	4.5	3.5	4.5			0.62		125.13	−60.56	29.97
	4.5	4.5	3.5	35.045	0.002	35.47	−0.43	0.16	1.94	0.50
	4.5	4.5	4.5			17.67		−2.05	3.02	−0.01
	4.5	4.5	5.5			4.09		21.43	−8.72	5.36
	4.5	5.5	4.5	40.512	0.001	40.03	0.49	0.34	1.80	0.55
	4.5	5.5	5.5			18.27		−2.05	3.03	0.03

reference 21-cm Hydrogen line has $K_\alpha = 2$, $K_\beta = 1$, and $K_{\rm nuc} = 1$. Parameter $\mathcal{F}$ according to Eq. (5) is given by the expression:

$$\mathcal{F} = \alpha^{\Delta K_\alpha}\beta^{\Delta K_\beta} g_{\rm nuc}^{\Delta K_{\rm nuc}} = \alpha^{3.14}\beta^{-1.55} g_{\rm nuc}^1\,, \qquad (14)$$

which is sufficiently close to Eq. (1). Sensitivity coefficients for the ground state $\Pi_{3/2}$, $J \le \frac{7}{2}$ and for the state $\Pi_{1/2}$, $J = \frac{3}{2}$, $\frac{5}{2}$ were calculated in Ref. [12]. For all these states our results are in good agreement with Ref. [12].

Table I shows that sensitivity coefficients depend on the rotational quantum number J. This is caused by decoupling of electron spin $\boldsymbol{S}$ from the molecular axis. For $J = \frac{7}{2}$ we are still far from case b values given by Eq. (10c). Because of that, it is interesting to look at higher rotational excitations. For Λ-doubles of $\Pi_{3/2}$ state we have monotonic approach to limit (10c). For $\Pi_{1/2}$ state the changes are not monotonic and more dramatic. Here the Λ-doubling splitting first grows, then decreases and changes sign at $J = \frac{9}{2}$ (note that tables give transition frequency, which is always positive). Sensitivity coefficients also change sign but their absolute values grow dramatically because they are inversely proportional to the frequency.

The ratio $|A/B|$ for CH molecule is smaller than for OH molecule and decoupling takes place much earlier, near $J = \frac{3}{2}$. Here A is positive and there is no change of sign of the splitting for $\Pi_{1/2}$ state and sensitivity coefficients slowly approach limit (10c). For $\Pi_{3/2}$ state, on the contrary, coefficients appear to be rather large and rapidly change with J. We see that for both molecules with intermediate coupling the doublets, which belong to the upper electronic fine structure state, have larger sensitivity coefficients with stronger dependence on the quantum number J.

Table III presents Λ-doubling spectrum for $^7Li^{16}O$. For this molecule $|A| \gg B$ and electron spin is strongly

TABLE V: Frequencies (in MHz) and sensitivity coefficients for Λ-doublet lines in $^{15}N^{16}O$. Experimental frequencies and their uncertainties are taken from Ref. [22].

Level	J	F	F'	ω (MHz)				K_α	K_β	$K_{\rm nuc}$
				Exper.	Uncert.	Theory	Diff.			
$^2\Pi_{1/2}$	0.5	1	1	290.657	0.0002	290.64	0.02	1.96	1.02	−0.18
	0.5	1	0	309.226	0.0002	309.02	0.21	1.96	1.02	−0.11
	0.5	0	1	482.621	0.0002	482.83	−0.20	1.98	1.01	0.29
	1.5	2	2	622.569	0.0003	622.60	−0.03	1.97	1.01	−0.10
	2.5	3	3	958.918	0.0003	958.95	−0.04	1.98	1.01	−0.07
	3.5	4	4			1294.89		1.99	1.00	−0.05
$^2\Pi_{3/2}$	1.5	2	2	0.780	0.005	0.78	0.00	−2.09	3.04	−0.05
	1.5	1	1			0.87		−2.09	3.05	0.07
	1.5	1	2	84.589	0.002	84.33	0.26	1.99	1.00	0.99
	1.5	2	1			82.67		2.07	0.96	1.01
	2.5	3	3	3.154	0.001	3.15	0.00	−2.08	3.04	−0.03
	2.5	2	2	3.393	0.005	3.39	0.00	−2.08	3.04	0.04
	2.5	2	3	55.738	0.003	55.54	0.19	1.84	1.07	0.94
	2.5	3	2			49.00		2.37	0.82	1.07
	3.5	4	4			7.91		−2.07	3.03	−0.02
	3.5	3	3			8.36		−2.07	3.03	0.03
	3.5	3	4			45.40		1.41	1.29	0.82
	3.5	4	3			29.13		3.36	0.32	1.28
	4.5	5	5			15.83		−2.05	3.02	−0.02
	4.5	4	4			16.54		−2.05	3.02	0.02
	4.5	4	5			44.35		0.71	1.65	0.64
	4.5	5	4			11.98		8.15	−2.08	2.35
	5.5	6	5	6.070	0.0005	6.25	−0.18	−18.25	11.18	−3.60
	5.5	6	6	27.657	0.0005	27.65	0.01	−2.03	3.01	−0.02
	5.5	5	5	28.664	0.0005	28.67	−0.01	−2.03	3.02	0.02
	5.5	5	6	50.251	0.0005	50.07	0.18	−0.07	2.03	0.44
	6.5	7	6	27.335	0.0005	27.53	−0.19	−4.96	4.50	−0.63
	6.5	7	7	44.092	0.0005	44.08	0.01	−2.01	3.00	−0.01
	6.5	6	6	45.461	0.0005	45.47	−0.01	−2.01	3.00	0.02
	6.5	6	7	62.218	0.0005	62.03	0.19	−0.71	2.35	0.28

coupled to the axis. Thus, we can expect Eqs. (10) to be applicable. Indeed, Eq. (10a) works nicely for all Λ-transitions of the $^2\Pi_{1/2}$ state. On the other hand, Eq. (10b) does not work for Λ-transitions with $J = \frac{3}{2}$ and $F' \neq F$ of the $^2\Pi_{3/2}$ state. This is because of the large hyperfine contribution to the transition energy. In fact, for some of these transitions there is strong cancelation between hyperfine energy and the Ω-splitting. This leads to the enhancement of the sensitivity to variation of FC similar to the one discussed by Flambaum [27]. Note, that for these transitions we also have noticeable sensitivity to the nuclear g-factor $K_{\rm nuc}$.

Tables IV and V list results for molecules $^{14}N^{16}O$ and $^{15}N^{16}O$. For these molecules coupling of the electron spin is also strong and general picture is similar to LiO. However, here much more low-frequency transitions are present. Sensitivity coefficients for the latter, including $K_{\rm nuc}$, are rather large. In principle, this opens possibility to make *full experiment* and place model independent bounds on the variation of all three fundamental constants. For this one needs to measure apparent redshifts at least for four lines with different sensitivity coefficients and obtain constrains for three independent combinations $\mathcal{F}$ (see Eq. (5)).

III. DISCUSSION

Tables I – V show that microwave Λ-doubling spectra of light molecules are very sensitive to the variations of FC. Moreover, the sensitivity coefficients strongly depend on quantum numbers J and F, so it is possible to study variation of FC using only lines of one molecule. This is particularly important for astrophysics, where different species may have different velocity distributions, which may lead to systematic frequency shifts.

As we have mentioned above, 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 1.6 GHz lines of OH [18, 19] and for 3.3 GHz lines of CH [20]. These lines can be used for new studies of the variation of 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. Among these lines the 0.7 GHz lines of CH 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 of 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-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 [28]:

$$\frac{\mathrm{d}\beta/\mathrm{d}t}{\beta} = (3.8 \pm 5.6)10^{-14}\,\mathrm{yr}^{-1}\,, \qquad (15)$$

and the limit on α-variation is three orders of magnitude stronger, on the level 10^{-17} [29]. To improve constrained (15) one needs to measure frequency shifts $\delta\omega < K_\beta\omega\delta\beta/\beta$. For the 1.6 GHz OH line this corresponds to the shift $\delta\omega \lesssim 4\times10^{-4}$ Hz. This is few orders of magnitude stronger than the accuracy of the best present measurements [18, 19]. Note, that the large dimensionless sensitivity coefficients (3) may be not sufficient for the laboratory experiments on time-variation. 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 (3), one has to look for large absolute sensitivities $K_i\omega$, which determine absolute frequency shifts $\delta\omega$. In astrophysics, on the contrary, all lines are Doppler-broadened and dimensionless sensitivity coefficients K_i become crucial.

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