

## Methanol as a Sensitive Probe for Spatial and Temporal Variations of the Proton-to-Electron Mass Ratio

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The 6.7 and 12.2 GHz masers, corresponding to the  $5_1 \rightarrow 6_0A^+$  and  $2_0 \rightarrow 3_{-1}E$  transitions in methanol ( $\text{CH}_3\text{OH}$ ), respectively, are among the brightest radio objects in the sky. We present calculations for the sensitivity of these and other transitions in the ground state of methanol to a variation of the proton-to-electron mass ratio. We show that the sensitivity is greatly enhanced due to a cancellation of energies associated with the hindered internal rotation and the overall rotation of the molecule. We find sensitivities of  $K_\mu = -42$  and  $K_\mu = -33$ , for the  $5_1 \rightarrow 6_0A^+$  and  $2_0 \rightarrow 3_{-1}E$  transitions, respectively. The sensitivities of other transitions in the different isotopologues of methanol range from  $-88$  to  $330$ . This makes methanol a sensitive probe for spatial and temporal variations of the proton-to-electron mass ratio.

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A possible spatial or temporal variation of the fine structure constant  $\alpha$  or the proton-to-electron mass ratio  $\mu$  can be detected by comparing transitions in atoms and molecules as a function of time and/or position. As these transitions have, in general, a different dependence on  $\alpha$  and  $\mu$ , a possible variation might be observed as a shift of the transition frequencies [1,2]. In astrophysical searches, the frequencies of two or more atomic and molecular absorptions from distant objects are compared with the frequencies as measured in the laboratory. This allows one to determine the apparent redshift—and hence distance to the object—and a possible variation. In this Letter, we discuss the use of molecules to detect a variation of  $\mu$ . The sensitivity of an experiment searching for a frequency shift  $\Delta\nu$  due to the variation of  $\mu$  depends both on the size of the shift, i.e., the inherent sensitivity of the molecular transition, and on the ability to measure this shift. As a measure for the inherent sensitivity of a transition, the sensitivity coefficient  $K_\mu$  is defined via

$$\frac{\Delta\nu}{\nu} = K_\mu \frac{\Delta\mu}{\mu}. \quad (1)$$

For a sensitive test, one needs molecular transitions that are observed with a good signal to noise and that exhibit high  $K_\mu$ . Transitions in hydrogen, the most abundant molecule in outer space and observed at high redshift ( $z = 3$ ), have sensitivities that range from  $K_\mu = -0.02$  to  $+0.05$  [2–4]. Rotational transitions in CO, the second most abundant molecule in space, have a sensitivity of  $K_\mu = -1$ . The inversion frequency in ammonia is exponentially dependent on  $\mu$ . As a consequence, the inversion frequency in ammonia has a sensitivity of  $K_\mu = -4.2$  [5–7].

It was noticed by Flambaum [8], Flambaum and Kozlov [9], DeMille *et al.* [10], and Bethlem and Ubachs [11] that the sensitivity to a variation of  $\alpha$  and  $\mu$  is enhanced when an accidental degeneracy occurs between levels which have substantially different dependences on  $\alpha$  and  $\mu$ —for instance, when rotational splittings are equal to a hyperfine structure splitting [8] or fine structure splitting [11] or when a vibrational splitting is equal to a fine structure splitting [9] or an electronic splitting [10]. However, the molecular transitions discussed in these papers are unlikely to be observed in interstellar objects. In this Letter, we show that a significant enhancement occurs in methanol due to a cancellation of energies associated with the hindered internal rotation and the overall rotation of the molecule. This is particularly relevant as methanol is abundantly present in the Universe.

Methanol is one of the simplest molecules that exhibits hindered internal rotation and has, therefore, been the subject of numerous experimental and theoretical studies [12–18]. The structure of methanol, depicted on the right-hand side of Fig. 1, consists of a methyl group, with a hydroxyl group attached. The center of mass of the OH group is slightly displaced from the symmetry axis of the methyl group. The overall rotation is described by three rotational constants  $A$ ,  $B$ , and  $C$ , associated with the moments of inertia  $I_a$ ,  $I_b$ , and  $I_c$ , respectively, along the three principal axes. The total angular momentum of the molecule is given by the quantum number  $J$ , while the projection of  $J$  onto the molecule fixed axis is given by  $K$ .

In addition to the overall rotation, methanol has internal rotation; the OH group rotates with respect to the methyl group. The angle between the two parts of the molecule is denoted by  $\gamma$ . The rotation is severely hindered, due to the

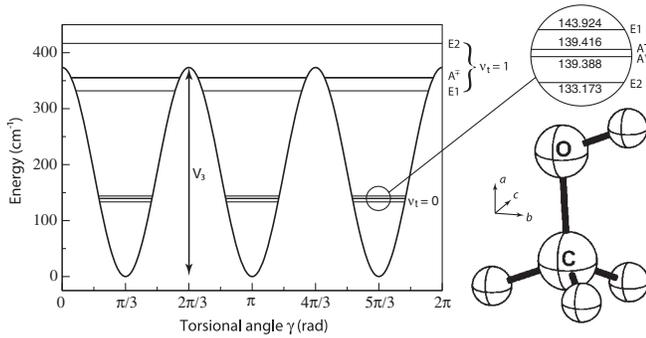


FIG. 1. Variation of the potential energy of methanol with the relative rotation  $\gamma$  of the OH group with respect to the methyl group about the molecular axis. Shown are the  $J = 1$ ,  $|K| = 1$  energies of the lowest torsion-vibrational levels. The splitting between the different symmetry levels is due to tunneling through the potential barriers. The  $A$ -symmetry species are split further due to the asymmetry of the molecule ( $K$  splitting).

repulsion of a threefold torsional potential energy curve, shown on the left-hand side of Fig. 1. The vibrational levels in this well are denoted by  $\nu_t$ . In lowest order—neglecting higher orders in the potential and centrifugal distortions—the Hamiltonian can be written as [12]

$$H = \frac{1}{2} \frac{P_a^2}{I_a} + \frac{1}{2} \frac{P_b^2}{I_b} + \frac{1}{2} \frac{P_c^2}{I_c} + \frac{1}{2} \frac{1}{I_{\text{red}}} p_\gamma^2 + \frac{1}{2} V_3(1 - \cos 3\gamma),$$

$$\text{with } I_{\text{red}} = \frac{I_{a1} I_{a2}}{I_a}. \quad (2)$$

The first three terms describe the overall rotation around the  $a$ ,  $b$ , and  $c$  axis, respectively. The fourth term describes the internal rotation around the  $a$  axis, with  $I_{\text{red}}$  the reduced moment of inertia along the  $a$  axis,  $I_{a2}$  the moment of inertia of the methyl group along its own symmetry axis, and  $I_{a1}$  the part of  $I_a$  that is attributed to the OH group;  $I_{a1} = I_a - I_{a2}$ . The fifth term is the lowest order term arising from the torsional potential. If the torsional potential were infinitely high, the threefold barrier would result in three separate harmonic potentials, with rotational

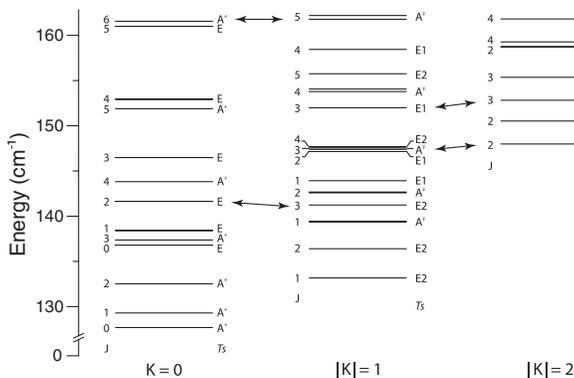


FIG. 2. Energy of the lowest rotational levels in the torsion-vibrational ground state ( $\nu_t = 0$ ) of methanol [18]. The levels are denoted by  $J$  and  $K$  and by their torsional symmetry  $T_s$ .

energies corresponding to the harmonic oscillator eigenvalues. In the case of a finite barrier, quantum-mechanical tunneling mixes the levels in the different wells of the potential. As a result, every  $K$  level is split into three levels, which can be labeled according to torsional symmetry,  $T_s$ , as  $A$ ,  $E1$ , or  $E2$ . Following Lees [14],  $E1$  and  $E2$  symmetries are labeled by the sign of  $K$ ; i.e., levels with  $E1$  symmetry are denoted by a positive  $K$  value, whereas levels with  $E2$  symmetry are denoted by a negative  $K$  value. For  $K \neq 0$ ,  $A$  levels are further split into  $+$  and  $-$  components by molecular asymmetry. For  $K = 0$ , only single  $E$  and  $A^+$  levels exist. The tunneling motion in the torsional potential is similar to the inversion motion in ammonia, which exhibits an increased sensitivity to a possible variation of the proton-to-electron mass ratio [5,6]. This similarity prompted us to study the methanol spectrum. In Fig. 2, the lowest energy levels of  $^{12}\text{CH}_3^{16}\text{OH}$  are shown.

The splitting between the different symmetry levels is related to the tunneling frequency between the different torsional potential wells, and hence, it is very sensitive to the reduced moment of inertia. In Fig. 3, the energy splittings between  $A$  and  $E$  levels of the  $J = 0$ ,  $K = 0$  and the energy splitting between  $E1$  and  $E2$  levels in the  $J = 1$ ,  $|K| = 1$  are plotted as a function of the reduced moment of inertia  $I_{\text{red}}$  along the  $a$  axis for six different isotopologues of methanol [18]. In analogy with ammonia [5], we expect the tunneling splitting to follow the formula

$$W_\gamma = \frac{a_0}{\sqrt{I_{\text{red}}}} e^{-a_1 \sqrt{I_{\text{red}}}}, \quad (3)$$

with  $W_\gamma$  the energy splitting due to hindered rotation and  $a_0$  and  $a_1$  constants. The fitted lines in Fig. 3 correspond to  $a_0 = 316$  and  $433 \text{ cm}^{-1} (\text{amu} \text{ \AA}^2)^{1/2}$  and  $a_1 = 4.9$  and  $5.1 (\text{amu} \text{ \AA}^2)^{-1/2}$  for  $K = 0$  and  $|K| = 1$ , respectively.

If we assume that possible variations of the proton and neutron masses scale in a similar manner, the reduced

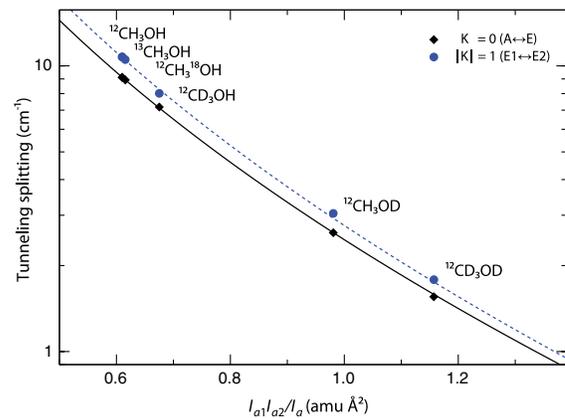


FIG. 3 (color online). Energy splitting between  $A$  and  $E$  levels of the  $J = 0$ ,  $K = 0$  (diamonds) and the energy splitting between  $E1$  and  $E2$  levels of the  $J = 1$ ,  $|K| = 1$  (circles) as a function of the reduced moment of inertia along the  $a$  axis for six different isotopologues of methanol [18]. The solid and dashed lines are fits according to Eq. (3).

moment of inertia is directly proportional to  $\mu$ . Thus, the sensitivity coefficient is given by

$$K_{\mu}^{\text{tors}} = \frac{I_{\text{red}}}{W_{\gamma}} \frac{\partial W_{\gamma}}{\partial I_{\text{red}}}. \quad (4)$$

From the above fits, we find for the  $K = 0$  and  $|K| = 1$  splitting a sensitivity coefficient of  $K_{\mu}^{\text{tors}} = -2.4$  and  $K_{\mu}^{\text{tors}} = -2.5$ , respectively.

In the case of ammonia, the tunneling frequency can be directly measured by inducing a transition between the two inversion levels. In the case of methanol, however, the different torsional levels of a specific  $J, K$  state have different torsional symmetries, and transitions between these levels are not allowed. Hence, we look for rotational transitions between levels which differ in  $K$  and/or  $J$ . The sensitivity coefficients of these transitions are given by

$$K_{\mu}(\nu_i'', J'', K'', T_s'' \rightarrow \nu_i', J', K', T_s') = \frac{\mu(\partial E/\partial \mu)_{\nu_i'', J'', K'', T_s''} - \mu(\partial E/\partial \mu)_{\nu_i', J', K', T_s'}}{E(\nu_i'', J'', K'', T_s'') - E(\nu_i', J', K', T_s')}, \quad (5)$$

with

$$\mu \left( \frac{\partial E}{\partial \mu} \right)_{\nu, J, K, T_s} = K_{\mu}^{\text{vib}} E_{\text{vib}} + K_{\mu}^{\text{rot}} E_{\text{rot}} + K_{\mu}^{\text{tors}} E_{\text{tors}}, \quad (6)$$

where  $K_{\mu}^{\text{vib}}$ ,  $K_{\mu}^{\text{rot}}$ , and  $K_{\mu}^{\text{tors}}$  are the sensitivities to a possible variation of the proton-to-electron mass ratio of a vibrational, rotational, and torsional energy level, respectively. In the first-order approximation,  $K_{\mu}^{\text{vib}} = -\frac{1}{2}$  and  $K_{\mu}^{\text{rot}} = -1$ . Equation (5) suggests that the sensitivity is enhanced for transitions between near degenerate levels. In Fig. 2, some of these transitions have been indicated. Let us, for instance, look at the  $5_1 \rightarrow 6_0 A^+$  transition, which corresponds to the strong 6.7 GHz maser line that is observed in many interstellar objects. Using the known energies of the rotational levels and  $K_{\mu}^{\text{tors}} = -2.4$ , we find  $K_{\mu} = -41$ . Similarly, for the  $2_0 \rightarrow 3_{-1} E$  transition, which corresponds to the 12.2 GHz maser line, we find  $K_{\mu} = -33$ .

In order to validate this simple model, we have simulated the methanol level energies by using BELGI [19]. This code was modified and improved by Xu *et al.* in a number of ways useful for treating the large data sets available for the methanol molecule [18]. Note that, rather than the Hamiltonian given in Eq. (2), BELGI uses an axis transformation (the so-called ‘‘rho-axis method’’) to simplify the calculation. This Hamiltonian is diagonalized in a two-step process to obtain the level energies. By using a set of 119 molecular constants for  $^{12}\text{CH}_3^{16}\text{OH}$  and 53 or more for the other isotopologues taken from Ref. [18], the lower energy levels are found typically with an accuracy  $< 50$  kHz. In order to obtain the sensitivity to a variation of the proton-to-electron mass ratio of each level, the molecular constants are scaled by using the relations given in Ref. [20].

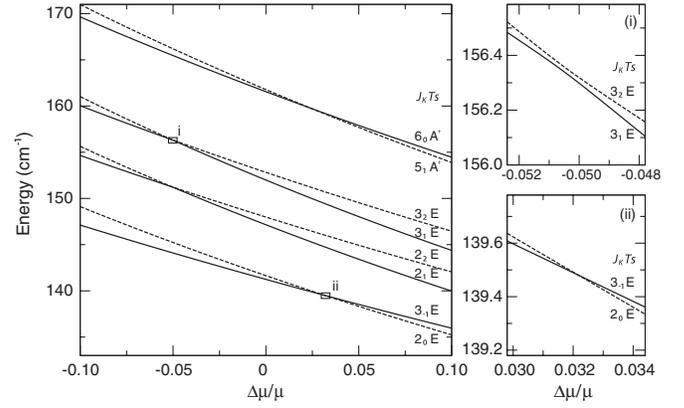


FIG. 4. Energies of selected rotational levels as a function of the fractional change in the proton-to-electron mass ratio. The panels on the right-hand side of the figure show enlargements of selected crossings. It is seen that levels with the same  $J$  give rise to avoided crossings, whereas levels with different  $J$  do not interact.

In Fig. 4, the energies of selected states (indicated in Fig. 2) are shown as a function of the fractional change of the proton-to-electron mass ratio. As expected, the energies of all rotational levels decrease for larger values of  $\Delta\mu/\mu$ . However, levels that have different  $J$  and  $K$  are seen to have a different dependence. The sensitivity coefficient for a transition connecting different levels is given by the difference of the slopes divided by their energy difference—in accordance with Eq. (5). Large sensitivity coefficients are expected when different levels cross in the vicinity of  $\Delta\mu/\mu = 0$ . If the levels cross at  $\Delta\mu/\mu < 0$ ,  $K_{\mu}$  will be positive; if the levels cross at  $\Delta\mu/\mu > 0$ ,  $K_{\mu}$  will be negative. Note that the behavior of the sensitivity coefficient very close to the resonance depends on the quantum numbers of the levels involved. For equal  $J$ , the levels will mix and  $K_{\mu}$  goes to zero, whereas if the levels have unequal  $J$ ,  $K_{\mu}$  goes to infinity.

We have calculated the sensitivity coefficients for several transitions in the most common isotopologues of methanol. The most sensitive transitions involving levels with  $J \leq 10$  are listed in Table I. The error in the last digit of the  $K_{\mu}$  coefficients is quoted in brackets. The error has 3 sources: (i) errors due to the uncertainty in the determination of the molecular constants, (ii) errors due to inexactness of the scaling relations of higher order constants, and (iii) errors due to neglecting the  $\mu$  dependence of the torsional potential. We estimate the error to be below 5% when  $K_{\mu} \geq 1$  or below 0.05 when  $K_{\mu} < 1$  (for further details, see [20]). It is seen that the values of the sensitivity coefficients for the  $5_1 \rightarrow 6_0 A^+$  and  $2_0 \rightarrow 3_{-1} E$  transitions agree well with those found by using Eq. (5). In Ref. [20], the sensitivity coefficients for all transitions that have been observed in interstellar masers [17] are listed.

It is important to note that the sensitivity coefficients of the transitions in Table I have both large positive and large negative values; i.e., if the proton-to-electron mass ratio

TABLE I. Selected transitions and  $K_\mu$  coefficients for different isotopologues of methanol, calculated with BELGI. All lines listed for  $^{12}\text{CH}_3^{16}\text{OH}$  are observed as maser lines [17], except for the two lines marked with an asterisk. The error in the last digit(s) is quoted within brackets.

Isotopologue	Transition, $J_K$	Transition (MHz)	$K_\mu$	
$^{12}\text{CH}_3^{16}\text{OH}$	$1_1 \rightarrow 1_1 A^+$	834.280	-1.03(5)	
	$3_1 \rightarrow 3_1 A^+$	5 005.302	-1.03(5)	
	$5_1 \rightarrow 6_0 A^+$	6 668.567	-42.(2)	
	$9_{-1} \rightarrow 8_{-2} E$	9 936.137	11.5(6)	
	$5_2 \rightarrow 4_3 A^+$	9 978.718*	53.(3)	
	$5_2 \rightarrow 4_3 A^-$	10 058.295*	52.(3)	
	$2_0 \rightarrow 3_{-1} E$	12 178.587	-33.(2)	
	$2_1 \rightarrow 3_0 E$	19 967.376	-5.9(3)	
	$9_2 \rightarrow 10_1 A^+$	23 120.916	-11.7(6)	
	$3_2 \rightarrow 3_1 E$	24 928.726	17.9(9)	
	$2_2 \rightarrow 2_1 E$	24 934.399	17.9(9)	
	$8_2 \rightarrow 9_1 A^-$	28 969.965	-9.5(6)	
	$4_{-1} \rightarrow 3_0 E$	36 169.259	9.7(5)	
	$6_2 \rightarrow 5_3 A^-$	38 293.273	-15.1(8)	
	$6_2 \rightarrow 5_3 A^+$	38 452.632	-15.0(8)	
	$7_0 \rightarrow 6_1 A^+$	44 069.364	5.2(3)	
	$1_0 \rightarrow 2_{-1} E$	60 531.477	-7.4(4)	
	$1_1 \rightarrow 2_0 E$	68 305.629	-2.4(1)	
	$^{12}\text{CD}_3^{16}\text{OH}$	$1_1 \rightarrow 2_2 E$	1 202.296	330.(20)
		$2_0 \rightarrow 1_1 E$	1 424.219	-42.(2)
$9_2 \rightarrow 8_3 E$		2 827.262	43.(2)	
$5_1 \rightarrow 6_0 A^+$		2 971.067	93.(5)	
$4_{-1} \rightarrow 3_0 E$		4 011.340	-73.(4)	
$6_4 \rightarrow 5_5 E$		6 723.841	167.(8)	
$9_6 \rightarrow 10_5 A^+$		20 088.522	-88.(4)	
$^{12}\text{CH}_3^{18}\text{OH}$	$9_6 \rightarrow 10_5 A^-$	20 088.522	-88.(4)	
	$9_2 \rightarrow 10_1 A^-$	2 604.912	93.(5)	
$^{12}\text{CD}_3^{16}\text{OD}$	$2_0 \rightarrow 3_{-1} E$	11 629.591	-34.(2)	
	$1_0 \rightarrow 1_{-1} E$	2 237.883	45.(2)	
$^{13}\text{CH}_3^{16}\text{OH}$	$7_{-4} \rightarrow 8_{-3} E$	2 329.088	-80.(4)	
	$9_{-1} \rightarrow 8_{-2} E$	1 989.502	-63.(3)	

varies, some transitions will shift to higher frequencies while others shift to lower frequencies. This makes it possible to perform a test of the variation of the proton-to-electron mass ratio by using transitions in methanol only, thus avoiding the many systematic effects that plague tests based on comparing transitions in different molecules. Detection of methanol at even modest redshift will facilitate more stringent bounds on a possible variation of  $\mu$  over cosmological time scales. Darling *et al.* [16] have performed a dedicated survey for 6.7 GHz methanol maser emission in OH megamaser galaxies at  $0.11 < z < 0.27$ . No detections were made in the 25 observed objects. It is our hope that this Letter will stimulate broader surveys.

The high sensitivity coefficients in methanol are also beneficial for probing variation of  $\mu$  as a result of chameleonlike scalar fields. These fields predict a dependence of  $\mu$  on the local matter density. Recently, Levshakov *et al.*

[21] compared ammonia spectra taken at high (terrestrial) and low (interstellar) densities of baryonic matter and observed a statistically significant variation of  $\mu$ . Using methanol, rather than ammonia, in these tests should result in an at least 1 order of magnitude increase in sensitivity.

Furthermore, methanol is a promising candidate for laboratory tests on a possible variation of  $\mu$ . For instance, when combined, the  $1_1 \rightarrow 2_1 E$  transition and the  $4_{-1} \rightarrow 3_0 E$  transition in  $\text{CD}_3\text{OH}$  have a sensitivity that is more than 400 times larger than a pure rotational transition. Note that the large dipole moment and low mass make it possible to manipulate methanol molecules by using electric fields.

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*Note added.*—Recently, Kozlov and Levshakov [22] reported an enhanced  $K_\mu$  for specific transitions in  $\text{H}_3\text{O}^+$ .

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