

Spectroscopic shifts in deuterated methanol induced by variation of  $m_e/m_p$ J. S. Vorotyntseva <sup>1,2</sup>, S. A. Levshakov <sup>1</sup> and M. G. Kozlov <sup>2,3</sup><sup>1</sup>*Ioffe Institute, Polytekhnicheskaya Str. 26, 194021 St. Petersburg, Russia*<sup>2</sup>*St. Petersburg Electrotechnical University "LETI", Prof. Popov Str. 5, 197376 St. Petersburg, Russia*<sup>3</sup>*Petersburg Nuclear Physics Institute of NRC "Kurchatov Institute", Gatchina, 188300 Leningrad District, Russia*

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Numerical calculations of the sensitivity coefficients,  $Q_\mu$ , of microwave molecular transitions in the ground torsion-rotation state of deuterated methanol ( $\text{CH}_3\text{OD}$ ,  $\text{CD}_3\text{OH}$ , and  $\text{CD}_3\text{OD}$ ) to small variations in the fundamental physical constant  $\mu = m_e/m_p$ —the electron-to-proton mass ratio—are reported. Theoretical motivation for changes in  $\mu$  comes from a variety of models beyond the standard model of particle physics which are invoked to explain the nature of dark matter and dark energy that dominate the Universe. The calculated values of  $Q_\mu$  range from  $-300$  to  $+73$  and, thus, make deuterated methanol promising for searches for small space-time changes in  $\mu$ . It is also shown that, among the calculated sensitivity coefficients  $Q_\mu$  using different Hamiltonians in the present and previous works, there are several pronounced outliers of unclear nature.

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## I. INTRODUCTION

Since the pioneering work of Thompson [1] the  $\mu$  test has been widely used in experimental studies of theoretical models beyond the standard model of particle physics which predict small variations of fundamental physical constants and, in particular, the electron-to-proton mass ratio,  $\mu = m_e/m_p$ , in space and time. Theories that connect varying constants to dark matter consider the dependence of  $\mu$  on the local density of dark matter which differs across the Milky Way (McMillan [2]). The coupling of physical constants to either dark matter or to gravitational fields is related to the chameleon scenario (e.g., Khoury and Weltman [3]; Olive and Pospelov [4]) and it can be probed in the Milky Way or in the nearby galaxies by astrophysical observations (Levshakov *et al.* [5,6]).

Regular quantitative measurements of fractional changes in  $\mu$  between its extraterrestrial ( $\mu_{\text{obs}}$ ) and terrestrial ( $\mu_{\text{lab}}$ ) values,  $\Delta\mu/\mu = (\mu_{\text{obs}} - \mu_{\text{lab}})/\mu_{\text{lab}}$ , became possible after the identification of molecular hydrogen lines in the absorption-line spectra of distant quasars (Levshakov and Varshalovich [7]) and calculation of sensitivity coefficients,  $Q_\mu$ , for individual molecular transitions of the Lyman and Werner bands of  $\text{H}_2$  (Varshalovich and Levshakov [8]).

It should be noted that at the first stage these studies were carried out mainly in the optical range on the  $\text{H}_2$  lines for which the sensitivity coefficients are not very high,  $|Q_\mu| \sim 10^{-2}$ , and the spectral resolution (channel width) does not exceed  $1 \text{ km s}^{-1}$ . The tightest upper limits on the variability of  $\mu$  on the cosmological time scale were obtained in the framework of the VLT/UVES Large Programme for testing fundamental physics,  $\Delta\mu/\mu < 10^{-5}$  (Rahmani *et al.* [9]), and at the highest redshift  $z = 4.22$  towards the quasar J1443+2724,  $\Delta\mu/\mu < 8 \times 10^{-6}$  (Bagdonaite *et al.* [10]).<sup>1</sup>

<sup>1</sup>All upper limits on  $\Delta\mu/\mu$  throughout the paper are given at the confidence level of  $1\sigma$ .

The second stage of development of the  $\mu$  tests took place in the microwave radio range after Flambaum and Kozlov [11] showed the enhanced sensitivity of the inversion tunneling transition at 23 GHz in ammonia molecule  $\text{NH}_3$ ,  $Q_\mu = +4.46$ . Comparing the positions of the ammonia inversion transition with pure rotation transitions in  $\text{CO}$ ,  $\text{HCO}^+$ , and  $\text{HCN}$ , for which  $Q_\mu = 1$ , they obtained a constraint on the changes in  $\mu$  at redshift  $z = 0.6847$  towards the quasar B0218+357,  $\Delta\mu/\mu < 2 \times 10^{-6}$ .

The accuracy of  $\Delta\mu/\mu$  estimates depends linearly on the accuracy of position measurements of spectral lines and is inversely proportional to the difference in the sensitivity coefficients of a pair of lines used in the analysis (Levshakov *et al.* [12]):

$$\frac{\Delta\mu}{\mu} = \frac{V_j - V_i}{c(Q_{\mu,i} - Q_{\mu,j})}, \quad (1)$$

where  $V_j$  and  $V_i$  are the local standard of rest radial velocities,  $V_{\text{LSR}}$ , of a pair of molecular transitions having sensitivity coefficients  $Q_{\mu,j}$  and  $Q_{\mu,i}$  and  $c$  is the speed of light.

The next step in improving  $\Delta\mu/\mu$  estimates was the search for molecules with large differences in the sensitivity coefficients of one molecule to avoid spectroscopic shifts (the so-called Doppler noise) caused by segregation effects in the spatial distribution of molecules within molecular clouds when  $\Delta\mu/\mu$  is calculated by comparing the positions of the lines of different molecules. The methanol molecule  $\text{CH}_3\text{OH}$  turned out to be most suitable for this purpose. The parent methanol and its isotopologues are among the most abundant molecules in interstellar space. The sensitivity coefficients for  $\text{CH}_3\text{OH}$  lie in the range  $-53 \leq Q_\mu \leq +43$  (Levshakov *et al.* [12], Jansen *et al.* [13]), which made it possible to obtain restrictions on cosmological variations of  $\mu$  at the level of  $5 \times 10^{-8}$  at  $z = 0.88582$  towards the quasar PKS1830-211 (Kanekar *et al.* [14]).

The same order of magnitude constraints on the spatial  $\mu$  variation in the Milky Way disk over the range of the

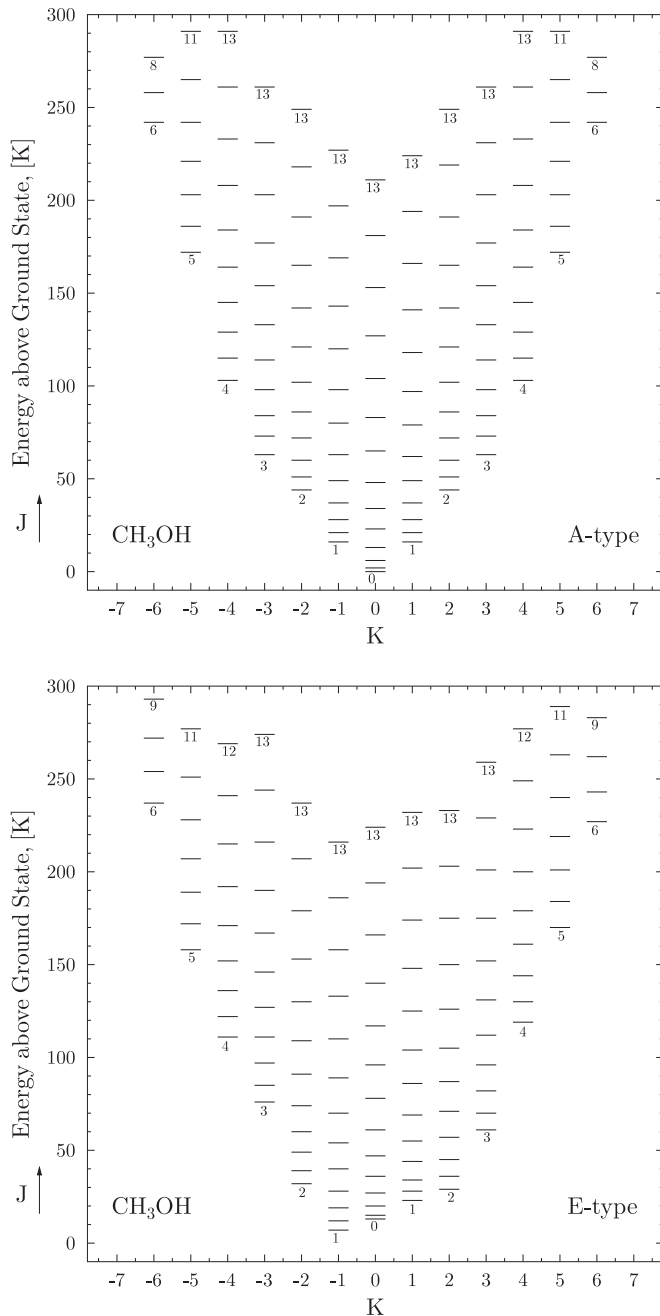


FIG. 1. Partial rotational level diagrams of A- and E-type methanol  $\text{CH}_3\text{OH}$  in the torsional ground state ( $\nu_t = 0$ ). Numbers below the horizontal bars are the values of the rotational angular momenta  $J$ .

galactocentric distances  $4 \leq R \leq 12$  kpc are based on the methanol thermal emission lines (Daprà *et al.* [15]) and methanol masers observations (Ellingsen *et al.* [16]; Levshakov *et al.* [17]):  $\Delta\mu/\mu < (2-3) \times 10^{-8}$ .

It should be emphasized that, over the past five decades, improvements in  $\Delta\mu/\mu$  estimates have always followed improvements in the quality of astronomical equipment and corresponded to the limiting parameters of observations in optical and radio ranges (see, e.g., Fig. 1 in Levshakov *et al.* [18]). Such extreme measurements may introduce

unaccounted systematic errors into the final results. Therefore, to obtain robust results, it is necessary to use various instruments and expand the list of molecular transitions with high sensitivity to changes in  $\mu$ . Among a number of complex organic molecules studied ( $\text{CH}_3\text{COH}$ ,  $\text{CH}_3\text{CONH}_2$ ,  $\text{CH}_3\text{OCOH}$ , and  $\text{CH}_3\text{COOH}$  in Jansen *et al.* [13],  $\text{CH}_3\text{NH}_2$  in Ilyushin *et al.* [19], and  $\text{CH}_3\text{SH}$  in Jansen *et al.* [20]), suitable transitions were found in methanol isotopologues (Jansen *et al.* [21]): for eight lines of deuterated methanol  $\text{CD}_3\text{OH}$  from the frequency interval  $1.202 < \nu < 20.089$  GHz, the sensitivity coefficients<sup>2</sup> lie between  $-330$  and  $+88$ , two lines of  $\text{CD}_3\text{OD}$  at 2.238 GHz and 2.329 GHz have, respectively,  $Q_\mu = -45$  and  $+80$ , two lines of  $\text{CH}_3^{18}\text{OH}$  at 2.605 GHz and 11.630 GHz have, respectively,  $Q_\mu = -93$  and  $+34$ , and  $Q_\mu = +63$  for one line of  $^{13}\text{CH}_3\text{OH}$  at 1.990 GHz.

A list of lines with high sensitivity coefficients of the  $^{13}\text{C}$ - and  $^{18}\text{O}$ -bearing methanol has recently been expanded to 27 transitions of  $^{13}\text{CH}_3\text{OH}$  from the frequency interval  $1.989 < \nu < 75.415$  GHz with  $Q_\mu$  ranging from  $-32$  to  $+78$  and to 30 transitions of  $\text{CH}_3^{18}\text{OH}$  with  $2.604 < \nu < 105.181$  GHz and  $-109 \leq Q_\mu \leq +33$  (Vorotyntseva *et al.* [22]). We have used these newly calculated  $Q_\mu$  values for  $^{13}\text{CH}_3\text{OH}$  to set constraints on  $\Delta\mu/\mu < 3 \times 10^{-8}$  from the thermal emission lines of  $^{13}\text{CH}_3\text{OH}$  detected in the star-forming region NGC 6334I by Wu *et al.* [23].

Astrophysical observations of deuterated methanol in galactic molecular clouds have been performed previously and are still an important goal of current studies. The  $\text{CH}_3\text{OD}$  lines were detected in the high-mass star-forming regions Sgr B2 (Gottlieb *et al.* [24], Turner [25], Belloche *et al.* [26]) and Orion-KL (Mauersberger *et al.* [27], Jacq *et al.* [28], Peng *et al.* [29], Wilkins and Blake [30]), which are both the reference sources to search for complex organic molecules. Besides the isotopologue  $\text{CH}_3\text{OD}$  was observed in the high-mass star-forming regions NGC 7538-IRS1 (Ospina-Zamudio *et al.* [31]), NGC 6334I (Bøgelund *et al.* [32]), DR 21 (Minh [33]), in the intermediate-mass star-forming regions CepE-mm and OMC2-FIR4 (Ratajczak *et al.* [34]), and in the low-mass star-forming regions IRAS 16293-2422 (Parise *et al.* [35], Jørgensen *et al.* [36]), IRAS 4A, IRAS 4B, and IRAS 2 (Parise *et al.* [37]), and SVS 13A (Bianchi *et al.* [38]) and HH 212 (Taquet *et al.* [39]). Triply deuterated methanol,  $\text{CD}_3\text{OH}$ , was observed in the low-mass protostar IRAS 16293-2242 (Parise *et al.* [40]). The search for quadruply deuterated methanol,  $\text{CD}_3\text{OD}$ , towards this object has not yet led to a reliable result but the research is currently ongoing (Ilyushin *et al.* [41]).

The present work is a continuation of our calculations of sensitivity coefficients for deuterated methanol  $\text{CH}_3\text{OD}$ ,  $\text{CD}_3\text{OH}$ , and  $\text{CD}_3\text{OD}$  in a wider spectral range as compared to the previous work by Jansen *et al.* [21].

## II. CALCULATIONS

Each of the deuterated methanol molecules ( $\text{CH}_3\text{OD}$ ,  $\text{CD}_3\text{OH}$ , and  $\text{CD}_3\text{OD}$ ) has, along with the overall rotation,

<sup>2</sup>Note that  $Q_\mu = -K_\mu$ , where  $K_\mu$  is used by Jansen *et al.* [21] who defined  $\mu$  as the *proton-to-electron* mass ratio.

internal torsion motions, the energy spectrum of which is similar to that of methanol CH<sub>3</sub>OH. The geometrical structure of these molecules is characterized by slight asymmetry which is the same for CH<sub>3</sub>OH and CD<sub>3</sub>OH, but increases for CH<sub>3</sub>OD and CD<sub>3</sub>OD resulting from the off-axis deuterium. Small differences in the degree of asymmetry between CH<sub>3</sub>OH and deuterated methanol molecules do not, however, affect the results of calculations of the energy spectra of deuterated molecules using the torsion-rotation Hamiltonian models developed for the parent methanol, as shown by Duan and McCoy [42] who demonstrated that for a particular molecule CH<sub>3</sub>OD a global fit of the observed transitions lies within the experimental uncertainties (a root-mean-square deviation of 0.098 MHz for  $J \leq 10$ ). Therefore, when calculating the sensitivity coefficients  $Q_\mu$  for lines in CH<sub>3</sub>OD, CD<sub>3</sub>OH, and CD<sub>3</sub>OD, we used the developed method from our previous works in which the sensitivity coefficients were calculated for CH<sub>3</sub>OH (Levshakov *et al.* [12]) and for two isotopologues <sup>13</sup>CH<sub>3</sub>OH and CH<sub>3</sub><sup>18</sup>OH (Vorotyntseva *et al.* [22]).

### A. Sensitivity coefficients and hyperfine corrections

Methanol in nature occurs in two types—*A* and *E*, which differ in the values of the total nuclear spin of the three hydrogen atoms in the methyl group CH<sub>3</sub>. The *A* methanol has parallel proton spins and the total nuclear spin  $I_{123} = 3/2$ , whereas the *E* methanol has one of the protons of the methyl group an antiparallel spin with respect to the others and  $I_{123} = 1/2$ . These nonzero total nuclear spins, interacting with the magnetic fields generated by the overall and torsion rotations of the molecule, lead to a hyperfine splitting of energy levels.

As noted by Lankhaar *et al.* [43], the hyperfine splitting of the torsion-rotation levels of molecules with hindered internal rotation such as methanol and its deuterated isotopologues may affect values of the sensitivity coefficients  $Q_\mu$ , since hyperfine effects shift the center of torsion-rotation lines which was not accounted for by effective torsion-rotation Hamiltonians used in previous calculations of  $Q_\mu$  in Jansen *et al.* [21] and Levshakov *et al.* [12]. Below we outline conditions when the hyperfine structure of the torsion-rotation levels can be neglected.

The frequency of a specific hyperfine transition,  $\nu$ , between upper and lower states consists of the rotation,  $\nu_r$ , torsion,  $\nu_t$ , and hyperfine,  $\nu_h$ , parts

$$\nu = \nu_r + \nu_t + \nu_h, \quad (2)$$

which are scaled with  $\mu$  as  $\mu^1$ ,  $\mu^\tau$ , and  $\mu^2$ , respectively, where  $\tau$  is a number attributed to a given transition.

The sensitivity coefficient  $Q_\mu$  is determined by two derivatives

$$\frac{d\nu}{\nu} = Q_\mu \frac{d\mu}{\mu}. \quad (3)$$

From (2) it follows that

$$\frac{d\nu}{d\mu} = \frac{1}{\mu}(\nu_r + \tau\nu_t + 2\nu_h) \quad (4)$$

and then

$$\frac{d\nu}{\nu} = \frac{d\mu}{\mu} \left[ 1 + (\tau - 1) \frac{\nu_t}{\nu} + \frac{\nu_h}{\nu} \right], \quad (5)$$

or, using the definition of  $Q_\mu$ , we have

$$Q_\mu \equiv Q_\mu^{(r)} + Q_\mu^{(t)} + Q_\mu^{(h)} = 1 + (\tau - 1) \frac{\nu_t}{\nu} + \frac{\nu_h}{\nu}. \quad (6)$$

Therefore, for a pure rotation transition, the sensitivity coefficient  $Q_\mu^{(r)} = 1$ . The energy difference between torsion-rotation levels of methanol in the microwave range is of the order of  $\sim 10$ s GHz, whereas the hyperfine splitting occurs at  $\sim 10$ s kHz, so that  $|\nu_h/\nu| \ll 1$  and, thus, we can neglect the hyperfine corrections in the effective Hamiltonian.

If, however, the hyperfine splitting is large compared to the transition frequency, then the third term in (2) and (6) must be included in calculations of the sensitivity coefficients. In this case the torsion-rotation transition splits into several lines with different frequencies and different  $Q_\mu$  values.

As for the second term in (2) and (6), it shows that transitions with enhanced sensitivities occur when  $\nu_t$  and  $\nu_r$  have different signs (i.e., energies associated with the hindered internal rotation and the overall rotation are canceled) and  $|\nu_t/\nu| \gg 1$ . We note in passing that different methanol isotopologues have slightly different rotation  $\nu_r$  and torsion  $\nu_t$  frequencies, but significantly different  $\nu$ . This results in different  $Q_\mu$  values for transitions with identical sets of quantum numbers in methanol isotopologues.

The microwave torsion-rotation transition can be defined by the quantum numbers  $J$  and  $K$  which are, respectively, the total angular momentum and its projection on the axis of the molecule. If subscripts  $u$  and  $\ell$  will denote the upper and lower energy levels, then the microwave torsion-rotation transition in emission can be written as  $J_{uK_u} \rightarrow J_{\ell K_\ell}$ . Figures 1–4 show diagrams of the methanol and its deuterated isotopologues' energy levels in the torsional ground state ( $\nu_t = 0$ ) which range up to an excitation temperature of 300 K above ground. The allowed transitions occur in accord with selection rules which have the following forms for *A*- and *E*-type methanol (e.g., Kalenskii and Kurtz [44]):

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#### *A* type

$$\Delta J = 0 \quad \Delta K = 0, \pm 1 \quad \pm \leftrightarrow \mp$$

$$\Delta J = \pm 1 \quad \Delta K = 0, \pm 1 \quad \pm \leftrightarrow \pm$$

#### *E* type

$$\Delta J = 0 \quad \Delta K = \pm 1$$

$$\Delta J = \pm 1 \quad \Delta K = 0, \pm 1$$


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It is interesting to note the inversion of energy levels in some transitions with identical sets of quantum numbers ( $J$ ,  $K$ ) when passing from one isotopologue to another, which affects the values of  $Q_\mu$  considerably. For instance, the transition  $J_{uK_u} \rightarrow J_{\ell K_\ell} = 2_1 - 3_0A^+$  in CH<sub>3</sub>OH has  $Q_\mu = +6.3$ , but its inverted analog  $J_{uK_u} \rightarrow J_{\ell K_\ell} = 3_0 - 2_1A^+$  in CH<sub>3</sub>OD has  $Q_\mu = -19.3$  or  $J_{uK_u} \rightarrow J_{\ell K_\ell} = 4_{-1} - 3_0E$  in CH<sub>3</sub>OH has  $Q_\mu = -9.6$ , but  $J_{uK_u} \rightarrow J_{\ell K_\ell} = 3_0 - 4_{-1}E$  in CD<sub>3</sub>OH has  $Q_\mu = +73$ , etc.

### B. Calculating procedure

The procedure for calculating sensitivity coefficients of methanol lines from microwave range was developed in Levshakov *et al.* [12]. It is based on an approach by Rabli and

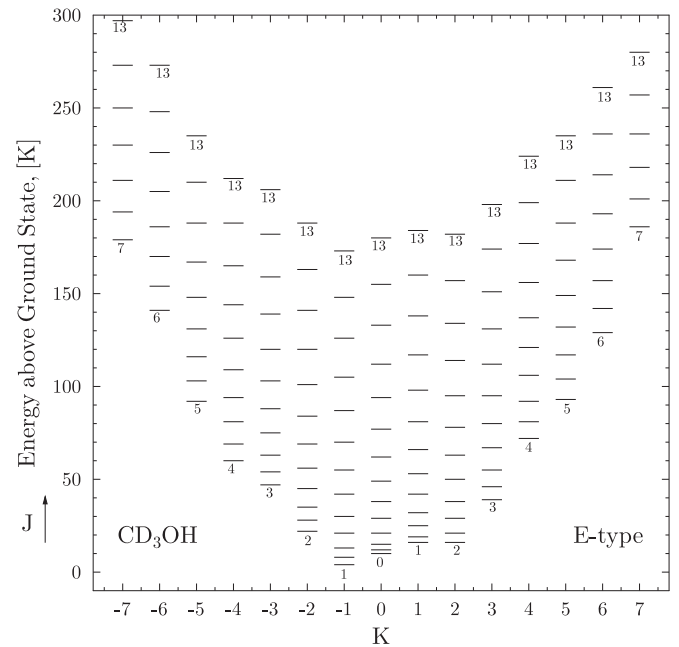
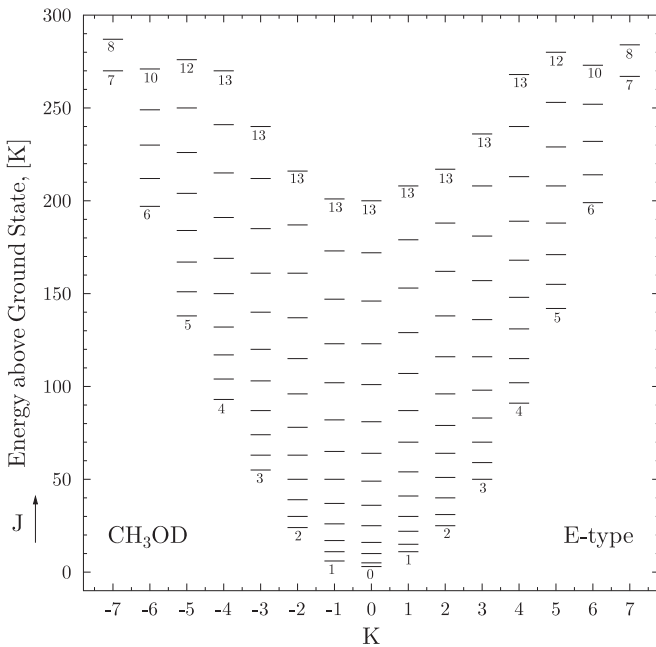
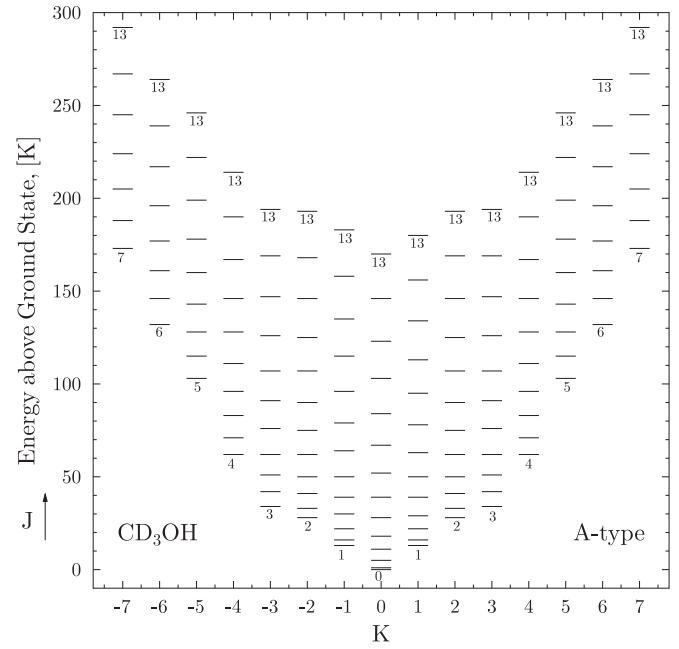
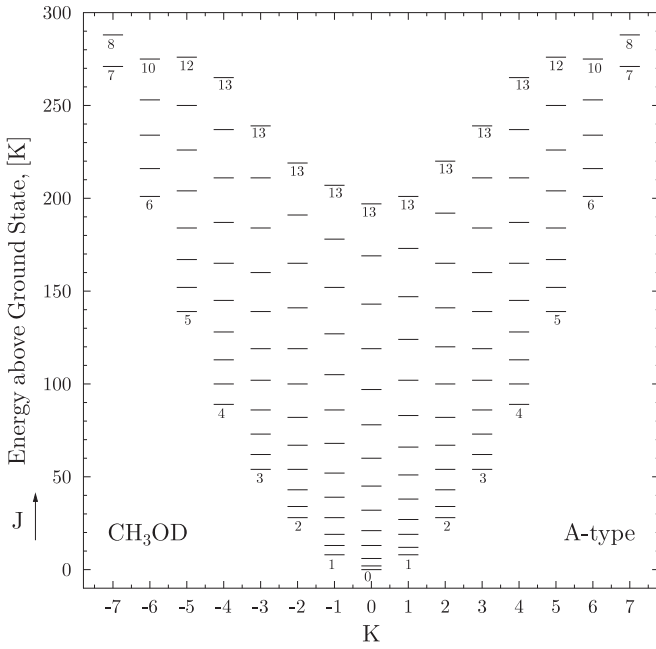


FIG. 2. Same as Fig. 1 but for the deuterated isotopologue  $\text{CH}_3\text{OD}$ .

FIG. 3. Same as Fig. 1 but for the deuterated isotopologue  $\text{CD}_3\text{OH}$ .

Flower [45] who suggested a convenient form of the effective Hamiltonian (hereafter RF Hamiltonian) which contains six spectroscopic constants having clear dependence on  $\mu$ . Comparison with the results of calculations using a more complex form of the Hamiltonian from Jansen *et al.* [21] showed that the RF Hamiltonian gives quite accurate values of the sensitivity coefficients (Levshakov *et al.* [12]; Vorotyntseva *et al.* [22]).

Seven parameters of the RF Hamiltonian are three rotation parameters  $A$ ,  $B$ ,  $C$ , one parameter  $D$ , describing interaction of the internal rotation with overall rotation, the kinetic coefficient  $F$ , and the depth of the threefold symmetric torsion

potential  $V_3$ ,

$$V(\omega) = \frac{V_3}{2}(1 - \cos 3\omega), \quad (7)$$

where  $0 \leq \omega \leq 2\pi$  is the torsion angle of the internal rotation of the  $\text{CH}_3$  group relative to the OH radical.

The values of all parameters, except  $V_3$ , were calculated from the moments of inertia of  $\text{CH}_3\text{OD}$ ,  $\text{CD}_3\text{OH}$ , and  $\text{CD}_3\text{OD}$  listed in Table I. The spectroscopic constants are defined as follows:

$$A = \frac{1}{2}\hbar^2 \left( \frac{I_a + I_b}{I_a I_b - I_{ab}^2} - \frac{I_b}{I_b^2 + I_{ab}^2} \right), \quad (8)$$

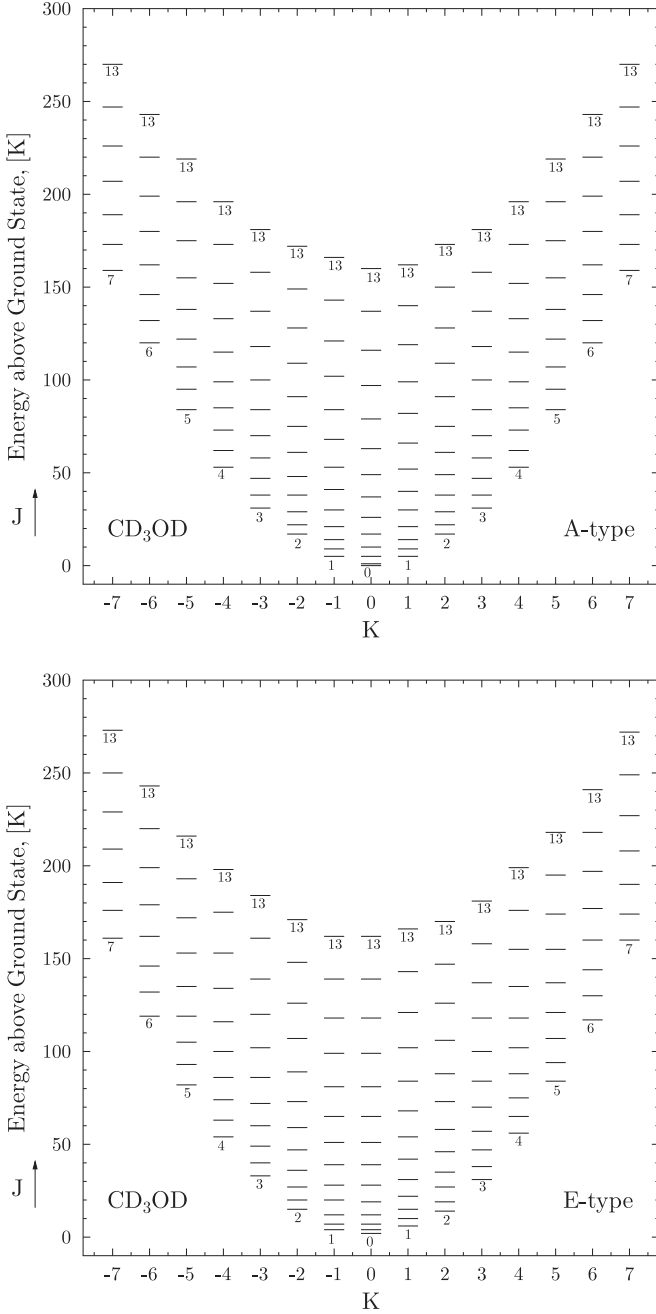


FIG. 4. Same as Fig. 1 but for the deuterated isotopologue  $\text{CD}_3\text{OD}$ .

TABLE I. Moments of inertia (in units  $\text{amu} \text{ \AA}^2$ ) for the parent methanol molecule and its deuterated isotopologues from Lees [46].

	$\text{CH}_3\text{OD}$	$\text{CD}_3\text{OH}$	$\text{CD}_3\text{OD}$	$\text{CH}_3\text{OH}$
$I_{a1}$	1.3946	0.7514	1.4082	0.7493
$I_{a2}$	3.2249	6.3872	6.3939	3.2122
$I_a^*$	4.6195	7.1386	7.8021	3.9615
$I_b$	21.5304	25.4621	26.7242	20.4771
$I_{ab}$	0.850	-0.125	0.8047	-0.065
$I_c$	22.9880	26.2203	28.1529	21.2614

\* $I_{a2}$  is the axial moment of inertia of the methyl group and  $I_{a1}$  is that of the hydroxyl group,  $I_a = I_{a1} + I_{a2}$ .

$$B = \frac{1}{2} \hbar^2 \frac{I_b}{I_b^2 + I_{ab}^2}, \quad (9)$$

$$C = \frac{1}{2} \hbar^2 \frac{1}{I_c}, \quad (10)$$

$$D = \frac{1}{2} \hbar^2 \frac{I_{ab}}{I_b^2 + I_{ab}^2}, \quad (11)$$

$$F = \frac{1}{2} \hbar^2 \frac{I_a I_b - I_{ab}^2}{I_{a2}(I_{a1} I_b - I_{ab}^2)}. \quad (12)$$

Here  $\hbar = h/2\pi$ ,  $I_a, I_b, I_c$  are the moments of inertia, and  $I_{ab}$  is the product of inertia about the  $a$  and  $b$  axes in the  $a, b, c$ -axis system, whose  $a$  axis is parallel to the internal rotation axis (assumed to be that of the methyl top) and  $c$  axis is perpendicular to the COH plane.  $I_{a2}$  is the axial moment of inertia of the methyl group and  $I_{a1}$  is that of the framework (the hydroxyl group), the sum of which determines  $I_a$ :  $I_a = I_{a1} + I_{a2}$  (for details, see Lees and Baker [47]). The RF Hamiltonian also includes a dimensionless parameter  $\rho$ —the internal rotation interaction constant, which is given for asymmetric molecules by

$$\rho = \frac{I_{a2} \sqrt{I_b^2 + I_{ab}^2}}{I_a I_b - I_{ab}^2}. \quad (13)$$

The degree of asymmetry is defined by the parameter  $\kappa$ :

$$\kappa = \frac{2B - A - C}{A - C}, \quad (14)$$

which is equal to 1 or  $-1$  when the molecule is symmetric (Townes and Schawlow [48]). Table II contains the calculated spectroscopic parameters for  $\text{CH}_3\text{OD}$ ,  $\text{CD}_3\text{OH}$ , and  $\text{CD}_3\text{OD}$  with the potential barriers  $V_3$  and the asymmetry parameter  $\kappa$ .

The calculated spectroscopic parameters were used to determine the Hamiltonian matrix, the nonvanishing elements of which are listed in Vorotyntseva *et al.* [22] for specific values of the rotational angular momentum  $J$ . Diagonalization of this matrix gives simultaneously the eigenenergies and eigenfunctions for  $A$ - and  $E$ -type methanol. The dependence of the found eigenvalues  $E_i$  on  $\Delta\mu/\mu$  defines the sensitivity coefficient  $Q_\mu$  through the following relations:

$$\Delta E_i = q_i \frac{\Delta\mu}{\mu} \quad (15)$$

and

$$Q_\mu = \frac{q_u - q_\ell}{\nu}. \quad (16)$$

Here  $q_i$  is the so-called  $q$  factor, individual for each level, which shows a response of the level  $E_i$  to a small change of  $\mu$ , when  $|\Delta\mu/\mu| \ll 1$ . This functional dependence is assessed through the diagonalization of the Hamiltonian matrix for three sets of parameters that correspond to  $\mu = \mu_0$  and  $\mu = \mu_0(1 \pm \varepsilon)$ , where  $\varepsilon$  is equal to 0.001 or 0.0001, and  $\mu_0 \equiv \mu_{\text{lab}}$  (Levshakov *et al.* [12]). The subscripts  $u$  and  $\ell$  denote the upper and lower levels, respectively.

For calculations we selected molecular transitions with  $0 \leq J \leq 13$  and  $|\Delta K| = 1$ , since transitions with  $\Delta K = 0$  are purely rotation and have  $Q_\mu \approx 1$ . Our calculations for the

TABLE II. Spectroscopic parameters of the RF Hamiltonian and the asymmetry parameter  $\kappa$  for CH<sub>3</sub>OD, CD<sub>3</sub>OH, CD<sub>3</sub>OD, and CH<sub>3</sub>OH.

	CH <sub>3</sub> OD	CD <sub>3</sub> OH	CD <sub>3</sub> OD	CH <sub>3</sub> OH
$A$ (cm <sup>-1</sup> )	3.679363	2.361733	2.169903	4.255604
$B$ (cm <sup>-1</sup> )	0.7818695	0.6620463	0.6302237	0.8232282
$C$ (cm <sup>-1</sup> )	0.7333172	0.6429177	0.5987836	0.7928686
$D$ (cm <sup>-1</sup> )	0.02923331	-0.003250156	0.01897685	-0.002613155
$F$ (cm <sup>-1</sup> )	17.58161	25.09238	14.81704	27.75181
$V_3$ (cm <sup>-1</sup> ) <sup>a</sup>	370.3	371.8	362.8	375.6
$\rho$	0.7031751	0.8948290	0.8224358	0.8109008
$\kappa$	-0.967	-0.978	-0.960	-0.982

<sup>a</sup>Values of  $V_3$  are taken from Lees [46].

three deuterated isotopologues of methanol CH<sub>3</sub>OD, CD<sub>3</sub>OH, and CD<sub>3</sub>OD cover the low frequency range 1–50 GHz, which contains transitions with the highest sensitivity to  $\mu$  variations.

The results of our calculations are reported in Table III (CH<sub>3</sub>OD)<sup>3</sup>, Table IV (CD<sub>3</sub>OH), and Table V (CD<sub>3</sub>OD). The structure of these tables is the following. The first column contains the quantum numbers  $J$  and  $K$  of the upper and lower levels. The second and third columns show the rest frequencies. The fourth column lists the sensitivity coefficients  $Q_\mu$  and their uncertainties, estimated according to the scheme described in Sec. III. Included in these tables are molecular transitions with large sensitivity coefficients,  $|Q_\mu| > 3$ , except for the  $8_{-1} - 8_0E$  transition in CD<sub>3</sub>OD with  $Q_\mu = -0.9$ , which is added to Table V for comparison with Jansen *et al.* [13].

Tables III–V show that deuterated isotopologues of methanol have high sensitivity coefficients of both signs. The calculated values of  $Q_\mu$  range from -32 to +25 for CH<sub>3</sub>OD, from -300 to +73 for CD<sub>3</sub>OH, and from -44 to +38 for CD<sub>3</sub>OD. The results obtained indicate that the most attractive

molecule for testing  $\mu$  variations is CD<sub>3</sub>OH, for which the maximum difference between the sensitivity coefficients [denominator in Eq. (1)] reaches the value of  $\Delta Q_\mu \approx 370$  in the narrow frequency range 1–5 GHz, which by itself minimizes possible systematic errors in the position measuring of spectral lines from a wide frequency range.

### III. ESTIMATION OF ERRORS OF THE SENSITIVITY COEFFICIENTS

Some of the sensitivity coefficients presented in Tables IV and V were calculated earlier in Jansen *et al.* [21] and Jansen *et al.* [13], which makes it possible to compare the results of calculations using different forms of the Hamiltonian. The footnotes to these tables show that the  $Q_\mu$  coefficients from Jansen *et al.* [21] and Jansen *et al.* [13] differ significantly from our calculations for a number of lines. The most striking cases are marked by superscripts  $c, f, g, h$  in Table IV and by  $b$  in Table V. For the case  $c$ , we even found  $Q_\mu$  of opposite signs.

Figure 5 illustrates the degree of agreement between common sensitivity coefficients calculated in Jansen *et al.* [21] and Jansen *et al.* [13] (red points) and in the present work (black points). To understand large differences marked by the blue

<sup>3</sup>The sensitivity coefficients for CH<sub>3</sub>OD are calculated here.

TABLE III. Numerical calculation of the sensitivity coefficients  $Q_\mu$  for the low-frequency torsion-rotation transitions ( $\Delta K = \pm 1$ ) in CH<sub>3</sub>OD. Given in parentheses are error estimates in the last digits. (Experimental frequencies are taken from Anderson *et al.* [49]; predicted frequencies are marked by an asterisk.)

Transition	Frequency	(MHz)		Transition	Frequency	(MHz)	
$J_u K_u \rightarrow J_l K_l$	Expt.	Theor.	$Q_\mu$	$J_u K_u \rightarrow J_l K_l$	Expt.	Theor.	$Q_\mu$
$11_4 - 12_3 A^-$	3983.678*	4839.8	-32(5)	$7_{-1} - 7_0 E$	17889.040	17982.9	-6.4(3)
$3_0 - 2_1 A^+$	4812.471*	4468.3	-19.3(1.0)	$6_{-1} - 6_0 E$	18454.760	18525.9	-6.5(3)
$10_{-3} - 11_{-2} E$	6346.731*	7012.6	25(2)	$5_{-1} - 5_0 E$	18792.970	18844.2	-6.6(3)
$9_2 - 8_3 A^-$	6362.584*	7195.5	15(2)	$4_{-1} - 4_0 E$	18957.170	18992.2	-6.6(3)
$9_2 - 8_3 E$	6761.206*	5619.9	11(2)	$1_{-1} - 1_0 E$	18957.950	18965.0	-6.8(3)
$9_2 - 8_3 A^+$	10279.780	11079.8	9.3(1.4)	$2_{-1} - 2_0 E$	18991.670	19004.8	-6.8(3)
$12_{-1} - 12_0 E$	11367.779*	11580.5	-6.4(6)	$3_{-1} - 3_0 E$	19005.640	19028.0	-6.7(3)
$11_{-1} - 11_0 E$	13033.065*	13225.9	-6.4(5)	$1_1 - 2_0 E$	19518.790	19404.9	3.67(17)
$10_{-1} - 10_0 E$	14588.875*	14758.9	-6.4(4)	$6_2 - 7_1 A^+$	23407.520	23200.3	6.6(6)
$3_2 - 4_1 E$	14920.430	14716.3	-8.8(6)	$5_1 - 4_2 E$	30839.200	31093.0	5.7(3)
$7_1 - 6_2 A^-$	15467.910	15510.4	-7.5(8)	$5_2 - 6_1 A^-$	34537.290	34559.4	4.8(3)
$8_1 - 7_2 A^+$	15720.990	16043.7	-7.3(1.0)	$1_1 - 2_0 A^+$	41858.774*	42261.2	3.34(11)
$9_{-1} - 9_0 E$	15948.140	16094.5	-6.4(3)	$9_{-3} - 10_{-2} E$	51926.768*	52658.7	3.9(3)
$8_{-1} - 8_0 E$	17057.090	17176.5	-6.4(3)				

TABLE IV. Numerical calculation of the sensitivity coefficients  $Q_\mu$  for the low-frequency torsion-rotation transitions ( $\Delta K = \pm 1$ ) in CD<sub>3</sub>OH. Given in parentheses are error estimates in the last digits. (Experimental frequencies are taken from Ilyushin *et al.* [50]; predicted frequencies are marked by asterisk.)

Transition $J_{uK_u} \rightarrow J_{lK_l}$	Frequency Expt.	(MHz) Theor.	$Q_\mu$	Transition $J_{uK_u} \rightarrow J_{lK_l}$	Frequency Expt.	(MHz) Theor.	$Q_\mu$
$2_2 - 1_1 E$	1202.3089*	1344.8	-300(12) <sup>a</sup>	$11_3 - 11_2 A^{++}$	17918.90	18210.8	-20.2(9)
$1_1 - 2_0 E$	1424.1693*	1330.4	47(2) <sup>b</sup>	$9_3 - 9_2 A^{+-}$	18081.20	18289.3	-20.4(9)
$12_{-7} - 13_{-6} E$	2656.1884*	2032.2	-103(9)	$12_3 - 12_2 A^{++}$	18097.00	18436.6	-19.8(9)
$10_{-2} - 9_{-3} E$	2754.4417*	3247.8	-84(5)	$13_3 - 13_2 A^{++}$	18317.15	18706.1	-19.4(9)
$8_3 - 9_2 E$	2827.2446*	2367.6	11(5) <sup>c</sup>	$10_3 - 10_2 A^{+-}$	18395.60	18650.2	-19.9(9)
$6_0 - 5_1 A^+$	2971.0289*	3360.0	-96(4) <sup>d</sup>	$8_6 - 9_5 A^+$	18988.36	18429.6	-16.9(1.1)
$6_1 - 5_2 A^-$	3130.6032*	3417.2	-46(3)	$8_6 - 9_5 A^-$	18988.36	18429.6	-16.9(1.1)
$3_0 - 4_{-1} E$	4011.3609*	3734.5	73(3) <sup>e</sup>	$12_3 - 12_2 A^{+-}$	19294.50	19651.5	-18.7(8)
$11_{-5} - 12_{-4} E$	4608.4386*	4030.4	5(3)	$13_3 - 13_2 A^{+-}$	19905.8	20318.1	-17.9(8)
$5_5 - 6_4 E$	6723.8853*	6293.0	-56(3) <sup>f</sup>	$10_5 - 9_6 A^+$	20088.47	20678.1	17.9(1.1) <sup>g</sup>
$5_2 - 6_1 A^+$	7662.4811*	7379.8	20.2(1.3)	$10_5 - 9_6 A^-$	20088.47	20678.1	17.9(1.1) <sup>h</sup>
$8_{-1} - 7_{-2} E$	9945.16	10418.8	-22.0(1.1)	$12_4 - 13_3 E$	24612.81	23996.1	13.5(7)
$11_3 - 10_4 A^+$	11125.37	11672.4	-6.5(1.2)	$9_4 - 10_3 A^-$	27981.73	27515.2	4.0(5)
$11_3 - 10_4 A^-$	11215.14	11764.1	-6.5(1.2)	$9_4 - 10_3 A^+$	28032.94	27567.5	4.0(5)
$3_3 - 3_2 A^{++}$	17328.19	17340.1	-21.9(1.0)	$6_{-2} - 7_{-1} E$	28811.25	28420.8	8.9(4)
$3_3 - 3_2 A^{+-}$	17335.14	17347.0	-21.9(1.0)	$7_1 - 6_2 A^+$	29550.25	29899.6	-4.0(4)
$4_3 - 4_2 A^{++}$	17353.94	17387.0	-21.8(1.0)	$7_4 - 6_5 E$	32352.307	32816.1	12.8(6)
$4_3 - 4_2 A^{+-}$	17374.42	17407.7	-21.8(1.0)	$5_{-1} - 4_0 E$	35748.571	36099.7	-6.2(3)
$5_3 - 5_2 A^{++}$	17388.63	17447.6	-21.7(9)	$8_{-3} - 9_{-2} E$	36663.008	36258.2	7.4(4)
$6_3 - 6_2 A^{++}$	17433.99	17523.4	-21.5(9)	$4_1 - 5_0 A^+$	37322.977	37013.0	8.7(3)
$5_3 - 5_2 A^{+-}$	17435.92	17495.7	-21.6(9)	$4_2 - 5_1 A^-$	37463.512	37242.4	5.0(2)
$7_3 - 7_2 A^{++}$	17492.27	17616.0	-21.3(9)	$3_2 - 2_1 E$	40649.426	40858.1	-7.1(3)
$6_3 - 6_2 A^{+-}$	17527.61	17618.3	-21.4(9)	$11_{-7} - 12_{-6} E$	41737.585	41149.7	-5.6(6)
$8_3 - 8_2 A^{++}$	17566.15	17727.7	-21.1(9)	$2_0 - 3_{-1} E$	43453.48	43245.6	8.5(3)
$7_3 - 7_2 A^{+-}$	17658.70	17784.6	-21.1(9)	$7_0 - 6_1 A^+$	43501.125	43975.9	-5.6(3)
$9_3 - 9_2 A^{++}$	17659.00	17861.6	-20.8(9)	$4_2 - 5_1 A^+$	45160.765	44941.7	4.3(2)
$10_3 - 10_2 A^{+-}$	17774.89	18021.1	-20.5(9)	$9_{-1} - 8_{-2} E$	48567.661	49130.7	-3.7(2)
$8_3 - 8_2 A^{+-}$	17839.40	18004.7	-20.8(9)				

<sup>a</sup> $Q_\mu$  from Jansen *et al.* [21]: -330 ± 20; <sup>b</sup>42 ± 2; <sup>c</sup>-43 ± 2; <sup>d</sup>-93 ± 5; <sup>e</sup>73 ± 4; <sup>f</sup>-167 ± 8; <sup>g</sup>88 ± 4; <sup>h</sup>88 ± 4.

TABLE V. Numerical calculation of the sensitivity coefficients  $Q_\mu$  for the low-frequency torsion-rotation transitions ( $\Delta K = \pm 1$ ) in CD<sub>3</sub>OD. Given in parentheses are error estimates in the last digits. (Experimental frequencies are taken from Ilyushin *et al.* [41]; predicted transition frequencies are marked by an asterisk.)

Transition $J_{uK_u} \rightarrow J_{lK_l}$	Frequency Expt.	(MHz) Theor.	$Q_\mu$	Transition $J_{uK_u} \rightarrow J_{lK_l}$	(MHz) Expt.	(MHz) Theor.	$Q_\mu$
$1_{-1} - 1_0 E$	2237.8224*	2229.4	-44.1(1.7) <sup>a</sup>	$4_3 - 5_2 A^-$	5276.6275*	5020.4	-19.7(1.6)
$8_{-3} - 7_{-4} E$	2328.9943*	2699.6	38(5) <sup>b</sup>	$12_0 - 12_{-1} E$	5432.1218*	5456.3	9.3(3)
$2_{-1} - 2_0 E$	2476.7516*	2472.2	-35.3(1.3)	$13_0 - 13_{-1} E$	5898.7376*	5913.7	9.5(3)
$3_{-1} - 3_0 E$	2777.7033*	2778.4	-27.0(1.0)	$1_1 - 2_0 A^+$	8147.610	8072.4	11.5(4)
$4_{-1} - 4_0 E$	3100.6415*	3107.6	-20.0(8)	$5_1 - 4_2 A^+$	11755.04	11985.1	-4.4(6)
$5_{-1} - 5_0 E$	3413.586*	3427.9	-14.4(6)	$3_2 - 4_1 A^-$	14172.74	14028.4	5.5(4)
$9_4 - 10_3 E$	3561.2687*	3225.4	32(3)	$3_2 - 4_1 A^+$	22792.07	22615.8	3.8(3)
$6_{-1} - 6_0 E$	3695.4856*	3717.7	-9.5(4)	$11_5 - 12_4 A^+$	24130.44	23768.0	5.7(6)
$7_{-1} - 7_0 E$	3940.3679*	3970.3	-5.1(3)	$11_5 - 12_4 A^-$	24141.87	23779.3	5.7(6)
$8_{-1} - 8_0 E$	4161.7206*	4197.5	-0.9(2) <sup>c</sup>	$6_2 - 5_3 A^-$	31381.11	31673.5	4.5(3)
$13_5 - 12_6 E$	4254.1923*	4971.5	23(4)	$6_2 - 5_3 A^+$	31980.59	32269.2	4.4(3)
$4_3 - 5_2 A^+$	4977.3938*	4723.0	-20.9(1.7)	$9_{-3} - 8_{-4} E$	39152.561	39556.0	3.2(3)
$11_0 - 11_{-1} E$	5012.0901*	5044.5	8.3(3)	$8_4 - 9_3 E$	40645.642	40372.7	3.8(3)
$11_4 - 10_5 E$	5049.9782*	5477.1	11(3)				

<sup>a</sup> $Q_\mu = -45 \pm 2$  (Jansen *et al.* [21]); <sup>b</sup> $Q_\mu = 80 \pm 4$  (Jansen *et al.* [21]); <sup>c</sup> $Q_\mu = -0.7$  (Jansen *et al.* [13]).

arrows in this figure, we checked the errors of our procedure following the approach developed in Levshakov *et al.* [12] and Vorotyntseva *et al.* [22].

Molecular transition frequencies depend on  $\mu$  via the parameters (7)–(13) of the effective Hamiltonian. Five of these parameters,  $A, \dots, F$ , are inversely proportional to the moments of inertia, which scales almost linearly with  $\mu^{-1}$ . Thus these parameters scale linearly with  $\mu$ . The deviation from the linearity was estimated to be on the level of 1–2% (Levshakov *et al.* [12]). It is mostly caused by the weak dependence of the internuclear distances on  $\mu$  due to the vibrational and centrifugal distortions. Up to the similar small corrections, the remaining two parameters ( $V_3$  and  $\rho$ ) of the effective Hamiltonian do not depend on  $\mu$ . All these corrections change the scaling of the three terms in Eq. (2). This, in turn, changes the sensitivity coefficients in Eq. (6). In order to estimate the scaling error for the sensitivity coefficients  $Q_\mu$  we independently change the scaling of each of the parameters of the effective Hamiltonian by 2% and calculate sensitivity coefficients using Eqs. (15) and (16).

Another possible source of theoretical errors comes from the interaction of the closely lying torsion-rotation levels with the same exact quantum numbers. Such interaction leads to the well-known level repulsion. Varying  $\mu$  changes the distance between the levels and, thus, changes repulsion. This may affect the sensitivity coefficients of the interacting levels (Dzuba *et al.* [51]). It is important that the  $q$  factors change in the opposite directions leaving their sum unchanged. Clearly, this source of errors is most important when there are close levels with significantly different  $q$  factors. Numerically it leads to the dependence of  $q_i$ , calculated from Eq. (16), on  $\mu$  (Konovalova *et al.* [52]). To estimate this error, we calculated  $q_i$  using  $\Delta\mu = \pm\epsilon$  and estimated the derivative  $\partial q_i/\partial\mu$ . Our analysis shows that this source of errors is subdominant for all levels considered in the present paper. The estimated theoretical errors are given in parentheses in Tables III–VI.

Coming back to the comparison of different sets of the  $Q_\mu$  values shown in Fig. 5, we note that in general there is a smooth dependence of  $Q_\mu$  on frequency, despite some scatter of points at low frequencies caused by interference of nearby energy levels. The highest  $Q_\mu$  values are found for transitions with the smallest differences between the energy levels,  $\Delta E \leq 0.1$  K. The results presented in Fig. 5 show a good concordance between Jansen *et al.* [21] calculations and ours for the parent molecule  $\text{CH}_3\text{OH}$ , but essential deviations in some cases for its isotopologues.

Among them, the most striking difference occurs at 20.088 GHz ( $10_5 - 9_6A$ ) in  $\text{CD}_3\text{OH}$  (Table IV), where Jansen’s point lies too far from the  $\pm 3\sigma$  uncertainty zone shown by the shadowed area, taking into account that  $\Delta E = 0.96$  K for this transition. The red point at 6.723 GHz ( $5_5 - 6_4E$ ) also deviates from the general trend, while the black one does not. However, this deviation is comparable to the overall spread at  $\Delta E \lesssim 0.3$  K. As for the  $Q_\mu$  values at 2.827 GHz ( $8_3 - 9_2E$ ), which have even opposite signs in our and Jansen’s calculations, we cannot state with certainty for the intermediate value of  $\Delta E = 0.14$  K for this transition whose result is more reliable since the found values of  $Q_\mu$  can belong either to the upper or to the lower curve. The isotopologue  $\text{CD}_3\text{OD}$  (Table V) also demonstrates one point

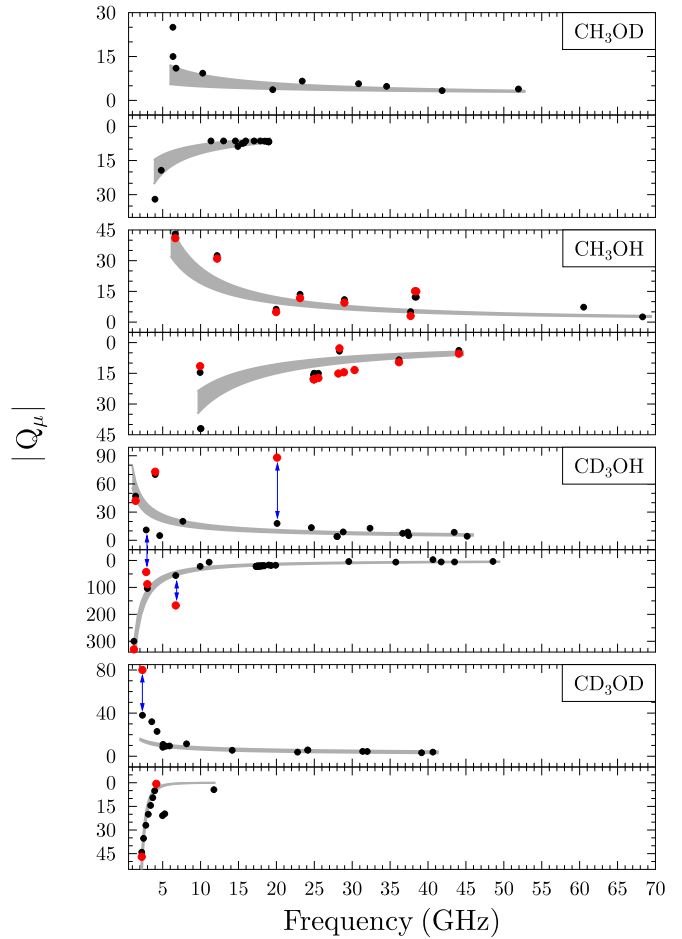


FIG. 5. Comparison of the sensitivity coefficients for methanol and its deuterated isotopologues: red dots, calculated by Jansen *et al.* [13,21]; black dots, current results. The shadowed area shows the  $\pm 3\sigma$  uncertainty zone. The blue arrows indicate maximum deviations in the  $Q_\mu$  values between Jansen *et al.* and the present calculations. Note that  $Q_\mu$  even changes sign in one case at 2.827 GHz for  $\text{CD}_3\text{OH}$  (see Table IV). The isotopologue  $\text{CH}_3\text{OD}$  is considered in the present paper. In general,  $Q_\mu$  decreases with increasing frequencies of molecular transitions in all four cases.

at 2.328 GHz ( $8_{-3} - 7_{-4}E$ ) where our and Jansen’s results differ significantly.

To illustrate the dependence of some values of the sensitivity coefficients on the Hamiltonian model used, we compare in Table VI the computational results obtained by three models of the effective Hamiltonian which are outlined below.

As mentioned above, Jansen *et al.* [21] used the complex model of the Hamiltonian based on 119 parameters and calculated numerically the torsion-rotation levels with the BELGI code. Despite the fact that this model calculates the transition frequencies with high accuracy, it provides limited insight.

For a clearer understanding of the physical meaning, Jansen *et al.* [13] used a “toy” model with six parameters:  $A, B, C, F, \rho$ , and  $V_3$ . Using this model, the authors calculated the sensitivity coefficients for some transitions in  $\text{CH}_3\text{OH}$ . To compare with our results, we recalculated the sensitivity coefficients  $Q_\mu$  for the same transitions using the seven spectroscopic parameters from the last column in Table II. The



TABLE VI. Sensitivity coefficients for CH<sub>3</sub>OH calculated with BELGI code,  $Q_\mu^{\text{BELGI}}$ , and “toy,”  $Q_\mu^{\text{toy}}$ , model from Jansen *et al.* [13], and, for comparison, the present paper  $Q_\mu$  values. Given in parentheses are errors in the last digits.

Transition $J_{uK_u} \rightarrow J_{lK_l}$	Frequency <sup>a</sup> (MHz)	$Q_\mu^{\text{BELGI}}$	$Q_\mu^{\text{toy}}$	$Q_\mu$
$5_1 - 6_0 A^+$	6668.52	42(2)	46	43(2)
$9_{-1} - 8_{-2} E$	9936.20	-11.5(6)	-16.7	-14.6(1.3)
$4_3 - 5_2 A^+$	9978.69	-53(3)	-35	-42(2)
$4_3 - 5_2 A^-$	10058.26	-52(3)	-35	-42(2)
$2_0 - 3_{-1} E$	12178.59	33(2)	32	32.5(1.3)
$2_1 - 3_0 E$	19967.40	5.9(3)	5.0	6.3(3)
$9_2 - 10_1 A^+$	23121.02	11.7(6)	10.8	13.6(1.0)
$3_2 - 3_1 E$	24928.72	-17.9(9)	-15.2	-16.7(7)
$2_2 - 2_1 E$	24934.38	-17.9(9)	-15.2	-16.7(7)
$8_2 - 9_1 A^-$	28969.95	9.5(6)	8.8	11.0(7)
$4_{-1} - 3_0 E$	36169.29	-9.7(5)	9.6	-9.6(4)
$6_2 - 5_3 A^+$	38293.29	15.1(8)	10.4	12.2(6)
$6_2 - 5_3 A^-$	38452.65	15.0(8)	10.4	12.2(6)
$7_0 - 6_1 A^+$	44069.48	-5.2(3)	-5.9	-5.4(3)
$1_0 - 2_{-1} E$	60531.49	7.4(4)	7.3	7.3(3)
$1_1 - 2_0 E$	68305.68	2.4(1)	2.2	2.55(7)

<sup>a</sup>Rest frequencies are taken from Lovas [53].

result of such comparison is presented in Table VI. As seen, there are some discrepancies between the listed  $Q_\mu$  values, the most pronounced of which are found for the following transitions:  $9_{-1} - 8_{-2}E$ ,  $4_3 - 5_2A^+$ ,  $4_3 - 5_2A^-$ ,  $6_2 - 5_3A^+$ , and  $6_2 - 5_3A^-$ .

The 119 parameters of the BELGI model have different dependence on  $\mu$ . Many of the higher-order parameters are products of operators and can be quite correlated. Therefore, the exact relationship between the higher-order parameters of moments of inertia (and hence masses) is poorly known. It can give some effects in calculating the sensitivity coefficients which were tested for CH<sub>3</sub>OH in Jansen *et al.* [13]

by using different forms of the effective Hamiltonian. The authors showed that the calculated sensitivity coefficients coincide within a few percent. However, it is possible that the effects produced by the high-order parameters may provide a more significant contribution for methanol deuterated isotopologues. In any case, care should be taken with those  $Q_\mu$  values where large deviations have been detected when different forms of the effective Hamiltonian were used. Elucidating the nature of the discrepancies found requires more detailed analysis.

#### IV. CONCLUSIONS

In this paper we calculated the sensitivity coefficients,  $Q_\mu$ , for different molecular transitions from the microwave range 1–50 GHz to small changes in the values of the electron-to-proton mass ratio,  $\mu = m_e/m_p$ . The considered molecular species include CH<sub>3</sub>OD, CD<sub>3</sub>OH, and CD<sub>3</sub>OD. The computational procedure is based on the effective Hamiltonian in the form suggested by Rabli and Flower [45]. The obtained main results are as follows.

(1) For CH<sub>3</sub>OD, the  $Q_\mu$  values lie in the interval from -32 to +25.

(2) For CD<sub>3</sub>OH, the sensitivity coefficients vary in a wide range from -300 at 1.202 GHz to +73 at 4.011 GHz.

(3) For CD<sub>3</sub>OD, the two neighboring transitions at 2.237 ( $Q_\mu = -44$ ) and 2.328 GHz ( $Q_\mu = +38$ ) confine the  $Q_\mu$  values from the whole sample in the frequency range 2–40 GHz.

(4) We also found that along with good agreement of the  $Q_\mu$  values for the parent methanol CH<sub>3</sub>OH calculated with different Hamiltonians in the present and previous works, there are several pronounced outliers of unclear nature in the isotopologues CD<sub>3</sub>OH and CD<sub>3</sub>OD.

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