Linear polyatomic molecules with $\Pi$ ground state: sensitivity to variation of the fundamental constants

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(Dated: May 5, 2014)

In polyatomic molecules with $\Pi$ electronic ground state the ro-vibrational spectrum can be strongly modified by the Renner-Teller effect. The linear form of $C_3H$ molecule has particularly strong Renner-Teller interaction and a very low lying vibronic $\Sigma^+_{1/2}$ level, which corresponds to the excited bending vibrational mode. This leads to the increased sensitivities of the microwave and submillimeter transition frequencies to the possible variation of the fine structure constant $\alpha$ and electron to proton mass ratio $\mu$.

PACS numbers: 06.20.Jr, 06.30.Ft, 33.20.Bx

I. INTRODUCTION

At present it is generally recognized that microwave and submillimeter molecular spectra from the interstellar medium provide us with a very sensitive tool to study possible variation of the fundamental constants $\alpha = e^2/\hbar c$ and $\mu = m_e/m_p$ on a large space-time scale. It was shown that certain types of transitions are particularly sensitive to such variations. The mixed tunneling-rotational transitions in such molecules as $H_2O^+$, $H_2O_2$, $CH_3OH$, and $CH_3NH_2$ can be very sensitive to $\mu$-variation [1–6]. Recently the submillimeter spectra of methanol have been used to place very stringent limits on $\mu$-variation on the cosmological timescale [5, 7]. On the other hand, the $\Lambda$-doublet transitions in such diatomic radicals, as OH and CH are very sensitive to variation of both constants [8–10]. The 18 cm OH line was observed at high redshifts, which allowed to constrain time variation of both constants [11]. In that work the 21 cm hyperfine hydrogen line was used as a reference. This constrain can be further improved if more than one $\Lambda$-doublet transition in OH, or CH is detected.

A rather general way to look for the enhanced sensitivity to variation of the fundamental constants is to search for the accidental degeneracy of the levels of different nature. This approach works for very different systems from nuclei, to atoms, and molecules (see, for example, the review [12] and [13]).

In this paper we want to draw attention to the microwave and submillimeter spectra of the linear polyatomic radicals with nonzero electronic angular momentum. First, these molecules have $K$-doublets, which are analogous to the $\Lambda$-doublets in diatomics. Second, the Renner-Teller interaction can lead to the anomalously low lying vibronic levels and cause enhanced sensitivities of the mixed ro-vibronic transitions. Finally, there are many linear polyatomic molecules, which are detected in the interstellar medium. In this context one of the most interesting species is the linear $C_3H$ molecule, where the excited vibronic $\Sigma^+_{1/2}$ level lies less than 30 cm$^{-1}$ above the ground level $\Pi_{1/2}$ and where several mixed transitions were recently measured in the molecular beam experiment [14]. Because of that we focus on this molecule here leaving other similar molecules for a separate discussion.

The interstellar carbon-chain radicals of hydrocarbon series $C_nH (n = 2–6)$ exist in linear and cyclic isomeric forms. Both forms are observed in the millimeter-wave range toward dark and translucent molecular clouds and circumstellar envelopes of carbon-rich stars [15–27]. A typical abundance of the linear radical $l-C_3H$, — the simplest odd carbon chain radical under consideration in the present study, — is $\sim 10^{-9}$ relative to hydrogen. The cyclic-to-linear abundance ratio $[c-C_3H]/[l-C_3H] \sim 5–10$ in dark clouds [23, 25], but decreases to $\sim 3$ in translucent clouds [23], and becomes less than unity around carbon stars [27]. The cyclic and linear isomers of $C_3H$ have also been detected in a star-forming region [28] and in two extragalactic sources: the star-burst galaxy NGC 253 [29] and the spiral galaxy located in front of the quasar PKS 1830–211 at the redshift $z = 0.89$ [30]. Thus, $l-C_3H$ lines have been detected in regions with kinetic temperature ranging from $T_{\mathrm{kin}} \sim 10$ K (dark clouds) to several hundred Kelvin (circumstellar envelopes, star-forming regions). The observed line intensities are less or about 0.1 K.

The lines observed from the interstellar medium (ISM) are Doppler broadened, so the linewidth $\Gamma \approx \Gamma_D = \omega \Delta V$, where $\Delta V$ is the velocity distribution for the ISM and $c$ is speed of light. This means that $\frac{\delta \omega}{\omega} \approx \frac{\Delta V}{c}$ characterizes ISM and to a first approximation is independent on the frequency of the transition $\omega$. Because of that for the astrophysical search of the possible variation of the fundamental constants it is crucial to find transitions with high dimensionless sensitivity coefficients defined as:

$$\frac{\delta \omega}{\omega} = Q_\alpha \frac{\delta \alpha}{\alpha} + Q_\mu \frac{\delta \mu}{\mu}. \quad (1)$$

In the optical waveband these sensitivity coefficients are typically of the order of $10^{-2}$. In the microwave waveband they are typically of the order of unity, but can be much bigger. Below we will calculate $Q$ factors for
some microwave and submillimeter transitions of the \( l\)-C\(_2\)H molecule and show that they can reach the order \( 10^4 \). As usual such enhanced sensitivities take place for the low frequency transitions between quasi degenerate levels of different nature.

II. RENNER-TELLER EFFECT

In this section we briefly recall the theory of the Renner-Teller effect in polyatomic linear molecules \([31, 32]\). The total molecular angular momentum \( J \) consists of several contributions. We have the overall rotation of the nuclei \( R \). Then we have the vibrational angular momentum \( G \) associated with the twofold degenerate bending vibration mode(s) and the electronic angular momentum \( L \). Momentum \( R \) is perpendicular to the molecular axis \( \zeta \); two others have \( \zeta \) projections \( l \) and \( \Lambda \). We define momentum \( N = R + G + L \) and its projection \( (N_\zeta) = K + l + \Lambda \). Finally, we add electronic spin: \( J = N + S \), \( (J_\zeta) = \Omega \).

Suppose we have \( \Pi \) electronic state \( | \Lambda = \pm 1 \rangle \) and \( v = 1 \) vibrational state of a bending mode \(| l = \pm 1 \rangle \). All together there are 4 states \(| \pm 1 \rangle | l = \pm 1 \rangle \). We can rewrite them as one doublet \( \Delta \) state \(| K = \pm 2 \rangle \) and states \( \Sigma^+ \) and \( \Sigma^- \). In adiabatic approximation all four states are degenerate. Renner \([31]\) showed that the states with the same quantum number \( K = l + \Lambda \) strongly interact, so \( \Sigma^+ \) and \( \Sigma^- \) states repel from each other, while \( \Delta \) doublet in the first approximation remains unperturbed. We are particularly interested in the case when one of the \( \Sigma \) levels is pushed close to the ground state \( v = 0 \).

This is what takes place in \( l\)-C\(_2\)H molecule \([14, 19, 33]\).

Consider linear polyatomic molecule with unpaired electron in the \( \pi \) state in the molecular frame \( \xi, \eta, \zeta \). Obviously, the bending energy is different for bendings in \( \xi \xi \) and in \( \xi \eta \) planes: \( V_\pm = \frac{1}{2} \kappa \chi^2 \) (here \( \chi \) is the supplement to the bond angle). That means that the electronic energy depends on the angle \( \phi \) between the electron and nuclear planes:

\[ H' = V' \cos 2\phi, \]

where \( 2V' = V_+ - V_- = k' \chi^2 \). There is no reason for \( V' \) to be small, so \( k' \sim k \pm \sim 1 \) a.u. and to a first approximation \( k' \) does not depend on \( \alpha \) and \( \mu \).

As long as interaction \([2] \) depends on the relative angle between electron and vibration it changes angular quantum numbers as follows: \( \Delta \Lambda = -\Delta l = \pm 2 \) and \( \Delta K = 0 \). This is exactly what is necessary to produce splitting between \( \Sigma^+ \) and \( \Sigma^- \) states with \( v = 1 \) as discussed above.

Interaction \([2]\) also mixes different vibrational levels with \( \Delta v = \pm 2, \pm 4, \ldots \). Thus, we have, for example, the nonzero matrix element (ME) \(| 0, 0, 1, 1 | H' | 2, 2, -1, 1 \rangle \) between states \(| v, l, \Lambda, K \rangle \). Such mixings reduce effective value of the quantum number \( \Lambda \) and, therefore, reduce the spin-orbital splitting between \( \Pi_{3/2} \) and \( \Pi_{1/2} \) states \([34]\).

\[ H_{so} \equiv A_{\text{eff}} \Lambda \Sigma, \quad A_{\text{eff}} = AA_{\text{eff}} / \Lambda. \]

Let us define the model more accurately. Following \([31]\) we write Hamiltonian as:

\[ H = H_e + T_v + A \Lambda \zeta S_\zeta. \]

Here “electronic” part \( H_e \) includes all degrees of freedom except for the bending vibrational mode and spin. For \( l\)-C\(_2\)H there are two bending modes, but for simplicity we include second bending mode in \( H_e \) too. Electronic MEs in the |\( \Lambda \rangle \) basis have the form:

\[ \langle \pm 1 | H_e | \pm 1 \rangle = \frac{V_{\pm} + V_{\mp}}{2} = \frac{k'}{2} \chi^2, \]

\[ \langle 1 | H_e | 1 \rangle &= \frac{k'}{2} \chi^2 \exp (\mp 2i\phi). \]

Here \( \chi \) and \( \phi \) are vibrational coordinates for the bending mode. Kinetic energy in these coordinates has the form:

\[ T_v = -\frac{1}{2MR^2} \left( \frac{\partial^2}{\partial \chi^2} + \frac{1}{\chi} \frac{\partial}{\partial \chi} + \frac{1}{\chi^2} \frac{\partial^2}{\partial \phi^2} \right). \]

We can use the basis set of 2D harmonic functions in polar coordinates \( \rho = \chi R \) and \( \phi \) for the mass \( M \) and force constant \( k \):

\[ \psi_{v,l}(\rho, \phi) = R_{v,l}(\rho) \frac{1}{\sqrt{2\pi}} \exp (il\phi). \]

It is important that radial functions are orthogonal only for the same \( l \):

\[ \langle R_{v',l} | R_{v,l} \rangle = \delta_{v',v}. \]

This allows for the nonzero MEs between states with different quantum number \( l \). Averaging operator \([4]\) over vibrational functions we get:

\[ \langle v', l' | H_e + T_v | v, l \rangle = \left[ \omega_v (v + 1) + AA_\zeta \right] \delta_{v',v} \delta_{l',l} \]

\[ + \frac{1}{2} (R_{v'} | k' \chi^2 | R_{v,l}) \exp (\mp 2i\phi) \delta_{v',l \pm 2}. \]

The exponent here ensures the selection rule \( \Lambda' = \Lambda \mp 2 \) for the quantum number \( \Lambda \) when we calculate MEs for the rotating molecule.

We solved eigenvalue problem for Hamiltonian \([4]\) using the basis set of the 2D-harmonic oscillator. Matrix elements were formed according to Eq. (9). As discussed above we neglected one of the bending modes leaving only the one that produces \( K = 0 \) level close to the ground state doublet \( K = 1, \Omega = 1/2, 3/2 \). Our model Hamiltonian has only 3 parameters, namely \( \omega_v \), \( A \), and the dimensionless Renner-Teller parameter \( \tilde{E} = k' / \tilde{E} k \). In Ref. \([33]\) the following values were obtained:

\[ \omega_v = 589 \text{ cm}^{-1}, \quad A = 29 \text{ cm}^{-1}, \quad \tilde{E} = 0.883. \]
We fixed the values for $\omega_v$ and $A$ and varied the Renner-Teller parameter $E$ to fit five lowest levels for the given bending mode: $\Pi_{1/2}$, $\Pi_{3/2}$, $\Sigma_{1/2}$, $\Delta_{3/2}$, and $\Delta_{5/2}$. The optimal value appeared to be $E = 0.788$. The difference with (10) is probably due to the neglect of the anharmonic corrections and second bending mode.

Our results are presented in Table I. The first two columns give nominal vibrational quantum number $v$ and its actual average value. We see that Renner-Teller term in (9) strongly mixes vibrational states. This mixing also affects $(\Lambda)$ and decreases spin-orbital splittings as explained by Eq. (3).

| $v_{\text{nom}}$ | $\langle v \rangle$ | $\langle \Lambda \rangle$ | $E$ | $\Delta$ | $Q_\alpha |Q_\mu$ | $\omega$ |
|----------------|-----------------|----------------|-----|-------|---------------|-----|
| 0              | 1.22            | 0.5            | 50  | 0.3765| 187.8 -14.6  | 18.78 |
| 1              | 1.35            | 1.5            | 0.46| 381.9 | 13.9         | 14.0 |
| 0              | 2.32            | 0.5            | -0.3942| 26.3| 27.0         | 197.3 |
| 1              | 3.57            | 1.5            | 0.21| 597.7 | 229.7        | 266.0 |
| 1              | 3.65            | 2.5            | 0.19| 603.5 | 235.5        | 232.0 |

The last two columns in Table I give sensitivity coefficients $q_\alpha$ and $q_\mu$ in cm$^{-1}$:

$$\delta E = q_\alpha \frac{\delta \alpha}{\alpha} + q_\mu \frac{\delta \mu}{\mu}.$$  

To get them we assumed that parameters (10) scale in a following way: $\omega_v \sim \mu^{1/2}$, $A \sim \alpha^2$, and $E$ does not depend on $\alpha$ and $\mu$. The dimensionless sensitivity coefficients (1) for the transitions $\omega_{i,k} = E_k - E_i$ can be found as:

$$Q_{i,k} = (q_k - q_i)/\omega_{i,k}.$$  

In Table II these coefficients are calculated for the same set of parameters as in Table I and for the slightly different parameters which better fit experimental frequencies from Ref. [14]. We see that $Q$-factors are practically the same for both sets.

| $K$ | $\Omega$ | $K'$ | $\Omega'$ | $Q_\alpha$ | $Q_\mu$ | $\omega$ |
|-----|---------|------|----------|------------|---------|-------|
| 1   | 0.5     | 1    | 1.5      | 13.9       | 14.0    | 2.00  |
| 1   | 1.0     | 0.5  | 12.4     | 0.78       | -1.11   | 13.3  |
| 0.5 | 0.5     | 1    | 2.035    | 0.51       | -0.03   | 204.4 |
| 2    | 1.5     | 2.5  | 5.8      | 0.00       | 2.00    | 6.0   |

Numerical values for these parameter will be obtained from the fit to experimental transition frequencies. Here we only need to determine the dependence of these parameters on fundamental constants. Table II shows that $A_{\text{eff}} \sim \alpha^2$ and $\Delta E_{\Sigma \Pi} \sim \mu^{1/2}$. Once again, this is because the Renner-Teller mixing depends on the dimensionless parameter $E$ and does not depend on $\alpha$ and $\mu$.

### III. EFFECTIVE HAMILTONIAN FOR ROTATING MOLECULE

In this section we mostly follow Ref. [14]. However, we prefer to use the basis set for the Hund’s case “a” as we did before in [10, 35]. We define the effective Hamiltonian for the subspace of the three lowest vibronic states $\Pi_{1/2}$, $\Pi_{3/2}$, and $\Sigma_{1/2}$. We neglect hyperfine interaction and some minor centrifugal corrections included in [14].

The basis ro-vibronic states for the Hund’s case “a” have the form:

$$|v, l, \Lambda, (K), S, \Sigma, J, \Omega, M\rangle = |v, l|\Lambda\rangle|S, \Sigma\rangle|J, \Omega, M\rangle.$$  

Here the quantum number $K$ does not appear explicitly, being defined as $K = l + \Lambda$. From these basic states we form parity states as described in [36]:
\[ |\Pi_{1/2}\rangle = |0, 0, 1, (1), \frac{1}{2}, -\frac{1}{2}, J, \frac{1}{2}, M, p\rangle = \frac{1}{\sqrt{2}}|0, 0\rangle \left( |\frac{1}{2}, -\frac{1}{2}\rangle J, \frac{1}{2}, M\rangle + \chi_p | -1\rangle |\frac{1}{2}, \frac{1}{2}\rangle J, -\frac{1}{2}, M\rangle \right), \]  
\[ |\Pi_{3/2}\rangle = |0, 0, 1, (1), \frac{1}{2}, -\frac{1}{2}, J, \frac{3}{2}, M, p\rangle = \frac{1}{\sqrt{2}}|0, 0\rangle \left( |\frac{1}{2}, \frac{1}{2}\rangle J, -\frac{3}{2}, M\rangle + \chi_p | -1\rangle |\frac{1}{2}, -\frac{1}{2}\rangle J, -\frac{1}{2}, M\rangle \right), \]  
\[ |\Sigma_{1/2}^{+}\rangle = |1, 1, 1, (0), \frac{1}{2}, \frac{1}{2}, J, \frac{1}{2}, M, p\rangle = \frac{1}{2} \left( |1, 1\rangle - |1, -1\rangle \right) \left( |\frac{1}{2}, \frac{1}{2}\rangle J, \frac{1}{2}, M\rangle + \chi_p |\frac{1}{2}, -\frac{1}{2}\rangle J, -\frac{1}{2}, M\rangle \right), \]  

where the parity dependent phase is \( \chi_p = (-1)^{J-S} p \).

We can write rotational energy by adding vibrational angular momentum \( \mathbf{G} \) to the usual expression:

\[
H_{\text{rot}} = B(J - \mathbf{G} - \mathbf{L} - \mathbf{S})^2 = B[J(J + 1) - \Omega^2] - 2B \sum_{q=\pm 1} [J_q G_q + J_q L_q + J_q S_q]
+ G_q L_{-q} + G_q S_{-q} + L_q S_{-q}
- B \sum_{q=\pm 1} [G_q G_{-q} + L_q L_{-q} + S_q S_{-q}] \tag{15c}
\]

Here we use the recipe from [36] that in the molecular frame all scalar products involving total angular momentum \( \mathbf{J} \) are written as \( J_q X_q \) rather than \((-1)^q J_q X_{-q}\). The last line [15c] can be skipped as it gives a constant independent of \( J, \Omega, \) and \( p \). The terms in [15b] linear in \( L_q \) turn to zero in the subspace \( \Lambda = \pm 1 \). We are left with the following operator for the rotational energy:

\[
H_{\text{rot}} = B[J(J + 1) - \Omega^2] - D[J(J + 1) - \Omega^2]^2 - 2B \sum_{q=\pm 1} [J_q G_q + J_q S_q + G_q S_{-q}], \tag{16}
\]

where we added standard centrifugal correction to the main diagonal term.

It is straightforward to calculate MEs of this operator on the states [12] – [14]. The term \( J_q S_q \) does not change quantum number \( l \) and can not mix \( \Sigma \) and \( \Pi \) states. The nonzero matrix elements are:

\[
\langle \Pi_{1/2} | -2BJ_q S_q | \Pi_{1/2}\rangle = -B \sqrt{(J - \frac{1}{2})(J + \frac{3}{2})}, \tag{17}
\]

\[
\langle \Sigma_{1/2}^{+} | -2BJ_q S_q | \Sigma_{1/2}^{+}\rangle = -B \chi_p (J + \frac{1}{2}). \tag{18}
\]

The operator \( J_q G_q \) changes quantum number \( l \) by one and mixes \( \Pi \) and \( \Sigma \) states:

\[
\langle \Sigma_{1/2}^{+} | -2BJ_q G_q | \Pi_{1/2}\rangle = -\beta \chi_p (J + \frac{1}{2}), \tag{19}
\]

\[
\langle \Sigma_{1/2}^{+} | -2BJ_q G_q | \Pi_{1/2}\rangle = \beta \sqrt{(J - \frac{1}{2})(J + \frac{3}{2})}, \tag{20}
\]

where \( \beta \) is defined as

\[
\beta = B(l = 1)G_1(l = 0). \tag{21}
\]

This ME can not be calculated within this formalism and is included as an independent parameter of the effective

Hamiltonian (see also Sec. IV). Finally, the term \( G_q S_{-q} \) mixes \( \Sigma \) and \( \Pi \) states, but can not change the quantum number \( \Omega \):

\[
\langle \Sigma_{1/2}^{+} | -2BG_q S_{-q} | \Pi_{1/2}\rangle = -\beta. \tag{22}
\]

In addition to the rotational energy the effective Hamiltonian must include spin-orbit interaction \( \mathbf{G} \), the energy splitting between \( \Sigma \) and \( \Pi \) states \( \Delta E_{\Sigma\Pi} \), and spin-rotation interaction. Following [36] we write the latter as:

\[
\gamma (\mathbf{NS}) = \gamma (\mathbf{J} - \mathbf{S}) \mathbf{S} = \gamma \left( \Omega \Sigma + \sum_{q=\pm 1} J_q S_q - S(S + 1) \right). \tag{23}
\]

The nontrivial part of this interaction is now reduced to the MEs [17] and [18].

Equations [16] – [22] show that the Coriolis terms involving vibrational angular momentum \( \mathbf{G} \) lead to the \( K \)-doubling via interaction between \( \Sigma \) and \( \Pi \) states. In contrast to the terms involving electronic angular momentum \( \mathbf{L} \) we do not need mixing with excited electronic states. Still, because of the relative smallness of the parameter \( \beta \) in [21], these latter terms can not be neglected. They have exactly the same form as for diatomic molecules and are defined in Ref. [36].

Transition amplitudes between spin-rotational states of the \( l \)-C3H molecule are expressed through MEs of the dipole moment operator \( \mathbf{D} \) on the basic states [12] – [14]. Generally speaking there are both diagonal and nondiagonal MEs in vibrational quantum numbers \( v, l \). Let us estimate them using atomic units (\( \hbar = m_e = |e| = 1 \)).

In the molecular frame the diagonal ME is reduced to the dipole moment of the molecule along the molecular axis \( \langle v, l | D \xi | v, l \rangle \approx D \). If we assume that the charge of the hydrogen atom in the molecule is \( q \), then \( D \sim 2qR_0 \sim 4q \), where \( R_0 \) is the bond length. Comparing this estimate with calculated value \( D = 1.40 \) [37] we get \( q = 0.35 \). Now we can estimate the nondiagonal ME: \( \langle 0, 0 | D_1 | -1 \rangle \sim q_\xi \sim q/\sqrt{M \omega} \sim q M^{-1/4} \sim 0.1q \sim 0.04 \), where \( \xi \) is the amplitude of the vibration and \( M \sim 10^4 \) is the reduced mass for this vibration mode. We conclude that nondiagonal MEs are much smaller than diagonal, so we will neglect them.

In this approximation we get the following expressions...
for the reduced MEs on the basis states \([12] - [14]\):

\[
\langle X, J', p' | D | Y, J, p \rangle = \delta_{X,Y} (-1)^{J'-\Omega} \sqrt{(2J'+1)(2J+1)} \left( J' \begin{array}{cc} 1 & 0 \\ \Omega & \Omega \end{array} \right) \frac{1-p'p}{2},
\]

where \(X\) and \(Y\) denote either \(\Pi\) or \(\Sigma\) state. Below we use these expressions and theoretical value \(D = 1.40\) a.u. \([37]\) to estimate reduced MEs for the microwave transitions in \(\text{I}-\text{C}_3\Pi\). The Einstein coefficients \(A\) for these transitions can be found as \([35]\):

\[
A_{i \rightarrow j} = \frac{4\omega_{ij}^3}{3\hbar c} \frac{|\langle i | D | j \rangle|^2 a_0^2}{2J_i + 1},
\]

where reduced ME is in a.u. and \(a_0\) is the Bohr radius.

**IV. SCALING OF THE PARAMETERS OF THE EFFECTIVE HAMILTONIAN WITH \(\alpha\) AND \(\mu\)**

Effective Hamiltonian described in Sec. \([13]\) is essentially equivalent to the one used in Ref. \([14]\). We included centrifugal corrections to most of the terms using the same definitions as in \([14]\). For the hyperfine structure we used usual parameters \(a\), \(b\), \(c\), and \(d\). Note that in \([14]\) the constant \(b_F = b + c/3\) was used instead of \(b\).

In this section we discuss how the parameters of the effective Hamiltonian depend on the constants \(\alpha\) and \(\mu\) (see Table \([3]\)). The scaling of the two largest parameters, \(\Delta E_{\Sigma\Pi} \sim \alpha^2\) and \(\Delta E_{\Pi\Sigma} \sim \alpha^2\), has been already discussed in Sec. \([1]\). The rotational constants \(B_\Sigma\) and \(B_\Pi\) linearly depend on \(\mu\). The spin-rotational interaction \([23]\) appears from the second order cross term in Coriolis and spin-orbit interactions, therefore \(\gamma \sim \alpha^2\mu\). For \(\Pi\) states there are two additional terms of the spin-rotational interaction with parameters \(p\) and \(q\). The first of them has the same scaling, as \(\gamma\), i.e. \(p \sim \alpha^2\mu\). The second term is quadratic in Coriolis interaction, so \(q \sim \mu^2\). These scalings are obvious from the expressions on pp. 362 and 531 of \([36]\).

Let us now discuss the parameter \(\beta\) defined by \([21]\). It is proportional to the non-diagonal ME \((1|G_1|0)\). According to Eq. (13) in \([32]\), the perpendicular component \(G_1\) simultaneously depends on the vibrational coordinates of the bending \((v_b)\) and stretching \((v_s)\) modes. In the harmonic approximation it has nonzero MEs only between different stretching vibrational states, i.e.:

\[\langle v_b = 1, v_s = 1 | G_1 | v_b = 0, v_s = 0 \rangle \neq 0.\]

The ME in \([21]\) is diagonal in stretching quantum number \(v_s\). It is nonzero due to the anharmonic corrections which mix vibrational modes. Such corrections appear in the first order of the adiabatic perturbation theory and are proportional to the adiabatic expansion parameter \(\mu^{1/4}\). Thus we can expect that \(\beta \sim 0.1B\). This estimate agrees well with the numerical value obtained in Sec. \([7]\). We conclude that \(\beta \sim \mu^{1/4}B \sim \mu^{5/4}\).

### Table III: Parameters of the effective rotational Hamiltonian and their scaling with \(\alpha\) and \(\mu\)

| Param. | This work | Ref. [14] | Units | Scaling |
| --- | --- | --- | --- | --- |
| \(\Delta E_{\Sigma\Pi}\) | 609.9811 | 609.9742 | GHz | \(\alpha^0\mu^{1/2}\) |
| \(B_\Sigma\) | 11.2124327 | 11.2126703 | GHz | \(\alpha^3\mu^0\) |
| \(D_\Sigma\) | 4.548 | 4.867 | kHz | \(\alpha^0\mu^4\) |
| \(\gamma_\Sigma\) | -35.800 | -35.525 | MHz | \(\alpha^0\mu^4\) |
| \(\gamma_\Sigma, p\) | 18.04 | 0.549 | kHz | \(\alpha^3\mu^0\) |
| \(c_\Sigma\) | -6.3 | -6.29 | MHz | \(\alpha^0\mu^4\) |
| \(c_\Sigma\) | 31.8 | 27.17 | MHz | \(\alpha^0\mu^4\) |
| \(A_{\text{eff}}\) | 432.7762 | 432.7898 | GHz | \(\alpha^0\mu^2\) |
| \(B_\Pi\) | 11.1892055 | 11.1891033 | GHz | \(\alpha^0\mu^2\) |
| \(D_\Pi\) | 5.356 | 5.3240 | kHz | \(\alpha^3\mu^0\) |
| \(\gamma_\Pi\) | -48.652 | -48.075 | MHz | \(\alpha^0\mu^4\) |
| \(\gamma_\Pi, p\) | 21.670 | 0.000 | kHz | \(\alpha^3\mu^0\) |
| \(p\) | -6.9021 | -7.0681 | MHz | \(\alpha^0\mu^4\) |
| \(q\) | -1.595 | 0.504 | kHz | \(\alpha^3\mu^0\) |
| \(q_D\) | -12.8556 | -12.9922 | MHz | \(\alpha^0\mu^4\) |
| \(q_D\) | -0.443 | -0.1432 | kHz | \(\alpha^3\mu^0\) |
| \(\beta\) | 1.2586 | 1.2342 | GHz | \(\alpha^0\mu^{1/4}\) |
| \(\beta_D\) | -28.3 | -19.2 | kHz | \(\alpha^0\mu^{1/4}\) |
| \(a_\Pi\) | 12.43 | 12.32 | MHz | \(\alpha^0\mu^4\) |
| \(b_\Pi\) | -22.57 | -23.04 | MHz | \(\alpha^0\mu^4\) |
| \(c_\Pi\) | 27.56 | 28.07 | MHz | \(\alpha^0\mu^4\) |
| \(d_\Pi\) | 16.21 | 16.26 | MHz | \(\alpha^0\mu^4\) |

Our effective Hamiltonian includes centrifugal corrections \((D, \gamma_\Pi, \beta_D, \text{etc.})\) to the most important terms. We assume that such corrections have the same \(\alpha\) dependence as the respective main term and an extra power in their \(\mu\) dependence. The magnetic hyperfine constants scale as the product of the nuclear and electronic magnetic moments, i.e. \(\alpha^2\mu\).

All scalings discussed above are approximate. There are relativistic corrections to all parameters, which modify their \(\alpha\)-dependence. These corrections are of the order of \((\alpha Z)^2 \sim 0.2\%\). The \(\mu\) dependence of parameters is changed by non-adiabatic corrections. To illustrate this point let us consider the rotational constants \(B\). To a first approximation the small difference between \(B_\Sigma\) and \(B_\Pi\) can be related to the vibrational corrections to the adiabatic value of the rotational constant \(B_0\).

We can use the data from Table \([1]\) and Table \([3]\) to estimate vibrational correction to the rotational constant:

\[
B_\Sigma = B_0 - \alpha (v + 1), \quad \text{(26)}
\]

\[
B_0 = \frac{(v_\Sigma + 1)B_\Pi - (v_\Sigma + 1)B_\Sigma}{v_\Sigma - v_\Pi} = 11137.1 \text{ MHz}, \quad \text{(27)}
\]

\[
\alpha = \frac{B_\Pi - B_\Sigma}{v_\Sigma - v_\Pi} = -22.8 \text{ MHz}. \quad \text{(28)}
\]

If we assume that \(B_0\) scales as \(\mu\) and \(\alpha\) scales as \(\mu^{3/2}\) \([3]\), we get following scalings of the rotational constants from Table \([3]\):

\[
B_\Sigma \sim \mu^{1.010}, \quad B_\Pi \sim \mu^{1.007}. \quad \text{(29)}
\]
Note that we neglected other vibrational degrees of freedom, so actual corrections can be somewhat bigger. We conclude that we know the scalings of the main parameters from Table III roughly to a percent accuracy. Further improvement of this accuracy requires extensive ab initio calculations.

V. NUMERICAL RESULTS FOR ROTATING MOLECULE

Our effective Hamiltonian has 22 parameters listed in Table III including 6 parameters for the hyperfine structure. The 16 non-hyperfine parameters were fitted using simplex method to the 44 experimentally observed transitions from Ref. [14] and to 12 experimental frequencies listed in the NIST database [39]. We added 8 theoretically predicted transitions for lower rotational quantum numbers from the same database to be sure we adequately reproduce this part of the spectrum.

In our fit the rms deviation for 64 fitted transition is 0.23 MHz with maximum deviation 0.52 MHz. This accuracy is lower than typical accuracy of the similar fits in the literature, but is absolutely sufficient for our purposes. Our main goal here is to calculate sensitivity coefficients for different transitions to the variation of the fundamental constants. Though the sufficiently complex effective Hamiltonians allow for very accurate predictions of the transition frequencies, the accuracy they can provide for the sensitivity coefficients is limited by the uncertainty in the dependence of the used parameters on the fundamental constants (see Sec. IV and [5]).

To fit the hyperfine structure parameters we used 30 lines from the Ref. [19] and 12 K-doublet transitions from [40]. The hyperfine structure is mostly too small to change the values of the sensitivity coefficients. This in not true only for several K-doublet transitions with frequencies $\lesssim 100$ MHz, comparable to the hyperfine splittings. We used the scalings from Table III to calculate the shifts of the spin-rotational levels due to the change

| $J\rightarrow J + 1$ transitions for $\Pi_{3/2}$ state | $J', p'$ | $J, p$ | $\omega$ | $Q_\alpha$ | $Q_\mu$ | $||D||^2$ |
|---|---|---|---|---|---|---|
| $2\frac{1}{2} - 0\frac{1}{2} + 22462.22$ | 0.00(0) 1.00(1) | 0.93 |
| $2\frac{1}{2} - 0\frac{1}{2} + 22420.66$ | 0.00(0) 1.00(1) | 1.87 |
| $2\frac{1}{2} - 1\frac{1}{2} - 44888.43$ | 0.00(0) 1.00(1) | 1.87 |
| $2\frac{1}{2} - 1\frac{1}{2} - 44853.34$ | 0.00(0) 1.00(1) | 3.36 |
| $23\frac{3}{2} - 22\frac{3}{2} + 517808.87^*$ | 0.05(0) 1.02(1) | 26.02 |
| $24\frac{3}{2} + 23\frac{3}{2} - 538178.20$ | 0.00(0) 1.00(1) | 32.57 |
| $24\frac{3}{2} + 23\frac{3}{2} - 542975.34$ | 0.11(0) 1.07(2) | 19.58 |
| $25\frac{3}{2} - 24\frac{3}{2} + 560575.62$ | 0.00(0) 1.00(1) | 33.93 |
| $25\frac{3}{2} - 24\frac{3}{2} + 540680.86$ | -0.11(1) 1.01(2) | 18.11 |
| $26\frac{3}{2} + 25\frac{3}{2} - 586696.44$ | -0.07(0) 0.94(1) | 23.27 |

† Transitions detected at the redshift $z = 0.89$ in Ref. [20].
* Transitions observed in Ref. [14].
of the constants $\alpha$ and $\mu$ by $\pm 0.1\%$. After that we found dimensionless sensitivities $Q_\alpha$ and $Q_\mu$ for the transitions described by the effective Hamiltonian.

There are three manifolds of levels, which belong to the vibronic states $\Pi_{1/2}$, $\Pi_{3/2}$, and $\Sigma_{1/2}$ (see Fig. [4]). According to [24] the strongest transitions take place between levels of the same manifold. The higher frequency transitions correspond to the change of the rotational quantum number $J \rightarrow J + 1$ (see Table [IV]). Such transitions usually have $Q_\alpha \approx 0$, $Q_\mu \approx 1$ [11]. We see that this is also true for $l$-C$_3$H.

For the $\Pi_{1/2}$ and $\Pi_{3/2}$ manifolds there is weak monotonic dependence of the sensitivities on $J$. This dependence is caused by the Coriolis interaction between these manifolds. For the upper part of the $\Pi_{3/2}$ spectrum we see some irregularities in sensitivities. They are caused by the resonant interactions with the nearby levels of the $\Sigma_{1/2}$ manifold, where similar irregularities are observed for $N \geq 22$. All these irregularities are weak because interaction energy is much smaller than respective transition frequencies.

For the $\Pi$ states there are also lower frequency transitions between the levels of different parity with the same

| $J F' J', F_p$ | $\omega$ | $Q_\alpha$ | $Q_\mu$ | $||D||^2$ |
|----------------|---------|-----------|--------|---------|
| 1/2, 0, $-1$  | 52.37   | 0.66(2)   | 1.7(2) | 0.333   |
| 0, 1, $-1$    | 39.12   | 0.20(2)   | 1.9(2) | 0.333   |
| 1, 0, $-1$    | 34.93   | -0.02(2)  | 2.0(2) | 0.667   |
| 1, 1, $+1$    | 85.55   | 0.65(2)   | 1.7(1) | 0.166   |
| 2, 1, $+1$    | 78.60   | 0.55(2)   | 1.7(1) | 0.033   |
| 1, 2, $+1$    | 75.23   | 0.43(2)   | 1.8(1) | 0.033   |
| 2, 2, $+1$    | 68.29   | 0.30(2)   | 1.8(1) | 0.299   |
| 2, 2, $-2$    | 107.19  | 0.95(2)   | 1.5(1) | 0.132   |
| 3, 2, $-2$    | 98.97   | 0.89(2)   | 1.5(1) | 0.009   |
| 2, 3, $-2$    | 98.83   | 0.82(2)   | 1.6(1) | 0.009   |
| 3, 3, $-2$    | 90.61   | 0.75(2)   | 1.6(1) | 0.188   |
| 3, 3, $+3$    | 112.38  | 1.63(2)   | 1.2(1) | 0.105   |
| 4, 4, $+3$    | 96.07   | 1.56(2)   | 1.2(1) | 0.136   |
| 4, 4, $-4$    | 95.75   | 3.22(4)   | 0.36(7) | 0.086 |
| 5, 5, $-4$    | 79.63   | 3.45(4)   | 0.23(7) | 0.105 |
| 5, 5, $+3$    | 52.81   | 9.1(6)    | -6.3(6) | 0.072 |
| 5, 5, $+6$    | 36.85   | 12.1(6)   | -4.1(3) | 0.085 |
| 6, 6, $+5$    | 8.25    | -34.2(2)  | 19.2(2) | 0.062 |
| 7, 7, $+5$    | 36.06   | -18.2(2)  | 11.2(2) | 0.071 |
| 7, 7, $+7$    | 126.59  | -7.6(2)   | 5.8(4)  | 0.054 |
| 8, 8, $+7$    | 142.24  | -6.5(2)   | 5.3(4)  | 0.061 |
| 8, 8, $+8$    | 268.76  | -4.7(1)   | 4.4(3)  | 0.047 |
| 9, 9, $+7$    | 284.25  | -4.3(1)   | 4.2(3)  | 0.053 |
| 9, 9, $+9$    | 448.75  | -3.5(7)   | 3.8(3)  | 0.042 |
| 10, 10, $+9$  | 464.07  | -3.39(7)  | 3.7(3)  | 0.046 |
| 10, 10, $+11$ | 668.02  | -2.97(6)  | 3.5(3)  | 0.038 |
| 11, 11, $+11$ | 683.18  | -2.85(6)  | 3.4(3)  | 0.041 |

| $J F' J', F_p$ | $\omega$ | $Q_\alpha$ | $Q_\mu$ | $||D||^2$ |
|----------------|---------|-----------|--------|---------|
| 1/2, 1, $+1$  | 5.61    | -2.63(8)  | 3.2(2) | 1.493   |
| 2/2, -1, $+1$ | 18.50   | 0.49(8)   | 1.7(2) | 0.299   |
| 2/2, 2, $-2$  | 7.30    | 5.28(8)   | -0.6(2) | 0.299 |
| 2/2, 2/2, $-2$| 5.58    | -2.63(8)  | 3.2(2) | 2.688   |
| 3/2, -2, $+2$ | 22.24   | -2.60(8)  | 3.2(2) | 1.186   |
| 3/2, 3/2, $+2$| 31.50   | -1.35(8)  | 2.6(2) | 0.085   |
| 3/2, 3, $+3$  | 12.88   | -5.67(8)  | 4.6(2) | 0.085   |
| 3/2, 3, $+3$  | 22.15   | -2.60(8)  | 3.2(2) | 1.694   |
| 3/2, 3/2, $+3$| 54.92   | -2.57(8)  | 3.2(2) | 0.943   |
| 4/2, 4, $+4$  | 54.76   | -2.57(8)  | 3.2(2) | 1.223   |

For the $\Pi_{3/2}$ states there are also lower frequency transitions between the levels of different parity with the same

$J$ ($K$-doubling). For diatomic radicals such transitions are known to be very sensitive to the variation of both constants [8][10]. Electron spin gradually decouples from the molecular axis with growing rotational energy. As a result, the $\Omega$-doubling for low $J$ values transforms to $\Lambda$-doubling for higher $J$s. In our case the electronic quantum number $\Lambda$ is substituted by the vibronic quantum number $K$, otherwise the effects are rather similar (see Tables [V] and [VI]). Decoupling of the electron spin happens around $J = \frac{15}{2}$ and causes the anomaly in sensitivities for the $\Pi_{1/2}$ doublets around $J = \frac{15}{2}$, where the frequency drops below 50 MHz. For the $l$-C$_3$H molecule we can expect additional anomalies in sensitivities due to the proximity and strong interaction of $\Pi$ and $\Sigma$ states [35]. One such anomaly is caused by the resonance between the levels $\Pi_{3/2}$ and $\Sigma^+_{1/2}$ with $J \approx \frac{17}{2}$. The tran-
sition frequency is higher here, about 1 GHz, but this is much smaller than for the neighboring rotational states.

The hyperfine structure is much larger for the K-doubllets of the $\Pi_{1/2}$ state. For this reason we do not neglect the hyperfine structure in Table V. For high $J$ values the transitions with $\Delta F \neq 0$ are strongly suppressed, so we list only transitions with $\Delta F = 0$. In Table VI the hyperfine splitting is neglected for all but the first few transitions. For transitions with $J \geq \frac{3}{2}$ the sensitivity coefficients for the hyperfine components of the transition are practically the same.

Because of the mixings [17] – [22] of the basic states there are also weaker transitions between $\Pi_{1/2}$, $\Pi_{3/2}$, and $\Sigma_{1/2}^\pm$ manifolds. Examples of such transitions are listed in Tables VII VIII. Sensitivities of these transitions depend on the quantum numbers in a less regular manner, than sensitivities within each manifold.

All transitions in Table VII have frequencies higher than 100 GHz. Because of that the sensitivity coefficients are not very high, but they are dispersed within intervals $0 \lesssim Q_\alpha \lesssim 4$ and $-1 \lesssim Q_\mu \lesssim 1$. Note that in order to study possible variations of fundamental constants we need to compare several transitions with different sensitivities. Thus, such a spread in sensitivities can be very useful [11].

In Table VIII there are several low frequency transitions with very high sensitivities. Among them there are few with sufficiently high transition amplitudes. In particular, there are three rather strong transitions at 27.6 GHz, 25.1 GHz, and 10.5 GHz with sensitivities $Q_\alpha$ from −5 to +19 and $Q_\mu$ from −3 to +11. This is comparable to the sensitivities of the K-doubllet transitions from Tables IV and VI but for higher transition frequencies.

| $N' J' p'$ | $J p$ | $\omega$ | $Q_\alpha$ | $Q_\mu$ | $|D|^2$ |
|------------|-------|----------|----------|--------|--------|
| 15 $\rightarrow$ 13 | 0.30(2) | −0.50(0) | 0.41 |
| 15 $\rightarrow$ 13 | 0.14(1) | 0.43(1) | 0.87 |
| 15 $\rightarrow$ 13 | 3.10(2) | −0.51(0) | 0.40 |
| 15 $\rightarrow$ 13 | 1.05(2) | 0.15(0) | 1.20 |
| 15 $\rightarrow$ 13 | 0.43(0) | 0.84 |
| 15 $\rightarrow$ 13 | 3.45(2) | −0.71(1) | 2.31 |
| 15 $\rightarrow$ 13 | 0.14(1) | 0.43(1) | 5.46 |
| 15 $\rightarrow$ 13 | 0.64(1) | 0.68(1) | 3.30 |
| 15 $\rightarrow$ 13 | 3.61(3) | −0.81(1) | 2.24 |
| 15 $\rightarrow$ 13 | 1.13(1) | 0.43(1) | 5.49 |
| 15 $\rightarrow$ 13 | 0.66(1) | 0.67(0) | 3.20 |
| 15 $\rightarrow$ 13 | 2.91(2) | −1.01(1) | 3.92 |
| 15 $\rightarrow$ 13 | 0.67(1) | 0.67(0) | 12.80 |
| 15 $\rightarrow$ 13 | 0.34(1) | 0.82(1) | 6.63 |
| 15 $\rightarrow$ 13 | 4.22(4) | −1.18(2) | 5.69 |
| 15 $\rightarrow$ 13 | 0.64(1) | 0.63(1) | 10.93 |
| 15 $\rightarrow$ 13 | 0.36(1) | 0.81(1) | 7.01 |

Table VIII: Frequencies (MHz), $Q$-factors and reduced MEs (a.u.) of some transitions $\Pi_{1/2}$ $J p$ $\rightarrow$ $\Pi_{1/2}$ $J p'$. Negative frequency means that final state lies lower.

| $N' J' p'$ | $J p$ | $\omega$ | $Q_\alpha$ | $Q_\mu$ | $|D|^2$ |
|------------|-------|----------|----------|--------|--------|
| 14 $\rightarrow$ 12 | −150987.95 | 2.00(2) | 1.90(7) | 0.10 |
| 16 $\rightarrow$ 14 | 535601.40* | −0.60(1) | 0.73(1) | 0.14 |
| 16 $\rightarrow$ 14 | 535512.07 | −0.60(1) | 0.73(1) | 0.11 |
| 16 $\rightarrow$ 14 | 161892.90 | −1.96(2) | 0.12(7) | 0.21 |
| 15 $\rightarrow$ 13 | −200166.07 | 1.55(2) | 1.74(6) | 0.14 |
| 14 $\rightarrow$ 12 | 540214.36* | −0.58(1) | 0.73(2) | 0.18 |
| 15 $\rightarrow$ 13 | 540229.47 | −0.57(1) | 0.73(2) | 0.15 |
| 15 $\rightarrow$ 13 | 144436.89 | −2.13(2) | −0.01(8) | 0.28 |
| 15 $\rightarrow$ 13 | −240483.13 | 1.25(1) | 1.63(6) | 0.19 |
| 15 $\rightarrow$ 13 | −544660.22* | −0.55(1) | 0.72(2) | 0.25 |
| 15 $\rightarrow$ 13 | −544628.26 | −0.55(1) | 0.72(2) | 0.22 |

| $N' J' p'$ | $J p$ | $\omega$ | $Q_\alpha$ | $Q_\mu$ | $|D|^2$ |
|------------|-------|----------|----------|--------|--------|
| 23 $\rightarrow$ 21 | −514442.07 | 0.17(0) | 1.20(2) | 7.13 |
| 25 $\rightarrow$ 23 | 579974.37 | −0.24(1) | 0.79(2) | 13.06 |
| 25 $\rightarrow$ 23 | 569214.13* | −0.15(0) | 0.90(1) | 6.18 |
| 24 $\rightarrow$ 22 | 18489.70 | −13.9(2) | −8.1(1) | 0.15 |
| 24 $\rightarrow$ 22 | 27624.21 | −5.28(7) | −3.0(5) | 9.40 |
| 26 $\rightarrow$ 24 | 1162035.24 | −0.22(0) | 0.85(1) | 9.14 |
| 25 $\rightarrow$ 23 | 230.75 | −1099.34 | −742.90 | 0.17 |
| 25 $\rightarrow$ 23 | −10529.49 | 18.8(2) | 11.1 | 6.95 |
| 27 $\rightarrow$ 25 | 1188561.69 | −0.21(0) | 0.85(1) | 1.5 |
| 24 $\rightarrow$ 22 | −571024.04 | 0.14(1) | 1.11(2) | 7.26 |
| 26 $\rightarrow$ 24 | 563386.99 | −0.34(1) | 0.79(3) | 10.93 |
| 26 $\rightarrow$ 24 | 556353.26 | −0.32(1) | 0.84(2) | 5.39 |
| 26 $\rightarrow$ 24 | −18063.18 | 13.6(2) | 11.1 | 0.18 |
| 25 $\rightarrow$ 23 | −25096.91 | 9.2(1) | 6.7(8) | 3.01 |
| 25 $\rightarrow$ 23 | 1215046.58 | −0.20(0) | 0.86(2) | 0.17 |

* Transitions observed in Ref. [11].

Because of the mixings [17] – [22] of the basic states there are also weaker transitions between $\Pi_{1/2}$, $\Pi_{3/2}$, and $\Sigma_{1/2}^\pm$ manifolds. Examples of such transitions are listed in Tables VII VIII. Sensitivities of these transitions depend on the quantum numbers in a less regular manner, than sensitivities within each manifold.

All transitions in Table VII have frequencies higher than 100 GHz. Because of that the sensitivity coefficients are not very high, but they are dispersed within intervals $0 \lesssim Q_\alpha \lesssim 4$ and $-1 \lesssim Q_\mu \lesssim 1$. Note that in order to study possible variations of fundamental constants we need to compare several transitions with different sensitivities. Thus, such a spread in sensitivities can be very useful [11].

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and $\beta \sim \mu^{3/2}$. Finally, in order to check, how the fitting procedure may affect the results, we did several calculations with slightly different sets of parameters. For example, we made a 13 parameter fit with three centrifugal corrections set to zero: $\gamma_{\Pi, D} = q_{D} = q_{D} = 0$. In terms of the obtained frequencies, such fit is only three times less accurate than our final 16 parametric one.

In Tables IV – VIII we give the average values of the $Q$ factors for all calculations, described above. The errors, given in the brackets, correspond to the maximum deviations from these average values for individual calculations. In most cases these errors are smaller than, or of the order of 10%, even for the large sensitivities. This accuracy is sufficient for the analysis of the experimental and observational data.

VI. CONCLUSION

We have studied sensitivity coefficients to the variation of the fundamental constants $\alpha$ and $\mu$ for the microwave and submillimeter spectra of the linear polyatomic molecule with strong Renner-Teller interaction. As an example we have chosen $l$-C$_3$H molecule, which is often observed in the interstellar molecular clouds and recently has been detected at the redshift $z = 0.89$. The Renner-Teller interaction depends on the dimensionless ratio $E = k' / k$ of the force constants in the two perpendicular planes, which include molecular axis. Parameter $E$ does not depend on the fundamental constants and vibrational intervals scale in the same way as for harmonic oscillator, i.e. $E_{v} \sim \mu^{1/2}$. However, the Renner-Teller interaction modifies vibrational spectrum and can lead to the close lying vibrational states. Such states then strongly interact with each other due to the Coriolis interaction. As a result, the molecules with strong Renner-Teller interaction can have low frequency mixed ro-vibronic transitions with strongly enhanced sensitivity coefficients to the variation of $\alpha$ and $\mu$. For the $l$-C$_3$H molecule we found several types of transitions with sensitivity coefficients varying in a wide range. This opens new possibilities to study variation of fundamental constants in astrophysics.

Acknowledgments

I am grateful to Sergei Levshakov for bringing $l$-C$_3$H molecule to my attention and for the constant interest to this work. I also want to thank Ed Hinds, Vadim Ilyushin, and Wim Ubachs for valuable discussions. This work is partly supported by the Russian Foundation for Basic Research Grants No. 11-02-00943 and No. 11-02-1284-ofi-m and by The Royal Society.
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