Note on CH_3NH_2

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Recent papers [1, 2] attract new attention to molecules with tunneling modes. Earlier the only tunneling transitions observed at high redshifts were ammonia inversion (J, K) lines around 24 GHz. All these lines have practically the same sensitivity to μ-variation ($\mu \equiv m_e/m_p$) and require additional anchor lines of different species as reference. Paper [2] reports observation of two more molecules with tunneling at redshift $z = 0.89$, namely methanol (CH_3OH) and methylamine (CH_3NH_2).

Both molecules have internal hindered rotation of the CH_3 group. The second one has another tunneling mode associated with the wagging of the NH_2 group. Existence of the large amplitude internal motions leads to very complex microwave spectra. In addition to usual rotational transitions they include mixed tunneling-rotational ones:

$$\nu_{\rm mix} \approx |\nu_{\rm rot} \pm \nu_{\rm tun}| \,. \tag{1}$$

When the frequency of such transition is small,

$$\nu_{\rm mix} \ll \nu_{\rm rot} \,, \nu_{\rm tun} \,, \tag{2}$$

its sensitivity to μ-variation is strongly enhanced [3]. Paper [1] reports a large number of such transitions in methanol. Typical tunneling energy there is $\nu_{\rm tun} \gtrsim 200$ GHz, so enhancement takes place for mixed transitions $\nu_{\rm mix} \lesssim 100$ GHz. To the best of our knowledge, there is no analysis yet of the sensitivity coefficients of methylamine. *Here we want to draw attention to this molecule as one more potential probe for μ-variation.* We also estimate the sensitivity coefficient for the single methylamine line, which was detected in [1]. General analysis will require more elaborate technique.

The theory of methylamine is more complex than that of methanol because of the interaction between two tunneling modes. At present it seems to be common practice to use the effective Hamiltonian developed by Ohashi *et al.* in Refs. [4, 5]. Parameters of this Hamiltonian were found from a gigantic fit in [6].

Interaction of the tunneling modes leads to a large number of tunneling frequencies even for non-rotating molecule [4]. The scale of these frequencies is determined by two tunneling parameters h_{2V} and h_{3V}, which correspond to the wagging mode and to hindered rotation respectively. According to [6] the numerical values of these parameters are: $h_{2V} = -1.5$ GHz and $h_{3V} = -2.5$ GHz. All other tunneling parameters are much smaller and do not change the general form of the spectrum. Applying theory from [4] we find that tunneling frequencies lie in the range $0 < \nu_{\rm tun} < 13.5$ (GHz). This is an order of magnitude smaller than the tunneling scale in methanol, so we can expect that enhanced sensitivity here takes place at much smaller frequencies $\nu_{\rm mix} \lesssim 10$ GHz.

Let us now estimate the sensitivity of the 78.135 GHz transition detected at the redshift $z = 0.89$ [1]. According to Ref. [6] this is $2_1(B_2)-2_0(B_1)$ transition in the J_{K_a} representation with additional symmetry label for G_{12} permutation group. If we neglect tunneling, this transition can be linked to two transitions of the rigid asymmetric top (J_{K_a,K_c} notation): $2_{1,1} - 2_{0,2}$ and $2_{1,2} - 2_{0,2}$. Using parameters from [6], we find frequencies of these transitions to be 82.3 and 79.7 GHz respectively. Therefore, we can estimate tunneling energy for this transition to be $1.6 \le \nu_{\rm tun} \le 4.2$ (GHz).

At this point we do not know sensitivity coefficients for the tunneling modes in methylamine. For the wagging mode it should be not very different from that of the inversion transition in a partly deuterated ammonia NH_2D ($\nu = 12$ GHz), where $Q_\mu \approx 5$ [7]. Taking this value, $Q_{\mu,\rm tun} = 5$, we get for the 78.1 GHz mixed transition $Q_{\mu,\rm mix} = 0.86(7)$. A two times bigger value, $Q_{\mu,\rm tun} = 10$, results in $Q_{\mu,\rm mix} = 0.7(2)$. Thus, we can conservatively estimate sensitivity of the observed methylamine transition to be

$$0.5 \le Q_\mu(78.1\,{\rm GHz}) \le 1.0 \,. \tag{3}$$

This is in accord with our expectation that enhancement takes place at much smaller frequencies. The relative offset between the detected CH_3NH_2 and CH_3OH lines then gives $|\Delta\mu/\mu| < 1.4 \times 10^{-6}$ at $z = 0.89$.

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