Acetaldehyde as a molecule for testing variations of electron-to-proton mass ratio

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We present the quantum-mechanical calculations of the dimensionless sensitivity coefficients Q for small changes in the fundamental physical constant $\mu = m_e/m_p$ (the electron-to-proton mass ratio) for a number of low-frequency (1–50 GHz) transitions of the acetaldehyde (CH_3CHO) molecule. The calculations show that Q varies in the range from 0.62 to 3.61. An example of the practical use of the CH_3CHO and CH_3OH lines tracing the same regions in three molecular clouds, located at large galactocentric distances ($D_{GC} \sim 8$ kpc), is considered. This results in a limit on the μ variations of $\Delta\mu/\mu = (0.1 \pm 0.4) \times 10^{-7}$, which is in line with the most stringent upper limits on changes in μ previously obtained based on other molecules and methods. The limit obtained restricts hypothetical violations of the Einstein principle of the local position invariance at the level of 4×10^{-8} in the Galactic disk at large galactocentric distances.

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I. INTRODUCTION

Complex organic molecules are carbon-bearing molecules that consist of at least six atoms. At astrophysical conditions these molecules are observed in the interstellar medium (ISM) and are present at all stages of star formation, from dense molecular clouds to protostellar and young stellar objects and protoplanetary disks. This prevalence makes it possible to investigate the physical and chemical conditions throughout the star- and planet-formation processes using spectral observations of such molecules.

Among complex organic molecules, a special class can be distinguished: molecules with hindered internal motion. Currently, simpler six-atom molecules (CH_3OH, CH_3SH) and the more complex (up to 12 atoms) molecule $C_2H_5OCH_3$ have been detected in the ISM [1–3]. They are listed in Table I.

Molecules with hindered internal motion have an important specificity: Torsion-rotational transitions of such molecules, which fall within the microwave spectral range, have high sensitivity coefficients Q for hypothetical variations in the electron-to-proton mass ratio $\mu = m_e/m_p$, which are individual for each transition. This makes such molecules not only a probe of the physical and chemical conditions in star-forming regions but also a tool for testing fundamental physical laws, such as Einstein's principle of local position invariance (LPI), which states that nongravitational measurements are independent of their location in space and time. A violation of the LPI has been predicted in a number of theories [4].

In general, sensitivity coefficients Q have previously been calculated for many molecules. The first molecule for these purposes was molecular hydrogen, H_2, for the Lyman and Werner electrovibrorotational transitions, for which the Q values turned out to be rather small, $Q \sim 10^{-2}$ [5] compared with those for pure rotational molecular transitions, $Q = 1$ [6]. It was also shown that the inversion transition $(J, K = 1, 1)$ of the ammonia molecule NH_3 has a rather high value of $Q = +4.46$ [7].

In 2012–2013, calculations were performed for the methyl mercaptan molecule (CH_3SH); for its various transitions, the values of Q range from –12.2 to +14.8 [8], and methylamine (CH_3NH_2) has $-24 \leqslant Q \leqslant +19$ [9]. For a number of complex organic molecules (CH_3CHO, CH_3CONH_2, CH_3OCOH, CH_3COOH), sensitivity coefficients for a few transitions were calculated in [10] as well.

However, as shown by two independent methods in 2011, the highest values of the sensitivity coefficients are for the transitions of methanol (CH_3OH): $-53 \leqslant Q \leqslant +42$ [11,12]. Compared with the pioneering work on molecular hydrogen, the use of methanol transitions yields an efficiency 1000 times greater in estimates of μ variations. Based on this fact, Q coefficients were recently calculated for methanol isotopologues, which showed that these molecules have even higher sensitivity coefficients than basic methanol: $-32 \leqslant Q \leqslant +78$ for $^{13}CH_3OH$, $-109 \leqslant Q \leqslant +33$ for $CH_3{}^{18}OH$, and $-32 \leqslant Q \leqslant +25$, $-300 \leqslant Q \leqslant +73$, $-44 \leqslant Q \leqslant +38$ for deuterated methanol (CH_3OD), CD_3OH, and CD_3OD, respectively [13,14].

The hypothetical variations in μ can be estimated from a pair of molecular transitions with different Q values [11]:

$$\frac{\Delta\mu}{\mu} = \frac{V_j - V_i}{c(Q_i - Q_j)}, \tag{1}$$

where V_j and V_i are the measured radial velocities in the local-standard-of-rest (LSR) velocity system V_{LSR} of a pair of molecular transitions having sensitivity coefficients Q_j and Q_i, c is the speed of light, and $\Delta\mu/\mu$ is the fractional difference between the astronomical (μ_{obs}) and terrestrial (μ_{lab}) values of μ, $\Delta\mu/\mu = (\mu_{obs} - \mu_{lab})/\mu_{lab}$. The radial velocity

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TABLE I. Complex organic molecules with hindered internal motion observed in the interstellar medium [1–3].

Number of atoms	Molecular formula		
6	CH_3OH	CH_3SH	
7	CH_3CHO	CH_3NH_2	CH_3NCO
8	$HC(O)OCH_3$	CH_3COOH	CH_3CHNH
9	CH_3OCH_3	CH_3CONH_2	CH_3NHCHO
10	CH_3COCH_3	CH_3CHCH_2O	CH_3OCH_2OH
	$HOCH_2CH_2OH$		
11	$CH_3C(O)OCH_3$		
12	$C_2H_5OCH_3$		

is defined according to the radio-astronomical convention:

$$V_{\rm LSR} = c(1 - f_{\rm obs}/f_{\rm lab}), \tag{2}$$

where $f_{\rm lab}$ and $f_{\rm obs}$ are the laboratory and observed transition frequencies, respectively.

The tightest upper limits on $\Delta\mu/\mu$ in the galactic disk at large galactocentric distances ($D_{\rm GC} \gtrsim 4$ kpc) are obtained with observations of the NH_3 (1, 1) inversion transition in combination with pure rotational transitions of HC_3N, HC_5N, and HC_7N, $\Delta\mu/\mu < 7 \times 10^{-9}$ [15], and with methanol lines (CH_3OH and $^{13}CH_3OH$), $\Delta\mu/\mu < (1-3) \times 10^{-8}$ [14,16–19].[1]

It should be noted that in the vicinity of the galactic center ($D_{\rm GC} \simeq 0.1$ kpc), which contains a supermassive black hole ($M_{\rm BH} \sim 4 \times 10^6 M_\odot$) and a massive complex of molecular clouds, Sagittarius (Sgr) B2 ($M_{\rm Sgr} \sim 6 \times 10^7 M_\odot$), an indication of a reduced value of μ was recently found from the microwave spectra of methanol (CH_3OH) observed in the hot core Sgr B2(N): $\Delta\mu/\mu = (-4.2 \pm 0.7) \times 10^{-7}$ [20], based on Herschel space telescope observations,[2] and $\Delta\mu/\mu = (-2.1 \pm 0.6) \times 10^{-7}$ [21], based on Institute for Radio Astronomy in the Millimeter Range (IRAM) 30-m telescope observations. At the same time, a set of methanol lines identical to that for Sgr B2(N) observed with Herschel for another complex of molecular clouds, Orion-KL ($D_{\rm GC} \simeq 8$ kpc), yields only an upper limit of $\Delta\mu/\mu = (-0.5 \pm 0.6) \times 10^{-7}$ [20].

This shows that the search for new molecules that are ubiquitous in space and that can be used to assess μ remains an urgent task to confirm previous evaluations of $\Delta\mu/\mu$ and to mitigate possible systematic effects.

One such molecule is acetaldehyde, CH_3CHO, which is widespread in the different environments of the ISM. The sensitivity coefficients for eight selected microwave transitions from the frequency range $\Delta f = 1.8$–47.8 GHz were calculated in [10].

In the present paper, we extend the list of acetaldehyde lines from the low-frequency range ($\Delta f = 1$–50 GHz) and calculate the corresponding Q values using a different method based on a simpler structure of the Hamiltonian. The results obtained are given in Sec. II. In Sec. III, we discuss an example of the $\Delta\mu/\mu$ estimation from a combined sample of methanol and acetaldehyde lines detected in the spectra of three molecular clouds. Finally, in Sec. IV, we conclude.

II. SENSITIVITY COEFFICIENTS OF THE SELECTED TRANSITION IN ACETALDEHYDE (CH_3CHO)

A. General remarks

Acetaldehyde (CH_3CHO) is a complex organic molecule similar in structure to methanol CH_3OH, which is also characterized by hindered internal rotation. CH_3CHO consists of seven atoms: three hydrogens and carbon in the methyl group (CH_3) and carbon, oxygen, and hydrogen in the CHO group. The internal rotation here is related to the quantum-mechanical tunneling effect. The methyl group (CH_3) can undergo torsional vibrations relative to the CHO group, where the hydrogen atom can be in one of three possible positions with equal energies.

There are two types of acetaldehyde that differ in symmetry properties: A type, for which the total nuclear spin of the methyl group is $I_{CH_3} = 3/2$, and E type, with $I_{CH_3} = 1/2$.

It is worth noting that transitions between A- and E-acetaldehyde are not observed since radiative and collisional transitions between the two types with proton spin flips are unlikely due to the extremely low efficiency of interaction of nuclear spins with magnetic and electric fields.

Figure 1 shows a diagram of the A and E levels of the CH_3CHO molecule. Note that the energy of the ground torsion state of E-type acetaldehyde ($v_t = 0, J = 0$) differs from zero and is 0.097 K. A similar characteristic is also observed for E-type methanol.

B. Calculating procedure

To calculate the sensitivity coefficients Q, the procedure described in [11] is used. This procedure is based on a simple and physically transparent model of the effective Hamiltonian [22], containing only seven spectroscopic parameters which have clear physical insight: three rotation parameters (A, B, C), one parameter (D) describing the interaction of the internal rotation with the overall rotation, the kinetic coefficient F, the depth of the threefold symmetric torsion potential V_3, and a dimensionless parameter ρ, which is the internal rotation interaction constant. The listed parameters can be calculated using the following formulas:

$$A = \frac{1}{2}\hbar^2\left(\frac{I_a + I_b}{I_a I_b - I_{ab}^2} - \frac{I_b}{I_b^2 + I_{ab}^2}\right), \tag{3}$$

$$B = \frac{1}{2}\hbar^2 \frac{I_b}{I_b^2 + I_{ab}^2}, \tag{4}$$

$$C = \frac{1}{2}\hbar^2 \frac{1}{I_c}, \tag{5}$$

[1]All upper limits on $\Delta\mu/\mu$ throughout the paper are given at the 1σ confidence level.

[2]Herschel is a European Space Agency space observatory with science instruments provided by European-led principal investigator consortia with important participation from NASA. IRAM is an international research institute and Europe's leading center for radio astronomy.

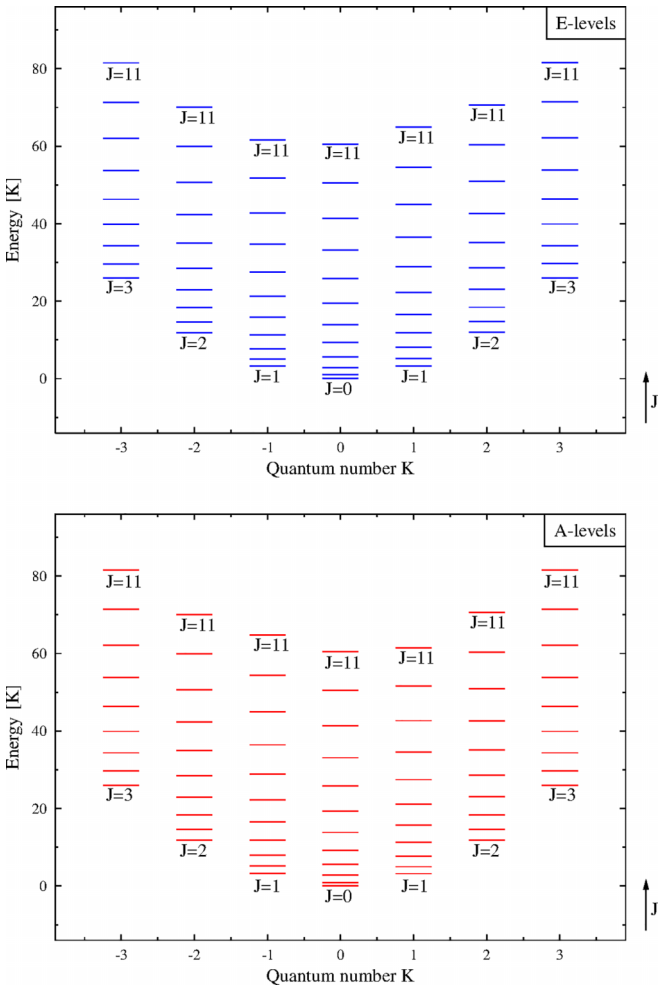

FIG. 1. Partial rotational level diagrams of the A and E levels of acetaldehyde (CH_3CHO) in the torsional ground state ($v_t = 0$). The energy of the ground torsion state of E-type acetaldehyde is 0.097 K.

$$D = \frac{1}{2}\hbar^2 \frac{I_{ab}}{I_b^2 + I_{ab}^2}, \tag{6}$$

$$F = \frac{1}{2}\hbar^2 \frac{I_a I_b - I_{ab}^2}{I_{a2}\left(I_{a1} I_b - I_{ab}^2\right)}, \tag{7}$$

$$\rho = \frac{I_{a2}\sqrt{I_b^2 + I_{ab}^2}}{I_a I_b - I_{ab}^2}. \tag{8}$$

Here $\hbar = h/2\pi$; I_a, I_b, and I_c are the moments of inertia. 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); the c axis is perpendicular to the CHO plane. I_{a2} is the axial moment of inertia of the methyl group, and I_{a1} is that of the framework (the CHO group), the sum of which determines I_a: $I_a = I_{a1} + I_{a2}$.

The moments of inertia, displayed in Table II, are assumed to be known from [23].

Table III shows the values of the spectroscopic constants calculated from the moments of inertia in accordance with formulas (3)–(6). Table III also contains an asymmetry parameter

TABLE II. Moments of inertia (in a.m.u. Å^2) for acetaldehyde (CH_3CHO) [23].

I_a	I_b	I_{ab}[a]	I_c
15.6230	43.0165	–15.1467	55.6095

[a]$I_{ab} = I_{ba}$ in [23].

κ, which is defined as [24]

$$\kappa = \frac{2B - A - C}{A - C}. \tag{9}$$

κ is equal to 1 or –1 when the molecule is a symmetric top. In Table III, the methanol parameters from [14] are also listed for comparison.

The calculated spectroscopic parameters were used to determine the Hamiltonian matrix, the nonvanishing elements of which are listed in [13] for specific values of the rotational angular momentum J. Diagonalization of this matrix simultaneously gives the eigenvalues (energies) and eigenfunctions for A- and E-type acetaldehyde. The dependence of the found eigenvalues E_i on $\Delta\mu/\mu$ defines the sensitivity coefficient Q through the following relations [11]:

$$\Delta E_i = q_i \frac{\Delta\mu}{\mu}, \tag{10}$$

$$Q = \frac{q_u - q_\ell}{hf}. \tag{11}$$

Here ΔE_i is the energy shift due to nonzero $\Delta\mu/\mu$; q_i is the so-called q factor, which is different for each level E_i, which shows a response of this level to a small changes in μ when $|\Delta\mu/\mu| \ll 1$. f is the laboratory frequency of a given transition, and h is Planck's constant. The subscripts u and ℓ denote the upper and lower levels, respectively. 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 ε is equal to 0.001 or 0.0001 and $\mu_0 \equiv \mu_{\text{lab}}$ [11].

C. Calculated sensitivity coefficients

For calculations we selected molecular transitions with $0 \leqslant J \leqslant 11$ and $|\Delta K| = 1$ since transitions with $\Delta K = 0$ are purely rotational and have $Q \approx 1$. However, for a number of

TABLE III. Spectroscopic parameters of the effective Hamiltonian and the asymmetry parameter κ for CH_3CHO and CH_3OH for comparison.

	CH_3CHO	CH_3OH
A (cm^{-1})	1.8846	4.2556
B (cm^{-1})	0.3487	0.8232
C (cm^{-1})	0.3031	0.7928
D (cm^{-1})	−0.1228	−0.0026
F[a] (cm^{-1})	7.6559	27.7518
V_3[a] (cm^{-1})	407.9	375.6
ρ[a]	0.3291	0.8109
κ	−0.0.942	−0.982

[a]Values for CH_3CHO are taken from [25].

TABLE IV. Calculated sensitivity coefficients Q for the low-frequency ($\Delta f = 1$–50 GHz) torsion-rotation transitions ($\Delta K = \pm 1$) in CH_3CHO measured in the laboratory [25]. Given in parentheses are errors in the last digits.

$J_{K_u} \to J_{K_\ell}$	f (MHz)	Q	$S\mu_D^2$ (D^2)
$1_{-1} \to 2_0 E$	7391.311	0.62(18)	0.4618
$1_1 \to 2_0 E$	9240.920	1.22(14)	0.1265
$7_2 \to 8_1 A^+$	9542.776	1.4(8)	1.1288
$3_0 \to 2_1 A^+$	12014.990	0.88(13)	1.2070
$3_0 \to 2_{-1} E$	12635.239	1.13(12)	1.1435
$10_3 \to 11_2 E$	14456.880	1.2(6)	0.9221
$10_3 \to 11_2 A^+$	14691.111	1.3(6)	1.8549
$6_2 \to 7_1 A^+$	23364.771	1.2(3)	0.9936
$10_{-3} \to 11_{-2} E$	24859.393	0.9(3)	0.8897
$10_3 \to 11_2 A^-$	27173.880	1.2(2)	1.7823
$8_1 \to 7_2 E$	29310.400	0.92(19)	0.2753
$8_1 \to 7_2 A^-$	30941.333	0.9(2)	1.7519
$4_0 \to 3_1 A^+$	32709.185	0.96(6)	1.8589
$4_0 \to 3_{-1} E$	33236.469	1.03(6)	1.8268
$5_{-2} \to 6_{-1} E$	35472.152	0.85(14)	0.3298
$9_3 \to 10_2 A^+$	36613.186	1.1(2)	1.5908
$4_2 \to 5_1 A^-$	37516.317	1.10(12)	0.7415
$5_2 \to 6_1 A^+$	38138.436	1.09(13)	0.8226
$2_{-1} \to 2_0 E$	45078.240	0.96(3)	0.1320
$9_3 \to 10_2 A^-$	45344.590	1.10(14)	1.5489
$1_{-1} \to 1_0 E$	45897.330	0.94(2)	0.3593

TABLE V. Calculated sensitivity coefficients Q for the low-frequency ($\Delta f = 1$–50 GHz) torsion-rotation transitions ($\Delta K = \pm 1$) in CH_3CHO predicted in [25]. Given in parentheses are errors in the last digits.

$J_{K_u} \to J_{K_\ell}$	f (MHz)	Q	$S\mu_D^2$
$9_{-1} \to 8_{-2} E$	8397.01	1.4(9)	0.0959
$6_{-2} \to 7_{-1} E$	20274.43	0.8(3)	0.2790
$11_{-1} \to 11_0 E$	21203.544	1.0(2)	0.0005
$10_{-1} \to 9_{-2} E$	21914.175	1.12(4)	0.0465
$10_{-1} \to 10_0 E$	24270.204	0.99(18)	0.0008
$4_0 \to 3_1 E$	26691.022	0.99(7)	0.0255
$9_{-1} \to 9_0 E$	27432.732	0.99(15)	0.0013
$8_{-1} \to 8_0 E$	30609.589	0.99(12)	0.0021
$7_{-1} \to 7_0 E$	33712.067	0.99(9)	0.0035
$11_{-1} \to 10_{-2} E$	34868.791	1.1(3)	0.0224
$6_{-1} \to 6_0 E$	36649.808	0.99(7)	0.0060
$4_2 \to 5_1 E$	37641.748	1.09(11)	0.3589
$5_{-1} \to 5_0 E$	39335.472	0.99(5)	0.0110
$4_{-1} \to 4_0 E$	41687.673	0.98(4)	0.0219
$9_{-3} \to 10_{-2} E$	43113.861	0.92(15)	0.8907
$5_0 \to 4_1 E$	43539.148	1.00(5)	0.0128
$3_{-1} \to 3_0 E$	43629.973	0.98(3)	0.0492
$2_1 \to 2_0 E$	48603.477	1.02(2)	2.6797
$2_1 \to 2_0 A^{-+}$	48902.831	1.03(2)	2.8232

lines with $\Delta K = 0, 1, 2$ observed in molecular clouds, we also calculated the sensitivity coefficients and their errors. Our calculations cover the low-frequency range ($\Delta f = 1$–50 GHz), which contains the CH_3CHO transitions most sensitive to μ variations.

The results of our calculations are reported in Tables IV–VI. In the first column of Table IV, the quantum numbers of the molecular transitions are shown: the total angular momentum J and its projection K onto the molecular axis for the upper (u) and lower (ℓ) states. The second column lists the laboratory frequencies f from [25], and the third column displays the calculated sensitivity coefficients Q and their errors. In the last column the line strengths are shown. The structure of Table V is similar, but instead of the measured laboratory frequency, the predicted frequency is shown. Table VI contains the same data as Table IV, but only for transitions observed in the ISM, with the references and object names listed in the last column.

The errors of the Q values shown in parentheses are calculated using the same procedure as for methanol [13,14]. From Eqs. (3)–(7) it can be seen that the Hamiltonian parameters A–F are inversely proportional to the moments of inertia, which provides a linear dependence of μ (each parameter is scaled as μ^{-1}). At the same time, the potential barrier V_3 is independent of μ and is scaled as μ^0. However, because of the weak dependence of the internuclear distances on μ, due to the vibrational and centrifugal distortions, the deviation from the above-mentioned scalings can be about 2% [11]. The resulting errors of Q are determined by the quadratic sum of the errors caused by changes in the values of each parameter within the 2% uncertainty.

It is worth noting that Tables IV–VI show CH_3CHO transitions whose Q coefficients have relative errors less than 50%.

It is also necessary to pay attention to the fact that the error calculation procedure described in [13,14] yields a majorizing estimate of uncertainty in Q since it includes the contribution from the change in each of the rotational constants. At the same time, it is not necessary for all constants to change simultaneously; therefore, the errors of Q should be taken as the maximum possible, although in reality they may have a smaller value.

For some lines listed in Table VI, sensitivity coefficients and their errors were calculated using another method in [10]. Both calculations show good agreement within the $\pm 1\sigma$ confidence interval (see footnotes to Table VI).

Analyzing the data obtained from Tables IV–VI, we can say that the CH_3CHO molecule does not exhibit very high sensitivity to possible changes in μ: Most transitions have $Q \sim 1$, and all of them have positive Q. The explanation for this is as follows. In methanol, for example, internal rotation is associated with the movement of only hydrogen, but here both hydrogen and oxygen rotate. Such movement is much more hindered, and therefore, the spectrum of acetaldehyde is much closer to purely rotational. Accordingly, the sensitivity coefficients Q are closer to unity. In the Hamiltonian, this manifests as follows: In methanol, the kinetic coefficient F is much higher than that in acetaldehyde ($\sim$7.6 in acetaldehyde vs $\sim$28 in methanol). Moreover, although acetaldehyde is a fairly common molecule and is observed in many astronomical objects, the stronger lines observed are purely rotational and are essentially the only ones observed in space; the transitions with $\Delta K \neq 0$ in Tables IV–VI are quite weak. Therefore, it is difficult to estimate the variations in μ using this molecule alone. However, this is possible in combination with methanol

TABLE VI. Calculated sensitivity coefficients Q for the low-frequency (Δf = 1–50 GHz) torsion-rotation transitions ($\Delta K = 0, 1, 2$) in CH_3CHO observed in the ISM. Given in parentheses are errors in the last digits.

$J_{K_u} \to J_{K_\ell}$	f (MHz)	Q	$S\mu_D^2$	Object and Ref.[a]
$1_1 \to 1_1A^{-+}$	1065.075	1.0(3)	9.4857	Sgr B2 [26]
$1_1 \to 1_{-1}E$	1849.634	3.61(12)[b]	3.1329	Sgr B2(N) [27]
$2_1 \to 2_1A^{-+}$	3195.167	1.0(3)	5.2690	Sgr B2 [26,28]
$3_1 \to 3_1A^{-+}$	6390.085	1.0(3)	3.6878	Sgr B2 [26]
$1_1 \to 2_0A^{+}$	8243.476	1.17(16)[c]	0.5906	Sgr B2(N) [27]
$4_1 \to 4_1A^{-+}$	10648.419	1.0(3)	2.8450	Sgr B2 [26]
$1_0 \to 0_0E$	19262.140	1.000(14)[d]	6.3282	Sgr B2, TMC-1, L134N [29]
$1_0 \to 0_0A^{+}$	19265.133	1.000(14)[d]	6.3239	Sgr B2, TMC-1, L134N [29]
$2_1 \to 1_1A^{+}$	37464.168	1.00(2)	9.4864	PMCs [30]
$2_{-1} \to 1_{-1}E$	37686.868	1.00(8)	8.8712	PMCs [30]
$2_0 \to 1_0E$	38505.999	1.000(14)[d]	12.6551	TMC-1 [31,32]
$2_0 \to 1_0A^{+}$	38512.113	1.000(14)[d]	12.6465	TMC-1 [31,32]
$2_1 \to 1_1E$	39362.504	1.00(18)	8.8688	PMCs [30]
$2_1 \to 1_1A^{-}$	39594.287	1.00(2)	9.4865	PMCs [30]
$1_1 \to 1_0E$	47746.980	1.04(2)[e]	1.3472	Sgr B2(M) [33]
$1_1 \to 1_0A^{-+}$	47820.668[f]	1.03(2)[g]	1.7133	Sgr B2(M) [33]

[a]Abbreviations are as follows: L, Lynds's catalog of dark nebulae [34]; PMC, Perseus molecular clouds; SGR, Sagittarius molecular clouds; TMC, Taurus molecular clouds.
[b]Q from[10] is 3.7(2).
[c]Q from [10] is 1.11(6).
[d]Q from [10] is 1.00(5).
[e]Q from [10] is 1.03(5).
[f]The line was not observed in the laboratory.
[g]Q from [10] is 1.02(5).

lines, as in the ammonia method mentioned above [7,15]. But this approach would require careful analysis of the spectral line shapes or other data confirming the origin of the transitions of both molecules in the same region. That such spatial coexistence between CH_3CHO and CH_3OH does take place is confirmed by direct observations of similar line profiles of these molecules in, e.g., Taurus molecular cloud-1 [32].

In the conclusion of this section, we note that in addition to the above-mentioned transitions, which fall within the frequency range Δf = 1–50 GHz from Table VI, purely rotational lines of acetaldehyde were also observed at higher frequencies. Lines from the range Δf = 70–120 GHz were detected for a good number of molecular clouds in the galactic disk [30,35–46]. Lines at even higher frequencies (200–350 GHz) were detected in [40,47–49]. Also, pure rotational transitions of CH_3CHO (50–80 GHz) were observed at the cosmological redshift $z = 0.89$ [50]. All such lines have sensitivity coefficients close to unity, $Q \approx 1$.

III. ESTIMATING $\Delta\mu/\mu$ USING CH_3CHO AND CH_3OH

In this section, we give an example of $\Delta\mu/\mu$ estimation from a comparison of torsion-rotation transitions in CH_3OH and purely rotational transitions in CH_3CHO, which have different sensitivity coefficients Q. Of course, among the methanol lines themselves there are purely rotational transitions with $Q = 1$, and such estimates could be made based on the lines of one molecule. However, for precision $\Delta\mu/\mu$ measurements, it is desirable to use close lines from narrow spectral ranges in which groups of methanol lines with significantly different Q are absent. In such cases, the acetaldehyde lines with $Q \approx 1$ could be used as references.

If the lines of methanol and acetaldehyde trace the same spatial region, they should have approximately the same excitation temperature and approximately equal widths (FWHM). The corresponding spectra are published in [40,51], where the results of observations of many organic molecules, including CH_3CHO and CH_3OH, are presented in the direction of the three molecular clouds L1544, Barnard-1, and IRAS4A.[3] The observations were carried out on the IRAM 30-m telescope with a spectral resolution of 200 kHz in several spectral bands: 3 mm (80–116 GHz), 2 mm (130–170 GHz), and 1.3 mm (200–276 GHz).

For the estimates of $\Delta\mu/\mu$, we selected methanol and acetaldehyde lines, satisfying the following criteria: (1) The lines should fall into the same spectral range of observations to exclude possible systematic shifts between different settings. (2) The transitions should have approximately the same upper-level energies (the difference is no more than 30 K). (3) The methanol lines should have $|Q| > 1$ since the strongest acetaldehyde lines are purely rotational, and (4) the laboratory frequencies should be known from the measurements.

The molecular clouds with emission lines that meet the listed criteria are shown in Table VII, where the first col-

[3]L1544 is a protostellar system from Lynds' catalog of dark nebulae [34], located in the Taurus molecular cloud complex. Barnard-1 is a dark nebula, and IRAS4A is a protostellar system, both embedded in the Perseus molecular cloud complex. IRAS stands for Infrared Astronomical Satellite.

TABLE VII. Selected CH_3OH and CH_3CHO transitions from [40,51]. Given in parentheses are errors in the last digits. Laboratory frequencies for the CH_3OH and CH_3CHO molecules are taken from Ref. [52] and Ref. [25], respectively.

Object	Molecule	Transition $J_{K_u} \to J_{K_\ell}$	f (MHz)	E_u (K)	$V_{\rm LSR}$ (km s^{-1})	FWHM (km s^{-1})	Q
L1544[a]	CH_3OH	$5_{-1} \to 4_0E$	84521.169(10)	40.4	7.24(4)	0.44	−3.6
	CH_3CHO	$5_1 \to 4_1A^+$	93580.859(100)	15.8	7.14(30)	0.44	1.0
	CH_3CHO	$5_{-1} \to 4_{-1}E$	93595.276(100)	15.8	7.19(30)	0.34	1.0
	CH_3CHO	$5_0 \to 4_0A^+$	95963.380(180)	13.8	7.18(60)	0.44	1.0
	CH_3CHO	$5_1 \to 4_1E$	98863.328(40)	16.6	7.11(12)	0.53	1.0
	CH_3CHO	$5_1 \to 4_1A^-$	98900.948(40)	16.5	7.17(12)	0.34	1.0
Barnard-1[b]	CH_3OH	$0_0 \to 1_{-1}E$	108893.960(7)	13.1	6.565(20)	1.37	4.6
	CH_3CHO	$5_1 \to 4_1A^+$	93580.859(100)	15.8	6.57(30)	1.43	1.0
	CH_3CHO	$5_{-1} \to 4_{-1}E$	93595.276(100)	15.8	6.58(30)	1.57	1.0
	CH_3CHO	$5_0 \to 4_0A^+$	95963.380(180)	13.8	6.66(60)	1.46	1.0
	CH_3CHO	$5_{-2} \to 4_{-2}E$	96425.618(40)	22.9	6.63(16)	1.66	1.0
	CH_3CHO	$5_2 \to 4_2E$	96475.536(40)	23.0	6.52(15)	0.97	1.0
	CH_3CHO	$5_1 \to 4_1E$	98863.328(40)	16.6	6.51(12)	1.04	1.0
	CH_3CHO	$5_1 \to 4_1A^-$	98900.948(40)	16.5	6.55(13)	1.25	1.0
IRAS4A[c]	CH_3OH	$0_0 \to 1_{-1}E$	108893.960(7)	13.1	7.402(20)	2.45	4.6
	CH_3CHO	$5_1 \to 4_1A^+$	93580.859(100)	15.8	7.32(30)	2.30	1.0
	CH_3CHO	$5_{-1} \to 4_{-1}E$	93595.276(100)	15.8	7.44(30)	2.34	1.0
	CH_3CHO	$5_{-2} \to 4_{-2}E$	96425.618(40)	22.9	7.54(16)	2.41	1.0
	CH_3CHO	$5_2 \to 4_2E$	96475.536(40)	23.0	7.17(15)	2.36	1.0
	CH_3CHO	$5_1 \to 4_1E$	98863.328(40)	16.6	7.36(13)	2.24	1.0
	CH_3CHO	$6_1 \to 5_1A^+$	112248.728(40)	21.1	7.29(12)	2.56	1.0
	CH_3CHO	$6_{-1} \to 5_{-1}E$	112254.520(40)	21.2	7.27(12)	3.06	1.0

[a]Weighted mean $\langle V_{\rm LSR}\rangle = 7.14(15)$; weighted mean $\langle$FWHM$\rangle = 0.42$.
[b]Weighted mean$\langle V_{\rm LSR}\rangle = 6.55(11)$; weighted mean $\langle$FWHM$\rangle = 1.34$.
[c]Weighted mean$\langle V_{\rm LSR}\rangle = 7.32(8)$; weighted mean $\langle$FWHM$\rangle = 2.47$.

umn indicates the object name, the second column shows the molecule, the third column displays the quantum numbers J and K for the upper (u) and lower (ℓ) levels, the laboratory frequency f and the energy of the upper-level E_u are listed in the fourth and fifth columns, and the measured velocity $V_{\rm LSR}$ and its error and the linewidth FWHM are shown in the sixth and seventh columns. The last column lists the sensitivity coefficient Q, with values for methanol from [10], while for acetaldehyde $Q = 1$. We also include the laboratory frequency uncertainties in the velocity uncertainty budget since they are the main source of errors in the $\Delta\mu/\mu$ calculations. These types of uncertainties were not considered in [40] because they were unnecessary.

Since the acetaldehyde transitions have the same sensitivity coefficient, $Q = 1$, their velocities can be averaged: Table VII shows the weighted mean velocity $\langle V_{\rm LSR}\rangle$ for CH_3CHO with the corresponding error, as well as the weighted mean linewidth $\langle$FWHM$\rangle$ for comparison with the widths of methanol lines.

Table VII demonstrates that the widths of the methanol lines and the mean values of the widths of the acetaldehyde lines are almost identical and that the energies of the upper levels differ by no more than 30 K in L1544 and no more than 10 K in Barnard-1 and IRAS4A.

The relative intensities of the methanol and acetaldehyde lines were also utilized in [40] to calculate the excitation temperatures $T_{\rm ex}$ characterizing the distribution of molecules over energy levels. Moreover, for the cospatially distributed molecules, $T_{\rm ex}$ should be approximately the same. The estimates of $T_{\rm ex}$ were carried out in [40] using two methods: rotational diagrams and Markov chain Monte Carlo fitting. In both cases, close values of the excitation temperatures were found, which may also indicate the origin of the emissions in the CH_3OH and CH_3CHO lines from the same regions.

Using the measured radial velocities $V_{\rm LSR}$ (CH_3OH) and $\langle V_{\rm LSR}\rangle$ (CH_3CHO) and the corresponding Q values, the following results were obtained: $\Delta\mu/\mu = (0.7 \pm 1.1) \times 10^{-7}$ (L1544), $\Delta\mu/\mu = (-0.1 \pm 1.0) \times 10^{-7}$ (Barnard-1), and $\Delta\mu/\mu = (-0.8 \pm 0.8) \times 10^{-7}$ (IRAS4A). Thus, no signal was detected at the level of $(0.8 - 1.1) \times 10^{-7}$ in these molecular clouds. The slightly higher values of the upper limits on $\Delta\mu/\mu$ for clouds L1544 and Barnard-1 are due to a larger uncertainty (180 kHz) of the laboratory frequency of the $5_0 \to 4_0A^+$ line of acetaldehyde. If we remove this line from the dataset, then the following values of $\Delta\mu/\mu$ can be obtained: $\Delta\mu/\mu = (0.7 \pm 0.5) \times 10^{-7}$ (L1544) and $\Delta\mu/\mu = (-0.1 \pm 0.4) \times 10^{-7}$ (Barnard-1). Now both upper limits are at the level of $(4-8) \times 10^{-8}$.

Since the measurements in these three molecular clouds are independent, we can average the obtained estimates of $\Delta\mu/\mu$. The results for the initial sample and for the reduced sample without line $5_0 \to 4_0A^+$ are as follows: $\langle\Delta\mu/\mu\rangle = (-0.2 \pm 0.5) \times 10^{-7}$ for the former and $\langle\Delta\mu/\mu\rangle = (0.1 \pm 0.4) \times 10^{-7}$ for the latter case. For the final result we take the second value. The constraint obtained is consistent with the LPI and gives an upper limit on its violation in the galactic disk at the level of 4×10^{-8}.

Thus, the analysis performed shows that CH_3CHO is a suitable molecule for differential assessments of μ in combination with CH_3OH. Along with other methods, acetaldehyde allows us to achieve the strongest limits to date on the spatial variations of μ in the galactic disk at large galactocentric distances.

IV. CONCLUSIONS

In this study, we calculated the sensitivity coefficients Q for small changes in $\mu = m_e/m_p$ (the electron-to-proton mass ratio) for various torsion-rotation transitions of CH_3CHO in the ground torsion state $v_t = 0$, which fall in the microwave range of $\Delta f = 1$–50 GHz. The main results obtained are as follows.

(1) The sensitivity coefficients for the torsion-rotation transitions with $\Delta K = \pm 1$ vary in a narrow range $0.62 \leqslant Q \leqslant 1.4$, and all of them have a positive sign.

(2) The $1_1 \rightarrow 1_{-1}E$ ($\Delta K = 2$) transition observed in astrophysics at a frequency of 1.849 GHz has the highest sensitivity coefficient ($Q = 3.61$) of all for CH_3CHO, which confirms the result previously obtained in [10].

(3) Analysis of astrophysical observations showed that acetaldehyde is often cospatially distributed with methanol, which allows the use of acetaldehyde and methanol lines, which have similar profiles and excitation temperatures, to probe $\Delta\mu/\mu$.

(4) An example of a combination of the CH_3CHO and CH_3OH lines to estimate $\Delta\mu/\mu$ was demonstrated using published data [40] for three molecular clouds located at galactocentric distances $D_{GC} \sim 8$ kpc. The most stringent upper limit on μ variation derived (4×10^{-8}) is in line with previously obtained constraints based on other molecules and methods. Thus, no violations of the LPI are currently seen at this level in the galactic disk at large galactocentric distances.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [51].

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