Sensitivity of microwave transitions in H_2O_2 to variation of the electron-to-proton mass ratio

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Recent observation of several microwave transitions in H_2O_2 from the interstellar medium [Bergman *et al.* Astron. Astrophys. **531**, L8 (2011)] raised interest in this molecule as yet another sensitive probe of the tentative variation of the electron-to-proton mass ratio μ. We estimate sensitivity coefficients of the microwave transitions in H_2O_2 to μ variation. The largest coefficient for 14.8-GHz transition is equal to 37, which is comparable to the highest sensitivities in methanol and an order of magnitude higher than the sensitivity of the tunneling transition in ammonia.

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I. INTRODUCTION

Molecules with an internal motion of large amplitude recently attracted much attention as high sensitive probes of the tentative variation of the electron-to-proton mass ratio $\mu = m_e/m_p$. In 2004 van Veldhoven *et al.* [1] pointed out that inversion transition in ammonia is very sensitive to μ variation. Later, several groups used this transition to place stringent limits on μ variation on a large time scale of the order of 10 Gyr [2–5]. At the same time ammonia spectra from our galaxy were used to study possible dependence of μ on the local mater density [6,7]. More recently the sensitivity to μ variation was studied for other molecules with tunneling motion, including hydronium (H_3O^+) [8,9], methanol (CH_3OH) [10–12], and methylamine (CH_3NH_2) [13]. All these molecules are observed in the interstellar medium (ISM) and potentially can be used as probes of μ variation. Sensitivities of the tunneling transitions are two orders of magnitude higher compared to optical transitions in molecular hydrogen, which is traditionally used to study μ variation at high redshifts (see [14] and references therein). Even higher sensitivities can be found for certain mixed tunneling-rotational transitions. Recently methanol and methylamine were detected at redshift $z = 0.89$ [15]. The first limit on μ variation using methanol is reported in [11].

Peroxide molecule (H_2O_2) is one of the simplest molecules with a large amplitude tunneling mode. It is very well studied both theoretically and experimentally. However, to the best of our knowledge, there is no analysis of the sensitivity of the microwave transitions in this molecule to μ variation. This is probably explained by the fact that H_2O_2 was not observed in ISM. The situation has changed after the first observation of four microwave lines of H_2O_2 from the molecular cloud core ρ Oph A in our Galaxy by Bergman *et al.* [16]. In this communication we estimate sensitivities of the microwave mixed tunneling-rotational transitions to μ variation.

II. CALCULATION OF SENSITIVITY COEFFICIENTS

In equilibrium geometry H_2O_2 is not flat; the angle 2γ between two HOO planes is close to 113°. Two flat configurations correspond to local maxima of potential energy; the potential barrier for *trans* configuration ($2\gamma = \pi$) is significantly lower, than for *cis* configuration ($\gamma = 0$): $U_\pi \approx 400$ cm^{-1} and $U_0 \approx 2500$ cm^{-1}. To a first approximation one can neglect the tunneling through the higher barrier. In this model peroxide is described by the slightly asymmetric oblate top with inversion tunneling mode, similar to ammonia and hydronium. A more accurate theory accounts for tunneling through both barriers [17]. In this case torsion motion can be described as hindered rotation. For sufficiently high angular quantum numbers J and K_A this internal motion strongly interacts with overall rotation. According to [18] this interaction becomes important for $K_A \geqslant 7$. Such levels lie very high and cannot be observed from ISM. Below 70 K there are only levels with quantum numbers $J \leqslant 6$ and $K_A \leqslant 2$. For such levels the simpler model is sufficiently accurate and we will use it here.

When tunneling through both barriers is taken into account the ground torsion state splits in four components designated by the quantum number $\tau = 1 - 4$. Because *trans* barrier is much lower than the *cis* one, the splittings between the pairs $\tau = 1,2$ and $\tau = 3,4$ is much larger then splittings within the pairs. The latter is usually not resolved experimentally. If we completely neglect second tunneling, we are left with only two states, but for consistency they are labeled as $\tau = 1$ and $\tau = 3$ states [17,18]. The low-energy effective Hamiltonian has the form (atomic units are used throughout the paper),

$$H_{\rm eff} = E_\tau + H_{\rm rot}, \tag{1}$$

where E_τ is tunneling energy and $H_{\rm rot}$ is the Hamiltonian of the rigid asymmetric top, whose constants A, B, and C weakly depend on the quantum number τ (see Table I).

The dimensionless sensitivity coefficient Q_μ of the transition ω to μ variation is defined so that

$$\frac{\Delta\omega}{\omega} = Q_\mu \frac{\Delta\mu}{\mu}. \tag{2}$$

In order to find these coefficients for transitions described by Hamiltonian (1) we need to know the μ dependence of the parameters from Table I. Rotational parameters A, B, and C scale linearly with μ. Thus, the purely rotational transition has sensitivity $Q_{\mu,\rm rot} = 1$. Sensitivity of the tunneling energy E_τ to the μ variation can be estimated with the help of the semiclassical Wentzel-Kramers-Brillouin approximation. Following [19], we can write

$$E_\tau = \frac{2E_0}{\pi} e^{-S}, \tag{3}$$

TABLE I. Parameters of the effective Hamiltonian (1) in GHz from Ref. [18].

τ	E_τ	A_τ	B_τ	C_τ
1	0.0	301.873	26.193	25.120
3	342.885	301.585	26.142	25.201

where S is the action over the classically forbidden region and E_0 is the zero-point energy for the inversion mode. Expression (3) gives the following sensitivity to μ variation:

$$Q_{\mu,\tau} = \frac{S+1}{2} + \frac{S\,E_0}{2(U_{\max} - E_0)}\,, \tag{4}$$

where $U_{\max}$ is the barrier hight. The numerical factor in the second fraction depends on the barrier shape. For the triangular and square barriers it is 2 times smaller and 1.5 times larger, respectively [2]. The factor $\frac{1}{2}$ in Eq. (4) corresponds to the parabolic barrier [9].

The potential for the tunneling coordinate γ was found by Koput *et al.* [20] in a form of Fourier expansion with $U_{\max} = U_\pi = 387\ \mathrm{cm}^{-1}$. Numerical solution of the one-dimensional Schrödinger equation for this potential gives $E_0 = 169\ \mathrm{cm}^{-1}$, $E_\tau = 13.1\ \mathrm{cm}^{-1}$, and $Q_{\mu,\tau} = 2.44$. Using this value for E_0 and tunneling energy from Table I we can find S from Eq. (3) and $Q_{\mu,\tau}$ from Eq. (4):

$$S = 2.28\,, \qquad Q_{\mu,\tau} = 2.54\,. \tag{5}$$

If we scale potential from [20] to fit experimental tunneling frequency from Table I, the numerical solution gives $Q_{\mu,\tau} = 2.56$. All three values for $Q_{\mu,\tau}$ agree to 5%. The semiclassical value corresponds to the experimental tunneling frequency and is less sensitive to the details of the potential shape. Therefore, we use it in our calculations and assign it 5% uncertainty.

We see that tunneling energy is 2.5 times more sensitive to μ variation than rotational energy. Sensitivity of the mixed tunneling-rotational transitions, $\omega = E_\tau \pm \omega_{\mathrm{rot}}$, is a weighted average of the tunneling and rotational contributions [21]:

$$Q_\mu = \frac{E_\tau}{\omega} Q_{\mu,\tau} \pm \frac{\omega_{\mathrm{rot}}}{\omega} Q_{\mu,\mathrm{rot}}. \tag{6}$$

This sensitivity is further enhanced for the frequencies $|\omega| \ll E_\tau$.

Results of the numerical calculations with Hamiltonian (1) are given in Table II. In this table we list six transitions in the range 200–700 GHz, which were studied in Ref. [16] (four of them were observed and the other two were not) and transitions from the JPL database [22] with frequencies below 100 GHz.

Note that pure rotational transitions with $\Delta\tau = 0$ for peroxide are not observed. Because of that all sensitivities in Table II significantly deviate from unity. As expected, lower frequency transitions have higher sensitivities. Transitions with the frequency $|\omega| < E_\tau$ fall in two categories. For transitions $\tau = 3 \to \tau = 1$ the tunneling energy is larger than rotational energy and $|\omega| = E_\tau - \omega_{\mathrm{rot}}$. For such transitions Q factors are positive. For transitions $\tau = 1 \to \tau = 3$, $|\omega| = \omega_{\mathrm{rot}} - E_\tau$ and Q factors are negative.

III. DISCUSSION OF ACCURACY

Let us discuss the accuracy of our estimates. Calculated frequencies agree with experiment to 0.1%, or better in spite of the simplicity of Hamiltonian (1). That means that centrifugal corrections to the rotational energy are indeed unimportant for the transitions with low rotational quantum numbers

TABLE II. Numerical calculation of the Q factors for low-frequency mixed transitions in peroxide using Hamiltonian (1) and Eq. (5). Experimental frequencies are taken from the JPL Catalogue [22]. E_{up} is upper-state energy in Kelvin.

$J_{K_A,K_C}(\tau)$		E_{up}	ω (MHz)		
Upper	Lower	(K)	Theory	Expt.	Q_μ
		Transitions below 100 GHz			
$0_{0,0}(3)$	$1_{1,0}(1)$	17	14818.8	14829.1	+36.5(2.9)
$2_{1,1}(1)$	$1_{0,1}(3)$	21	37537.0	37518.28	−13.0(1.2)
$1_{0,1}(3)$	$1_{1,1}(1)$	19	67234.5	67245.7	+8.8(6)
$2_{0,2}(3)$	$2_{1,2}(1)$	24	68365.3	68385.0	+8.7(6)
$3_{0,3}(3)$	$3_{1,3}(1)$	31	70057.4	70090.2	+8.5(6)
$4_{0,4}(3)$	$4_{1,4}(1)$	41	72306.0	72356.4	+8.3(6)
$5_{0,5}(3)$	$5_{1,5}(1)$	53	75104.6	75177.4	+8.0(6)
$6_{0,6}(3)$	$6_{1,6}(1)$	68	78444.7	78545.4	+7.7(6)
$3_{1,2}(1)$	$2_{0,2}(3)$	28	90399.8	90365.51	−4.8(5)
		Transitions observed from ISM in Ref. [16]			
$3_{0,3}(3)$	$2_{1,1}(1)$	31	219163.2	219166.9	+3.4(2)
$6_{1,5}(1)$	$5_{0,5}(3)$	66	252063.6	251914.68	−1.1(2)
$4_{0,4}(3)$	$3_{1,2}(1)$	41	268963.7	268961.2	+3.0(2)
$5_{0,5}(3)$	$4_{1,3}(1)$	53	318237.7	318222.5	+2.7(1)
		Transitions attempted to observe in Ref. [16]			
$5_{1,4}(3)$	$6_{0,6}(1)$	67	318635.6	318712.1	+2.7(1)
$1_{1,0}(3)$	$0_{0,0}(1)$	32	670611.9	670595.8	+1.8(1)

considered here. Even in this case the scaling of the rotational energy with μ is not exactly linear as rotational constants of the effective Hamiltonian are averaged over the vibrational wave functions of the states $\tau = 1,3$. Respective corrections to the rotational sensitivity coefficients are of the order of 1%–2% [11]. Note that τ dependence of the rotational constants can be considered as centrifugal corrections to the tunneling energy [9]. According to Refs. [9,11] the accuracy of the semiclassical expressions for tunneling (3), (4) is comparable, about 3%. Additional uncertainty is associated with the zero-point energy E_0, which is not directly observable and we take it from calculation with potential [20]. This potential was used in a number of later papers, including [23,24]. We estimate the accuracy of the tunneling sensitivity coefficient (5) to be 5%, which agrees with numerical estimates made above. Uncertainties in rotational and tunneling sensitivities result in the final uncertainties for mixed transitions given in Table II. These uncertainties are typically about 10%. Such accuracy is sufficient for the analysis of the astrophysical spectra.

To summarize, we have estimated sensitivity coefficients for the low-frequency mixed tunneling-rotational transitions in H_2O_2. Transitions below 100 GHz appear to be highly sensitive to μ variation with sensitivity coefficients of both signs. Maximal relative sensitivity is found for transitions 14.8 and 37.5 GHz, where $\Delta Q_\mu = +36.5 - (-13.0) \approx 50$. This is comparable to the highest sensitivities in methanol [10,11] and an order of magnitude larger than for ammonia [1,2]. The lines recently observed by Bergman *et al.* [16] have frequencies above 200 GHz and significantly lower sensitivities. Three of the observed transitions have sensitivities, which are close to each other. However, the sensitivity of the fourth observed transition is significantly different. Transitions 219 GHz and 252 GHz have relative sensitivity $\Delta Q_\mu = 4.5$. This is close to the sensitivity of the ammonia method, where $\Delta Q_\mu = 3.5$, but with the advantage that both lines belong to one species. This eliminates a very important source of systematic errors caused by the difference in spatial and velocity distributions of species [7]. We conclude that microwave transitions in H_2O_2 potentially can be used for a μ-variation search in astrophysics. Note that high-sensitivity transitions correspond to low rotational quantum numbers J. This makes peroxide a potential candidate for laboratory tests on μ variation using the molecular beam technique [25].

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