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Sensitivity to a possible variation of the proton-to-electron mass ratio of torsion-wagging-rotation transitions in methylamine CH_3NH_2

Vadim V. Ilyushin,[1] Paul Jansen,[2] Mikhail G. Kozlov,[3] Sergei A. Levshakov,[4] Isabelle Kleiner,[5]
Wim Ubachs,[2] and Hendrick L. Bethlem[2]
[1]*Institute of Radio Astronomy of NASU, Chervonopraporna 4, 61002 Kharkov, Ukraine*
[2]*Institute for Lasers, Life and Biophotonics, VU University Amsterdam, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands*
[3]*Petersburg Nuclear Physics Institute, Gatchina 188300, Russia*
[4]*Ioffe Physical-Technical Institute, St. Petersburg 194021, Russia*
[5]*Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), CNRS UMR 7583 et Universités Paris 7 et Paris Est, 61 avenue du Général de Gaulle, 94010 Créteil Cédex, France*
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We determine the sensitivity to a possible variation of the proton-to-electron mass ratio μ for torsion-wagging-rotation transitions in the ground state of methylamine (CH_3NH_2). Our calculation uses an effective Hamiltonian based on a high-barrier tunneling formalism combined with extended-group ideas. The μ dependence of the molecular parameters that are used in this model are derived, and the most important ones of these are validated using the spectroscopic data of different isotopologues of methylamine. We find a significant enhancement of the sensitivity coefficients due to energy cancellations between internal rotational, overall rotational, and inversion energy splittings. The sensitivity coefficients of the different transitions range from −19 to +24. The sensitivity coefficients of the 78.135, 79.008, and 89.956 GHz transitions that were recently observed in the disk of a $z = 0.89$ spiral galaxy located in front of the quasar PKS 1830-211 [S. Muller *et al.*, Astron. Astrophys. **535**, A103 (2011)] were calculated to be −0.87 for the first two and −1.4 for the third transition. From these transitions a preliminary upper limit for a variation of the proton to electron mass ratio of $\Delta\mu/\mu < 9 \times 10^{-6}$ is deduced.

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I. INTRODUCTION

Recently, it was shown that transitions between accidently degenerate levels that correspond to different motional states in polyatomic molecules are very sensitive to a possible variation of the proton-to-electron mass ratio, $\mu = m_p/m_e$. Kozlov *et al.* [1] showed that transitions that convert rotational motion into inversion motion, and vice versa, in the different isotopologues of hydronium (H_3O^+) have K_μ coefficients ranging from −219 to +11 [2]. Similarly, Jansen *et al.* [3,4] and Levshakov *et al.* [5] showed that transitions that convert internal rotation into overall rotation in the different isotopologues of methanol have K_μ coefficients ranging from −88 to +330. Here, the sensitivity coefficient K_μ is defined by

$$\frac{\Delta\nu}{\nu} = K_\mu \frac{\Delta\mu}{\mu}. \tag{1}$$

For comparison, pure rotational transitions have $K_\mu = -1$, while pure vibrational transitions have $K_\mu = -\frac{1}{2}$ and pure electronic transitions have $K_\mu = 0$.

Accidental degeneracies between different motional states in polyatomic molecules are likely to occur if the energies associated with the different types of motions are similar. In this paper, we present a calculation of the sensitivity coefficients for microwave transitions in methylamine (CH_3NH_2). Methylamine is an interesting molecule for several reasons: (i) it displays two large amplitude motions; hindered internal rotation of the methyl (CH_3) group with respect to the amino group (NH_2), and tunneling associated with wagging of the amino group. The coupling between the internal rotation and overall rotation in methylamine is rather strong resulting in a strong dependence of the torsional energies on the K quantum number, which is favorable for obtaining large enhancements of the K_μ coefficients [4]. (ii) Methylamine is a relatively small and stable molecule that is abundantly present in our galaxy and easy to work with in the laboratory. Recently it was also detected in the disk of a high redshift ($z = 0.89$) spiral galaxy located in front of the quasar PKS 1830-211 [6].

This paper is organized as follows. In Sec. II, we introduce the effective Hamiltonian used for calculating the level energies in the vibrational ground state of methylamine. In Sec. III, we derive how the constants that appear in this Hamiltonian scale with μ. Finally, in Sec. IV, we use the Hamiltonian and the scaling relations to determine the sensitivity coefficients of selected transitions.

II. HAMILTONIAN AND ENERGY LEVEL STRUCTURE

Methylamine, schematically depicted in Fig. 1, is a representative of molecules exhibiting two coupled large-amplitude motions, the torsional motion of a methyl group and the wagging (or inversion) motion of an amine group. A combination of intermediate heights of the potential barriers with a leading role of the light hydrogen atoms in the large-amplitude motions results in relatively large tunneling splittings even in the ground vibrational state. On the right-hand side of Fig. 1, a contour plot of the potential energy is shown with the relative angle between the methyl and the amino group, γ, on the horizontal axis and the angle between the NH_2 plane and the CN bond, τ, on the vertical axis. The methyl torsion motion is indicated with the arrow labeled by h_{3v} whereas the amino wagging motion is indicated with the arrow labeled by h_{2v}. From the contour plot, it is seen that amino wagging motion of the NH_2 group is accompanied by a $\pi/3$ rotation of the CH_3 group about the CN bond with respect to the NH_2 group. Consequently, the

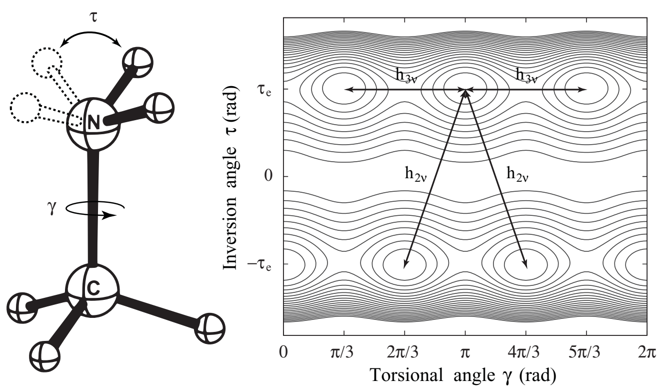

FIG. 1. Schematic representation of methylamine and variation of the potential energy of methylamine as function of the relative rotation γ of the CH_3 group with respect to the amine group about the CN bond and the angle τ of the two hydrogen atoms of the NH_2 group with respect to the CN bond. The two large amplitude motions, corresponding to inversion h_{2v} and hindered rotation h_{3v} are schematically indicated by the arrows. Note that inversion of the NH_2 group is accompanied by a $\pi/3$ rotation about the CN bond of the CH_3 group with respect to the amine group.

amino wagging motion is strongly coupled to the hindered methyl top internal rotation resulting in a rather complicated computational problem.

In Fig. 2 the lowest rotational levels of the ground vibrational state of CH_3NH_2 are shown. The level ordering resembles that of a near-prolate asymmetric top molecule. In addition to the usual asymmetric splitting, every J, K level is split due to the different tunneling motions. The internal rotation tunneling splits each rotational level into one doubly degenerate and one nondegenerate sublevel. Each of these sublevels are further split into two due to the inversion motion. Together, this results in eight levels with overall symmetry A_1, A_2, B_1, B_2, E_1+1, E_2+1, E_1-1, and E_2-1 for $K>0$ and four levels for $K=0$. The $+1$ and -1 levels in the E_1 and E_2 symmetry species correspond to $K>0$ and $K<0$, respectively. Because of nuclear-spin statistics, in the ground vibrational state the nondegenerate levels of J =even, $K=0$ are only allowed to possess the overall symmetry A_1, B_1, whereas levels with J =odd, $K=0$ are only allowed to possess the overall symmetry A_2, B_2. The $K=0$ doubly degenerate levels of E_1 and E_2 symmetry are denoted by $+1$ levels, i.e., by E_1+1, E_2+1 levels. The exact ordering of the different symmetry levels within a certain J, K level is determined by the relative contributions of the h_{3v} and h_{2v} parameters (see, for example, Fig. 3 of Ref. [7]). The internal motions are strongly coupled to the overall rotation resulting in a strong dependence of the torsional-wagging energies on the K quantum number. Thus the level ordering may differ from one K ladder to another. This turns out to be important for obtaining large enhancement factors, as it may result in closely spaced energy levels with a different functional dependence on μ that are connected by a symmetry allowed transition.

The panel on the right-hand side of Fig. 2 shows an enlarged view of the $J=2$, $K=0$ and $J=1$, $K=1$ levels, with all symmetry allowed transitions assigned with roman numerals. Note that transitions with $\Delta J=0$ in the $K=0$ manifold are not allowed. The transitions labeled by III,IV,VI,VII,VIII, and X are of particular interest as these connect the closely spaced levels of different K manifolds and have an enhanced sensitivity to a variation of μ. A similar enhancement occurs for transitions between the $J=5$, $K=1$, and $J=4$, $K=2$ levels as well as for transitions between the $J=6$, $K=1$, and $J=5$, $K=2$ levels. In what follows, we will outline the procedure to calculate the sensitivities of these transitions.

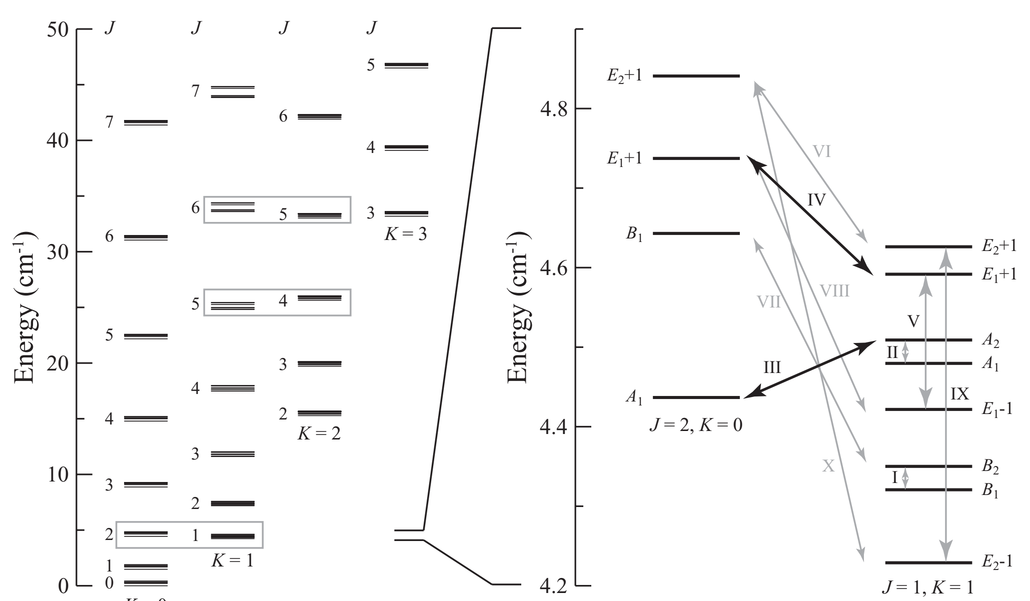

FIG. 2. Energy of the lowest rotational levels in the ground state of methylamine ($^{12}CH_3^{14}NH_2$). The levels are denoted by J, K and the overall symmetry. The panel on the right-hand side of the figure shows an enlarged view of the $J=2, K=0$ and $J=1, K=1$ levels, with all symmetry allowed transitions assigned with roman numerals. The sensitivity of these transitions are listed in Table III. The two transitions that are designated with bold arrows and are labeled by III and IV have sensitivity coefficients equal to $K_\mu=-19$ to $+2$, respectively.

The resulting sensitivity coefficients are presented in Tables II and III and discussed in Sec. IV.

In the present work, we use the group-theoretical high-barrier tunneling formalism developed for methylamine by Ohashi and Hougen [8], which is capable of reproducing observations of the rotational spectrum of the ground vibrational state of CH_3NH_2 to within a few tens of kilohertz [9,10]. The high-barrier formalism assumes that the molecule is confined to one of n equivalent equilibrium potential minima for many vibrations, but that it occasionally tunnels from one of these n minima to another. The formalism fits in between the infinite-barrier approximation, where no tunneling splittings are observed, and the low-barrier approximation, where the present formalism breaks down. A backward rotation of the whole molecule is introduced to cancel the angular momentum generated by one of the large amplitude motions—the so-called internal axis method—requiring the usage of extended group ideas. The reader is referred to Refs. [7–11] for a detailed description of the high-barrier tunneling formalism and the used Hamiltonian.

Table I lists the molecular constants used in our calculations. It includes three types of parameters: "nontunneling" or pure rotational parameters; parameters associated with pure methyl torsion motion (odd numerical subscripts n); and parameters associated with the NH_2 wagging motion (even numerical subscripts n). The obtained μ-scaling relations for the different parameters of the high-barrier tunneling formalism of methylamine are listed in the 2nd, 5th and 8th column of Table I. In the next sections, we will discuss the scaling relations for the lowest order parameters. The scaling relations for the higher order parameters, and the problems encountered in determining these, are discussed in the Supplemental Material [12].

III. SCALING RELATIONS OF THE MOLECULAR PARAMETERS

We will use two different approaches for determining the μ dependence of the molecular constants that appear in the Hamiltonian:

(i) The first approach is based on the fact that the tunneling model essentially assumes that for each large-amplitude tunneling motion the system point travels along some path in coordinate space. In zeroth approximation, we may represent each large amplitude motion as a one-dimensional mathematical problem after parameterizing the potential along the path and the effective mass that moves along it. Thus, for each large amplitude motion, we will set up a Hamiltonian that contains one position coordinate and its momentum conjugate. The parameters of this one dimensional Hamiltonian may be connected with the observed splittings which are fitting parameters of the high-barrier

TABLE I. Molecular parameters P_s of the ground torsional state of methylamine CH_3NH_2 [9], and their sensitivity to a variation of the proton-to-electron mass ratio μ defined as $K_\mu^{P_s} = \frac{\mu}{P_s}\frac{\partial P_s}{\partial \mu}$. All molecular parameters are in MHz, except ρ and ρ_K, which are dimensionless.

Rotation[a]			Inversion[b]			Torsion[c]		
	$K_\mu^{P_s}$			$K_\mu^{P_s}$			$K_\mu^{P_s}$	
$\bar{B}$	−1	22 169.36636(30)	h_{2v}	−5.5	−1549.18621(77)	h_{3v}	−4.7	−2493.5140(12)
A-$\bar{B}$	−1	80986.3823(11)	h_{4v}	−8.2	2.73186(96)	h_{5v}	−8.8	2.88398(55)
B-C	−1	877.87717(53)	h_{2J}	−5.5	0.101759(11)	h_{3J}	−4.7	−0.052546(20)
D_J	−2	0.0394510(18)	h_{2K}	−5.5	1.73955(16)	h_{5J}	−8.8	0.0002282(55)
D_{JK}	−2	0.170986(15)	h_{4K}	−8.2	−0.004778(37)	h_{3K}	−4.7	1.16676(22)
D_K	−2	0.701044(24)	h_{2JJ}	−6.5	−0.000005466(88)	h_{5K}	−8.8	−0.002667(73)
δ_J	−2	0.00175673(17)	h_{2KK}	−6.5	−0.0009016(63)	h_{3JJ}	−5.7	−0.000017296(44)
δ_K	−2	−0.33772(13)	h_{2JK}	−6.5	−0.00015400(94)	h_{3KK}	−5.7	−0.0002995(42)
Φ_J	−3	−0.0000000485(16)	h_{2JKK}	−7.5	0.0000001923(56)	h_{3JJK}	−6.7	−0.00000004702(67)
Φ_{JK}	−3	0.000002442(50)	q_2	−5.5	21.54923(52)	f_3	−4.7	−0.173439(24)
Φ_{KJ}	−3	−0.00000855(10)	q_4	−8.2	−0.03071(20)	f_{3J}	−5.7	−0.00000261(13)
Φ_K	−3	0.00003322(29)	q_{2J}	−6.5	−0.0037368(45)	f_{3K}	−5.7	−0.0001359(32)
ϕ_K	−3	0.0002366(48)	q_{2K}	−6.5	−0.019676(43)	f_{3JK}	−6.7	−0.0000000646(27)
			q_{2JJ}	−7.5	0.000002098(62)	$f_3^{(2)}$	−5.7	−0.000003021(89)
			q_{2KK}	−7.5	0.00001023(54)	$f_{3J}^{(2)}$	−6.7	0.00000000220(13)
ρ	0	0.64976023(13)	f_2	−5.5	−0.096739(38)			
ρ_K	−1	−0.0000011601(77)	f_4	−8.2	0.0002153(39)			
			f_{2J}	−6.5	0.000004452(67)			
			f_{2K}	−6.5	0.001188(37)			
			f_{2KK}	−7.5	−0.000001600(47)			
			$f_2^{(2)}$	−6.5	−0.000002443(55)			
			r_2	−5.5	10.979(37)			
			r_{2K}	−6.5	−0.7206(73)			

[a]These parameters do not involve tunneling motions.

[b]These parameters arise from the NH_2 inversion tunneling motion.

[c]These parameters arise from the CH_3 torsional tunneling motions.

tunneling formalism. The parameters of the one-dimensional Hamiltonians are functions of the moments of inertia and the potential barrier only, and their μ dependence can be found in a similar fashion as was done for methanol and other internal rotors [3,4]. Application of this approach is straightforward in the case of the leading tunneling parameters of methylamine but some ambiguities appear for the J and K dependences of the main terms, because there are several ways of representing these dependences in a one-dimensional model.

(ii) In the second approach, we use the spectroscopic data of different isotopologues of methylamine to estimate the dependence of the tunneling constants. In analogy with methanol, we expect the tunneling splittings to follow the formula [3]:

$$W_{\text{splitting}} = \frac{a_0}{\sqrt{I_{\text{red}}}} e^{-a_1\sqrt{I_{\text{red}}}}. \quad (2)$$

This formula originates from the semiclassical [Wentzel-Kramers-Brillouin (WKB)] approximation that assumes that the effective tunneling mass, represented by I_{red}, changes with isotopic substitution, but that the barrier between different wells remains unchanged. This expression was successfully applied to the $J = 0$, $K = 0$ A-E splittings and the $J = 1$, $|K| = 1$ splittings in methanol [3]. In methylamine, the h_{nv} parameters correspond to the splittings in the $J = 0$, $K = 0$ level due to tunneling between framework $|1\rangle$ and framework $|n\rangle$ (the set of frameworks represent the equivalent potential wells between which the system can tunnel), and application of the WKB approach to these parameters is straightforward. Moreover, since in fact all tunneling parameters in methylamine may be related to the same type of overlap integral as the h_{nv} parameters, we may expect that the isotopologue dependence of all tunneling terms can be described by Eq. (2). Unfortunately, ambiguities appear again when we apply this approach to higher order terms in the methylamine Hamiltonian. These ambiguities are connected to the fact that vibrational basis set functions $|n\rangle$ localized near various minima are not orthogonal, but in fact have nonzero overlap integrals with each other. The correlation problems that arise in the high-barrier tunneling formalism due to nonorthogonality of the basis functions are discussed in some detail in Ref. [13]. The main consequence which affects the isotopologue approach is that there may be "leakage" from one parameter to another; each fitted parameter appears as a sum of the "true" parameter value plus a small linear combination of all other parameters with a coefficient that goes to zero when the overlap integral goes to zero. While this effect should be insignificant for the main tunneling parameters of methylamine, it may be important for higher order terms because even a small leakage of the low order parameters may be comparable in magnitude with the true values of the higher order parameter.

In order to verify the mass dependence coefficients for the parameters of the methylamine Hamiltonian, we have refitted available data on the CH_3ND_2 [14], CD_3NH_2 [15], and CD_3ND_2 [16] isotopologues of methylamine using the high-barrier tunneling formalism. Unfortunately, the amount of data available in the literature was rather limited: 66 transitions for CH_3ND_2 [14], 41 transitions for CD_3NH_2 [15], and 49 transitions for CD_3ND_2 [16]. Therefore, many of the higher order terms were not determined in the fits, while some low order parameters were determined with a few significant digits only. As a result, it was possible to obtain the μ dependence of the main tunneling parameters h_{2v} and h_{3v} only. In order to obtain information on higher order terms, we have undertaken a new investigation of the CH_3ND_2 spectrum with the Kharkov millimeter wave spectrometer. The newly obtained data set for CH_3ND_2 contains 614 transitions, comparable to the number of microwave transitions available for CH_3NH_2 (696 transitions). The CH_3NH_2 and CH_3ND_2 fits have an almost equal number of varied parameters and obtained similar weighted root-mean-square deviations. The results of the CH_3ND_2 investigation will be published elsewhere [17]; here we will use only those results necessary for obtaining the scaling relations.

A. Pure rotational constants

The pure rotational or nontunneling parameters in the model are connected to the usual moments of inertia of the molecule and to the centrifugal distortion parameters. Therefore, we will assume the same μ dependence for these parameters as used for methanol [4].

B. CH_3 torsion and the h_{3v} parameter

The h_{3v} parameter in the high-barrier-tunneling formalism corresponds to a pure torsion motion. The quantity $|3h_{3v}|$ may be related to the usual E-A internal rotation splitting in a molecule that contains a group of C_{3v} symmetry. Assuming that the potential barrier is described by a cosine function and taking the moment of inertia of the methyl top to represent the mass that tunnels, we may set up a one-dimension internal rotation Hamiltonian

$$H_{\text{tors}} = F_\gamma p_\gamma^2 + \frac{V_n}{2}(1 - \cos n\gamma), \quad (3)$$

with $n = 3$ for a threefold barrier, $p_\gamma = -i\partial/\partial\gamma$ is the angular momentum operator associated with the internal rotation coordinate, F_γ is the internal rotation parameter, and V_3 the barrier height. Using a value for F_γ derived from the molecular constants, we may fit the barrier height V_3 to the observed value for $|3h_{3v}|$ and estimate the μ dependence of h_{3v}.

In the used axis system, the off-diagonal contribution to the inertia tensor is represented by the s_1 parameter. For methylamine, this parameter is set to zero as it is not required by the fit. Thus, we may assume that the methyl top axis coincides with the principal axis a, $\rho = I_\gamma/I_a$, and $F_\gamma = C_{\text{conv}}/[(1-\rho)I_\gamma]$, with C_{conv} being a conversion factor ($C_{\text{conv}} = 16.8576291$ amu Å cm^{-1}). Using values for ρ and I_a (recalculated from rotational parameters) from Table I, we obtain $I_\gamma = 3.18$ amu Å^2 and $F_\gamma = 15.12$ cm^{-1} (*ab initio* value 15.1684 cm^{-1} [18]). The value for I_γ is close to the expected one which supports the validity of the present analysis. Now, using this value for F_γ and the value for h_{3v} from Table I, a fit to Eq. (3) yields the effective barrier height $V_3 = 683.7$ cm^{-1} (*ab initio* value 708.64 cm^{-1} [18]). The one-dimensional model with this value for V_3 predicts values for the first torsional band and the A-E splitting in the first excited torsional state that are in a good agreement with the observed values (269 versus 264 cm^{-1} [19] for the band origin

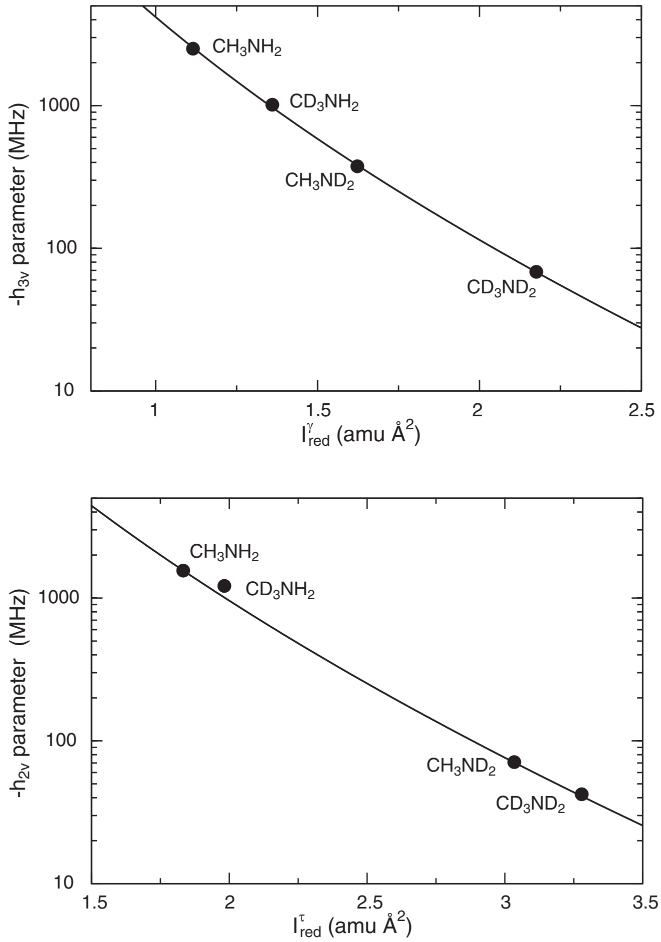

FIG. 3. h_{2v} and h_{3v} parameters as a function of the reduced moment of inertia for the torsional and inversion motions for four different isotopologues of methylamine. The solid lines are fits according to Eq. (2) through the values of CH_3NH_2 and CH_3ND_2.

and 186 versus 180 GHz [19] for the splitting in the $\nu_t = 1$). All this indicates that the one-dimensional model is physically sound and sufficiently accurate for our purposes.

Finally, we obtain the μ dependence of h_{3v} via

$$K_\mu^{h_{3v}} = \frac{\mu}{h_{3v}}\frac{\partial(h_{3v})}{\partial\mu} = -\frac{F_\gamma}{h_{3v}}\frac{\partial(h_{3v})}{\partial F_\gamma}, \tag{4}$$

where we have used the fact that F_γ scales as μ^{-1}, i.e., we assume that the neutron mass has a similar variation as the proton mass. The numerical evaluation $\partial(h_{3v})/\partial F_\gamma$ using Eq. (4) yields $K_\mu^{h_{3v}} = -4.66$.

In the upper panel of Fig. 3, the value of the h_{3v} parameter is plotted as a function of the reduced moment of inertia, $I_{\rm red}^\gamma = C_{\rm conv}/F_\gamma$, for four different isotopologues of methylamine. As mentioned, the quantity $|3h_{3v}|$ corresponds to the usual *A*-*E* internal rotation splitting in a methyl top molecule; hence, we expect the tunneling splitting to follow Eq. (2). The solid line in the upper panel of Fig. 3 corresponds to $a_0 = 10.3\,\text{THz}\,(\text{amu Å}^2)^{1/2}$ and $a_1 = 7.84\,(\text{amu Å}^2)^{-1/2}$, obtained using the CH_3NH_2 and CH_3ND_2 data. The reduced moment of inertia is directly proportional to μ. Thus, the sensitivity coefficient is given by

$$K_\mu^{h_{3v}} = \frac{I_{\rm red}^\gamma}{h_{3v}}\frac{\partial(h_{3v})}{\partial I_{\rm red}^\gamma} = -\frac{1}{2} - \frac{a_1\sqrt{I_{\rm red}^\gamma}}{2}. \tag{5}$$

From the above expression, we find for the h_{3v} parameter of CH_3NH_2 a sensitivity coefficient of $K_\mu^{h_{3v}} = -4.64$, in excellent agreement with the value found from the one-dimensional Hamiltonian model.

C. Inversion and the h_{2v} parameter

The interpretation of the h_{2v} parameter in terms of an effective mass moving in a one-dimensional effective potential is not straightforward. For instance, *ab initio* calculations of the kinetic parameter for the inversion motion in the equilibrium geometry range from 9.6017 [18] to 26.7291 cm^{-1} [20], while the barrier height in different studies varies from 1686 [21] to 2081 cm^{-1} [22]. Since the system needs to tunnel six times in order to return to its initial configuration, we will treat this large amplitude motion as a six-fold periodic well problem, following Ohashi *et al.* [23]. Furthermore, we assume that the potential along the path can be represented by a rapidly converging Fourier series. Thus, we use Eq. (3) with γ replaced by τ and $n = 6$ as a zeroth order model. The effective inversion-torsion constant F_τ and barrier height V_6 can be determined from the splittings in the ground state and NH_2 wagging band origin (780 cm^{-1} [24]). From this, we obtain $F_\tau = 9.19$ cm^{-1} and $V_6 = 2322$ cm^{-1}, close to the values obtained by Ohashi *et al.* [23]. Following the same procedure as for h_{3v}, we obtain the μ dependence of h_{2v}, $K_\mu^{h_{2v}} = -5.49$.

In the lower panel of Fig. 3, the value of the h_{2v} parameter is plotted as a function of the reduced moment of inertia, $I_{\rm red}^\tau = C_{\rm conv}/F_\tau$ for four different isotopologues of methylamine. The solid line in Fig. 3 corresponds to $a_0 = 44.4\,\text{THz}\,(\text{amu Å}^2)^{1/2}$ and $a_1 = 7.35\,(\text{amu Å}^2)^{-1/2}$, obtained using the CH_3NH_2 and CH_3ND_2 data. From this fit, we find for the h_{2v} parameter of CH_3NH_2 a sensitivity coefficient equal to $K_\mu^{h_{2v}} = -5.48$, again in excellent agreement with the one-dimensional Hamiltonian model.

D. q_2 and r_2 parameters

The linear terms q and r correspond to the interaction of components of the total angular momentum with the angular momentum generated in the molecule-fixed axis system by the two large amplitude motions. In methylamine, q_2 and r_2 represent the interaction of the angular momentum generated by the NH_2 inversion and the "corrective" $\pi/3$ rotation of the CH_3 group with the J_z and J_y components of the total angular momentum, respectively. It can be shown in different ways that q_2 has the same dependence on μ as h_{2v}. For instance, it follows from a study of the correlations between the q_2, q_3, and ρ parameters carried out by Ohashi and Hougen [8]. In methylamine, two possible choices exist for ρ. ρ can be chosen such that Coriolis coupling due to the inversion plus corrective rotation is eliminated (q_2 fixed to zero), or such that Coriolis coupling due to the internal rotation of the CH_3 group is eliminated (q_3 fixed to zero). These two choices result in a difference $\Delta\rho = (3/\pi)q_2/h_{2v}$ [8]. Since ρ is in both cases a (dimensionless) ratio between different moments of inertia and independent of μ, the above equation implies that q_2 and h_{2v} should have the same μ dependence.

From the CH_3ND_2 isotopologue data, a sensitivity coefficient $K_\mu^{q_2} = -5.53$ was found, in good agreement with the $K_\mu^{q_2} = -5.50$ obtained from the one-dimensional model and close to the value for $K_\mu^{h_{2v}}$. The r_2 term is expected to have the same μ dependence as q_2. We were not able to check the isotopologue dependence for this term, since it was not required by the CH_3ND_2 fit.

E. Higher order terms

The μ dependence of the higher order terms, including the J and K dependences of the h_{2v} and h_{3v} parameters, was determined in a similar fashion (see the Supplemental Material to this paper [12]). Unfortunately, some ambiguities and discrepancies between the different approaches appeared in the determination of the scaling relations for some higher order terms, which is reflected by the rather large error for these parameters (see Sec. IV). This is not a serious concern as the higher order tunneling parameters only marginally affect the K_μ coefficients of the considered transitions.

IV. SENSITIVITY OF SELECTED TRANSITIONS

Using the scaling relations for the high-barrier tunneling Hamiltonian determined in the previous section, we are now able to calculate the sensitivity coefficient of any desired transition in the ground state of methylamine. In order to do numerical calculations, we rewrite Eq. (1) as

$$K_\mu^{\nu_{mn}} = \frac{\nu_{mn}^{+} - \nu_{mn}^{-}}{2\epsilon \nu_{mn}}, \tag{6}$$

with ν_{mn} the transition frequency between states m and n for the present value of μ and $\nu_{mn}^{\pm}$, the transition frequency when μ is replaced by $\mu(1 \pm \epsilon)$ with ϵ a number much smaller than 1 (in our calculations, we typically use $\epsilon = 0.0001$). ν_{mn} is calculated using values for the molecular constants as listed in Table I, and ν_{mn}^{+} and ν_{mn}^{-} are calculated using the molecular constants scaled according to the relations that were determined in the previous section.

We have calculated the K_μ coefficients for all rotational transitions in the ground state of methylamine with $J < 30$, $K_a < 15$, and ν_{mn} below 500 GHz. The two largest coefficients $K_\mu \approx -19$ and $K_\mu \approx +24$, respectively were found for the $1_1A_2 \leftarrow 2_0A_1$ and $13_3E_1+1 \leftarrow 12_4E_1+1$ transitions at 2166 and 1458 MHz, respectively.

In Table II, the transitions of methylamine that are detected in astrophysical objects in our local galaxy are listed together with their transition strengths and sensitivity coefficients. Table III lists transitions involving levels that have an excitation energy below 10 cm^{-1}, i.e., transitions involving levels that are expected to be populated in cold molecular clouds. The rotational transitions labeled with an asterisk have recently been detected by Muller *et al.* [6] via absorption in a cold cloud at a redshift $z = 0.89$. Due to their rather large transition frequency, their sensitivity coefficients are only slightly enhanced. The transitions in Table III that are labeled by the roman numerals I–X, correspond to transitions in the $J = 1, K = 1$ and $J = 2, K = 0$ levels that are shown in the right-hand side panel of Fig. 2. The transitions labeled by I and II correspond to transitions between the levels of K doublets; hence these have sensitivities of approximately -1. The transitions labeled by V and IX are transitions between levels in which splittings are significantly affected by tunneling motions. The sensitivities of these transitions are on the order of -5, comparable to the sensitivity of the h_{2v} and h_{3v} parameters. The transitions labeled by III,IV,VI,VII,VIII, and X are of particular interest as these are transitions between levels that differ in overall rotational energy as well as torsional-wagging energy. Consequently, cancellations may take place that lead to an enhancement of the sensitivity coefficients. Of these, the transition labeled by III has the smallest transition frequency (2166 MHz) and the highest sensitivity coefficient ($K_\mu = -19$). The transition labeled by IV at 4364 MHz has a sensitivity coefficient equal to $K_\mu = +2$.

The estimated uncertainties of the K_μ coefficients are quoted in brackets in units of the last digits. There are two sources of the uncertainty in the K_μ coefficients: (i) the uncertainty in the determination of the molecular constants and (ii) the inexactness of the scaling relations of the Hamiltonian parameters including errors due to neglecting the μ dependence of the torsion-wagging potential of the molecule. We have assumed the error in the scaling coefficients to be ± 0.02 for the rotational parameters, ± 0.1 for the tunneling parameters h_{2v}, h_{3v}, q_2, r_2, and ± 1 for higher order tunneling terms. Since the uncertainties for the measured transition frequencies in the ground torsional state of methylamine are less than 10^{-4} (and below 5×10^{-6} for the low-J transitions of interest in the present study [10]), we assume that the main errors in sensitivity coefficients are due to the inexactness of the scaling relations of the Hamiltonian parameters. Therefore, similarly to the procedure adopted in Ref. [5], the K_μ coefficients were calculated taking either the upper or the lower bound for the scaling relations, corresponding to the upper and lower bounds of the assumed uncertainties. The difference was taken as an estimate of the uncertainty of the K_μ coefficients. In spite of the large uncertainties of the scaling relations for the higher order terms, the resulting errors in the K_μ coefficients of the different transitions are below 3%. To test the influence of the uncertainties in the scaling relations of the higher order terms, we have performed an additional calculation where only the nontunneling parameters and h_{2v}, h_{3v}, q_2, and r_2 were used to calculate the K_μ coefficients for different transitions. The difference between this calculation and the calculation with the full set of scaling relations was less than 1.7%, i.e., within the uncertainties presented in Tables II and III.

It is interesting to note that almost identical values for the sensitivity coefficients are obtained by using an equation that directly connects the sensitivity coefficient of a transition with the sensitivity coefficients of the Hamiltonian parameters:

$$K_\mu^{\nu_{mn}} = \frac{1}{\nu_{mn}} \sum_s K_\mu^{P_s} P_s \left[\frac{\partial E_n}{\partial P_s} - \frac{\partial E_m}{\partial P_s} \right], \tag{7}$$

where

$$\frac{\partial E_m}{\partial P_s} = \langle m | \hat{O}_s | m \rangle \tag{8}$$

is the derivative of the energy level E_m with respect to the Hamiltonian parameter P_s used in the program to build up the least-squares-fit matrix, and $K_\mu^{P_s}$ is the sensitivity

TABLE II. Transitions in methylamine (CH_3NH_2) that are detected in astrophysical objects in our local galaxy as listed in Lovas *et al*. [25]. The fourth column lists the transition strength multiplied by the electric dipole moment μ_e squared. The last column lists the sensitivity of the transitions to a possible variation of the proton-to-electron mass ratio.

Upper state			Lower state					
J	K	Sym	J	K	Sym	Transition (MHz)	$S\mu_e^2$ (D^2)	K_μ
2	0	B_1	1	1	B_2	8 777.827	0.779	−2.14(6)
5	1	B_1	5	0	B_2	73 044.474	9.024	−0.86(3)
4	1	B_2	4	0	B_1	75 134.858	7.290	−0.87(3)
3	1	B_1	3	0	B_2	76 838.932	5.611	−0.87(3)
1	1	B_1	1	0	B_2	79 008.693	2.373	−0.87(3)
5	1	A_1	5	0	A_2	83 978.941	9.024	−1.47(4)
2	1	E_1+1	2	0	E_1+1	84 598.202	1.065	−1.14(3)
4	1	A_2	4	0	A_1	86 074.729	7.290	−1.45(4)
3	1	A_1	3	0	A_2	87 782.494	5.613	−1.45(4)
2	0	B_1	1	0	B_2	88 667.906	0.189	−1.00(3)
2	0	E_2+1	1	0	E_2+1	88 668.681	0.189	−1.00(3)
2	0	E_1+1	1	0	E_1+1	88 669.543	0.188	−1.00(3)
2	0	A_1	1	0	A_2	88 669.626	0.188	−1.00(3)
8	2	E_1-1	8	1	E_1+1	219 151.221	3.519	−0.84(3)
7	0	B_2	6	1	B_1	220 826.705	4.295	−1.05(3)
9	2	E_2+1	9	1	E_2+1	220 888.443	7.496	−0.94(3)
5	0	E_2+1	4	0	E_2+1	221 527.438	0.472	−1.00(3)
5	0	E_1+1	4	0	E_1+1	221 530.404	0.470	−1.00(3)
5	0	B_2	4	0	B_1	221 530.481	0.473	−1.00(3)
5	0	A_2	4	0	A_1	221 536.285	0.470	−1.00(3)
5	2	E_2+1	4	2	E_2+1	221 717.567	0.395	−1.00(3)
5	2	E_1+1	4	2	E_1+1	221 721.771	0.396	−1.00(3)
5	2	E_1-1	4	2	E_1-1	221 724.256	0.395	−1.00(3)
5	2	E_2-1	4	2	E_2-1	221 728.700	0.396	−1.00(3)
10	2	B_2	10	1	B_1	227 545.019	8.759	−1.15(3)
8	2	E_1+1	8	1	E_1+1	227 997.002	3.320	−1.00(3)
4	2	E_1-1	4	1	E_1+1	229 310.604	0.848	−0.83(3)
7	2	E_2-1	7	1	E_2+1	229 452.729	0.628	−0.96(3)
9	2	B_1	9	1	B_2	231 844.268	7.784	−1.16(3)
5	2	E_2+1	5	1	E_2+1	232 003.755	3.580	−0.89(3)
7	2	A_1	7	1	A_2	233 368.424	5.922	−1.03(3)
14	6	A_1	15	5	A_2	235 337.423	2.367	−1.17(4)
14	6	A_2	15	5	A_1	235 337.540	2.367	−1.17(4)
8	2	B_2	8	1	B_1	235 734.967	6.840	−1.14(3)
6	2	A_2	6	1	A_1	236 408.779	5.020	−1.03(3)
2	2	E_1-1	2	1	E_1-1	237 143.512	1.230	−0.88(3)
4	2	E_1-1	4	1	E_1-1	239 427.017	2.299	−0.87(3)
3	2	E_1+1	3	1	E_1+1	239 446.258	1.937	−0.98(3)
5	2	E_1-1	5	1	E_1-1	241 501.243	2.554	−0.87(3)
6	2	B_2	6	1	B_1	242 261.957	5.020	−1.14(3)
6	2	E_1-1	6	1	E_1-1	244 151.624	2.725	−0.87(3)
10	5	B_1	11	4	B_2	245 463.443	1.506	−1.09(3)
10	5	B_2	11	4	B_1	245 464.483	1.506	−1.09(3)
2	2	A_1	2	1	A_2	246 924.172	1.298	−1.03(3)
4	2	B_2	4	1	B_1	247 080.140	3.235	−1.14(3)
7	2	E_1-1	7	1	E_1-1	247 362.353	2.807	−0.86(3)
3	2	B_1	3	1	B_2	248 838.499	2.317	−1.14(3)
3	2	E_2-1	3	1	E_2-1	248 999.871	2.182	−1.09(3)
8	0	A_1	7	1	A_2	250 702.202	4.891	−0.84(3)
6	2	E_1+1	6	1	E_1-1	252 908.786	1.740	−1.01(3)
6	2	E_2-1	6	1	E_2-1	253 768.569	3.999	−1.06(3)
4	1	E_1-1	3	0	E_1+1	254 055.766	0.259	−1.01(3)
9	2	E_1-1	9	1	E_1-1	255 444.689	2.612	−0.87(3)
4	2	B_1	4	1	B_2	255 997.777	3.065	−1.13(3)
5	2	B_2	5	1	B_1	258 349.240	3.804	−1.13(3)
7	2	A_2	7	1	A_1	258 857.426	5.080	−1.03(3)
10	2	E_1-1	10	1	E_1-1	260 293.984	2.308	−0.87(3)
11	1	B_2	10	2	B_1	260 963.400	3.943	−0.87(3)
4	1	E_2+1	3	0	E_2+1	261 024.312	3.128	−1.00(3)
4	1	B_1	3	0	B_2	261 219.282	3.924	−0.96(3)
8	0	B_1	7	1	B_2	261 562.178	4.881	−1.04(3)
8	0	E_2+1	7	1	E_2+1	263 377.814	4.613	−1.04(3)

TABLE III. Transitions in methylamine (CH_3NH_2) involving levels with an excitation energy lower than 10 cm^{-1} (i.e., both the upper and lower level of the transition have an excitation energy below 10 cm^{-1}). The fourth column lists the transition strength multiplied by the electric dipole moment μ_e squared. The last column lists the sensitivity of the transitions to a possible variation of the proton-to-electron mass ratio. The transitions labeled by roman numerals correspond to the ones depicted in Fig. 2. The transitions labeled with an asterisk have recently been detected by Muller *et al.* [6] in a cold cloud at $z = 0.89$.

	Upper state			Lower state					
	J	K	Sym	J	K	Sym	Transition (MHz)	$S\mu_e^2$ (D^2)	K_μ
I	1	1	A_2	1	1	A_1	879.859	0.141	−1.02(3)
II	1	1	B_2	1	1	B_1	881.386	0.142	−1.02(3)
III	1	1	A_2	2	0	A_1	2 166.305	0.779	−19.1(6)
	2	1	A_1	2	1	A_2	2 639.491	0.078	−0.99(3)
	2	1	B_1	2	1	B_2	2 644.073	0.080	−0.98(3)
IV	2	0	E_1+1	1	1	E_1+1	4 364.348	0.456	1.95(6)
V	1	1	E_1+1	1	1	E_1-1	5 094.897	0.004	−4.0(1)
	2	1	E_1+1	2	1	E_1-1	5 669.477	0.017	−3.5(1)
VI	2	0	E_2+1	1	1	E_2+1	6 437.552	0.418	−0.42(3)
VII	2	0	B_1	1	1	B_2	8 777.827	0.779	−2.14(6)
VIII	2	0	E_1+1	1	1	E_1-1	9 459.246	0.322	−1.29(4)
IX	1	1	E_2+1	1	1	E_2-1	11 911.000	0.001	−4.9(1)
	2	1	E_2+1	2	1	E_2-1	12 167.419	0.004	−4.8(1)
X	2	0	E_2+1	1	1	E_2-1	18 348.552	0.360	−3.3(1)
	3	0	A_2	2	1	A_1	41 263.780	1.541	−0.05(3)
	1	0	B_2	0	0	B_1	44 337.938	0.095	−1.00(3)
	1	0	E_2+1	0	0	E_2+1	44 338.468	0.094	−1.00(3)
	1	0	A_2	0	0	A_1	44 338.755	0.094	−1.00(3)
	1	0	E_1+1	0	0	E_1+1	44 338.876	0.094	−1.00(3)
	3	0	E_1+1	2	1	E_1+1	48 385.595	1.128	−0.75(3)
	3	0	E_2+1	2	1	E_2+1	50 615.856	0.936	−0.94(3)
	3	0	B_2	2	1	B_1	52 202.362	1.540	−1.19(4)
	3	0	E_1+1	2	1	E_1-1	54 055.072	0.412	−1.04(3)
	3	0	E_2+1	2	1	E_2-1	62 783.275	0.603	−1.68(5)
	2	1	E_2-1	2	0	E_2+1	70 199.113	2.420	−0.40(3)
	1	1	E_2-1	1	0	E_2+1	70 320.128	1.274	−0.39(3)
	2	1	E_2-1	1	1	E_2+1	76 636.665	0.001	−0.40(3)
	2	1	B_2	2	0	B_1	78 135.504*	3.976	−0.87(3)
	2	1	E_1-1	2	0	E_1+1	78 928.726	2.914	−0.98(3)
	1	1	B_1	1	0	B_2	79 008.693*	2.373	−0.87(3)
	1	1	E_1-1	1	0	E_1+1	79 210.297	1.392	−0.97(3)
	1	1	E_2+1	1	0	E_2+1	82 231.128	1.099	−1.05(3)
	2	1	E_2+1	2	0	E_2+1	82 366.532	1.558	−1.04(3)
	2	1	E_1-1	1	1	E_1+1	83 293.074	0.003	−0.82(3)
	1	1	E_1+1	1	0	E_1+1	84 305.195	0.982	−1.15(3)
	2	1	E_1+1	2	0	E_1+1	84 598.202	1.065	−1.14(3)
	2	1	B_2	1	1	B_1	87 794.717	0.141	−1.00(3)
	2	1	A_2	1	1	A_1	87 795.016	0.141	−1.00(3)
	2	1	E_1-1	1	1	E_1-1	88 387.971	0.138	−1.01(3)
	2	1	E_2-1	1	1	E_2-1	88 547.665	0.140	−1.01(3)
	2	0	B_1	1	0	B_2	88 667.906	0.189	−1.00(3)
	2	0	E_2+1	1	0	E_2+1	88 668.681	0.189	−1.00(3)
	2	0	E_1+1	1	0	E_1+1	88 669.543	0.188	−1.00(3)
	2	0	A_1	1	0	A_2	88 669.626	0.188	−1.00(3)
	2	1	E_2+1	1	1	E_2+1	88 804.084	0.141	−0.99(3)
	2	1	E_1+1	1	1	E_1+1	88 962.550	0.138	−0.99(3)
	2	1	A_2	2	0	A_1	89 081.463	3.978	−1.44(4)
	2	1	A_1	1	1	A_2	89 554.649	0.141	−1.00(3)
	2	1	B_1	1	1	B_2	89 557.404	0.141	−1.00(3)
	1	1	A_1	1	0	A_2	89 956.072*	2.374	−1.44(4)
	2	1	E_1+1	1	1	E_1-1	94 057.448	0.003	−1.16(3)
	2	1	E_2+1	1	1	E_2-1	100 715.084	0.001	−1.46(4)
	1	1	E_2-1	0	0	E_2+1	114 658.597	0.733	−0.63(3)
	1	1	E_1-1	0	0	E_1+1	123 549.174	0.655	−0.98(3)
	1	1	B_2	0	0	B_1	124 228.018	1.582	−0.92(3)
	1	1	E_2+1	0	0	E_2+1	126 569.597	0.850	−1.03(3)
	1	1	E_1+1	0	0	E_1+1	128 644.071	0.928	−1.10(3)
	3	0	B_2	2	0	B_1	132 981.939	0.284	−1.00(3)
	3	0	E_2+1	2	0	E_2+1	132 982.388	0.283	−1.00(3)
	3	0	E_1+1	2	0	E_1+1	132 983.797	0.282	−1.00(3)
	3	0	A_2	2	0	A_1	132 984.734	0.282	−1.00(3)
	1	1	A_2	0	0	A_1	135174.686	1.583	−1.29(4)
	2	1	E_2-1	1	0	E_2+1	158 867.793	0.929	−0.73(3)
	2	1	E_1-1	1	0	E_1+1	167 598.269	0.636	−0.99(3)
	2	1	B_1	1	0	B_2	169 447.483	2.373	−0.94(3)
	2	1	E_2+1	1	0	E_2+1	171 035.212	1.444	−1.02(3)
	2	1	E_1+1	1	0	E_1+1	173 267.745	1.739	−1.07(3)
	2	1	A_1	1	0	A_2	180 390.580	2.374	−1.22(4)

coefficient with respect to the sth Hamiltonian parameter. Equation (7) is based on the assumption that the energy of state $|m\rangle$ may be represented as $E_m = \sum_s P_s \langle m|\hat{O}_s|m\rangle$. This assumption is valid when the Hamiltonian depends linearly on the parameters, i.e., that the Hamiltonian may be written as $H = \sum_s P_s \hat{O}_s$. The high-barrier tunneling Hamiltonian used for methylamine depends nonlinearly on ρ, but as $K_\mu^\rho = 0$, the transition sensitivity coefficients calculated using Eq. (7) agree well with the results obtained by using Eq. (6); the ≈0.4% difference is attributed to the ρ_K term, which is also nonlinear and whose scaling coefficient is nonzero.

From Eq. (7) it is seen that contributions to $K_\mu^{\nu_{mn}}$ from different terms in the Hamiltonian are proportional to the relative contributions of these terms to the transition frequency. From this fact, it is obvious that the resulting sensitivity coefficients are mainly determined by the largest terms in the Hamiltonian, and uncertainties in the scaling relations for the high order parameters do not significantly affect our results.

Equation (7), illustrates that the largest enhancement is obtained for transitions that connect two near degenerate levels that have substantially different dependences on μ. The different dependence on μ is provided when the two levels contain nonequal contributions from different types of motions in the molecule. In that case, a transition "converts" one superposition of rotation-torsion-wagging motion to another superposition of rotation-torsion-wagging motion. A significant enhancement is obtained when a "cancellation" takes place, i.e., when two levels have nearly the same total energy due to quantitatively different contributions from various types of motion in the molecule.

From Eq. (7), it is possible to obtain an upper limit for the sensitivity coefficient that we may hope to find in the ground vibrational state of methylamine. Considering the main, low order terms, the maximum splitting due to the tunneling motions, i.e., the maximum torsional-wagging energy difference between levels n and m may be roughly taken to be $4(h_{2v} + h_{3v})$. Large enhancements of the sensitivity are expected for transitions that convert a considerable fraction of this energy into rotational energy. Using Eq. (7) and the values and sensitivities of the molecular parameters as listed in Table I, the maximum sensitivity that we may hope to find is

$$K_\mu = K_\mu^{\mathrm{rot}} \pm \frac{1}{\nu_{nm}}\left(4h_{2v}\left[K_\mu^{h_{2v}} - K_\mu^{\mathrm{rot}}\right] + 4h_{3v}\left[K_\mu^{h_{3v}} - K_\mu^{\mathrm{rot}}\right]\right) \approx -1 \pm 64\,800/\nu_{nm}, \quad (9)$$

with $K_\mu^{\mathrm{rot}} = -1$ (i.e., the K_μ of a rotational parameter) and ν_{nm} the transition frequency in MHz. The sensitivities obtained from our numerical calculations are indeed found within these bounds.

V. CONCLUSION

Spectra of molecular hydrogen in highly redshifted objects have been used to constrain a possible variation of the proton-electron mass ratio μ since the 1970s [26]. However, as the observed absorptions in H_2 correspond to transitions between different electronic states, these are rather insensitive to μ; the sensitivity coefficients K_μ are in the range (−0.01,+0.05) [27,28]. For this reason even the highest quality H_2 absorption spectra involving over 90 lines, observed with the large dish Keck Telescope [29] and the Very Large Telescope [30], yield constraints $|\Delta\mu/\mu|$ of only 5×10^{-6} at a redshift $z \sim 2$.

The notion that specific molecules exhibit an enhanced sensitivity to μ variation is changing the paradigm for searching drifting constants on cosmological time scales from the optical to the radio domain. The use of NH_3 inversion transitions in the microwave range that have K_μ coefficients of −4.2 [31,32] has led to much tighter constraints [33] with currently the lowest limit on temporal variations in μ of $|\Delta\mu/\mu| < 0.4 \times 10^{-6}$ at $z \sim 0.68$ [34]. It was recently pointed out that microwave transitions in the methanol molecule (CH_3OH) have sensitivity coefficients in the range (−42,+53) [3,5], which was used to obtain a limit on $|\Delta\mu/\mu| < 0.3 \times 10^{-6}$ at $z \sim 0.89$ based on two methanol lines at 12.2 and 60.5 GHz [35]. In the Milky Way, the methanol method was used to test the variation of μ by looking at the 9.9 and 104 GHz maser transitions resulting in $|\Delta\mu/\mu| < 0.03 \times 10^{-6}$ [5]. This limit can be improved by one order of magnitude if new and more accurate laboratory rest frequencies of methanol transitions are measured. Improvements beyond the level of $\sim 10^{-9}$ are hindered by segregation effects within the methanol emitters [36].

In this paper, we show that the sensitivity of microwave transitions in methylamine, CH_3NH_2, are in the range (−19, +24). Methylamine is particularly relevant as it was recently observed at $z = 0.8859$ in the intervening galaxy toward the quasar PKS 1830-211 [6]. The sensitivity coefficients of the observed transitions at 78.135, 79.008, and 89.956 GHz were calculated to be $K_\mu = -0.87$ for the first two and $K_\mu = -1.4$ for the third transition (see Table III). These three methylamine lines have a mean radial velocity of $v_{CH_3NH_2} = -6.2 \pm 1.6$ km s^{-1} [6]. With $|\Delta K_\mu| = 0.563$ and the uncertainty interval $\Delta v = 1.6$ km s^{-1}, we obtain a preliminary estimate of $\Delta\mu/\mu$:

$$\left|\frac{\Delta\mu}{\mu}\right| = \left|\frac{\Delta v}{c\Delta K_\mu}\right| < 9 \times 10^{-6}, \quad (10)$$

where c is the speed of light.

A tighter constraint on $\Delta\mu/\mu$ is obtained from the comparison of $v_{CH_3NH_2}$ with the radial velocity of the methanol line at 60.531 GHz, also detected at $z = 0.8859$; $v_{CH_3OH} = -5.3 \pm 0.5$ km s^{-1} [6]. According to Ref. [3], this transition has a sensitivity coefficient $K_\mu = -7.4$. In this case we have $|\Delta K_\mu| = 6.5$ and $\Delta v = 0.9 \pm 1.7$ km s^{-1}, which yields $|\Delta\mu/\mu| < 10^{-6}$. This estimate contains an unknown input due to possible noncospatial distribution of CH_3OH and CH_3NH_2. More robust constraints on $\Delta\mu/\mu$ are derived from observations of lines of the same molecule. In this approach the low frequency transitions of CH_3NH_2 at 2166 and 4364 MHz would be particularly attractive as the difference of their sensitivity coefficients is $\Delta K_\mu \approx 21$.

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[1] M. G. Kozlov, S. G. Porsev, and D. Reimers, Phys. Rev. A **83**, 052123 (2011).

[2] In Kozlov *et al.* [1], μ is defined as the electron-to-proton mass ratio; consequently, the sensitivity coefficient used in that work is minus times the sensitivity coefficient used here, $Q_\mu = -K_\mu$.

[3] P. Jansen, L.-H. Xu, I. Kleiner, W. Ubachs, and H. L. Bethlem, Phys. Rev. Lett. **106**, 100801 (2011).

[4] P. Jansen, I. Kleiner, L.-H. Xu, W. Ubachs, and H. L. Bethlem, Phys. Rev. A **84**, 062505 (2011).

[5] S. A. Levshakov, M. G. Kozlov, and D. Reimers, Astrophys. J. **738**, 26 (2011).

[6] S. Muller, A. Beelen, M. Guélin, S. Aalto, J. H. Black, F. Combes, S. Curran, P. Theule, and S. Longmore, Astron. Astrophys. **535**, A103 (2011).

[7] V. V. Ilyushin, E. A. Cloessner, Y.-C. Chou, L. B. Picraux, J. T. Hougen, and R. Lavrich, J. Chem. Phys. **133**, 184307 (2010).

[8] N. Ohashi and J. T. Hougen, J. Mol. Spectrosc. **121**, 474 (1987).

[9] V. V. Ilyushin, E. A. Alekseev, S. F. Dyubko, R. A. Motiyenko, and J. T. Hougen, J. Mol. Spectrosc. **229**, 170 (2005).

[10] V. V. Ilyushin and F. J. Lovas, J. Phys. Chem. Rev. Data **36**, 1141 (2007).

[11] J. T. Hougen and B. M. DeKoven, J. Mol. Spectrosc. **98**, 375 (1983).

[12] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevA.85.032505 for the scaling relations of the higher order terms of the high-barrier tunneling Hamiltonian.

[13] N. Ohashi and J. T. Hougen, J. Mol. Spectrosc. **112**, 384 (1985).

[14] K. Takagi and T. Kojima, J. Phys. Soc. Jpn. **30**, 1145 (1971).

[15] M. Kréglewski, W. Jager, and H. Dreizler, J. Mol. Spectrosc. **144**, 334 (1990).

[16] M. Kréglewski, D. Stryjewski, and H. Dreizler, J. Mol. Spectrosc. **139**, 182 (1990).

[17] V. V. Ilyushin *et al.* (unpublished).

[18] Y. G. Smeyers, M. Villa, and M. L. Senent, J. Mol. Spectrosc. **177**, 66 (1996).

[19] M. Kréglewski and G. Wlodarczak, J. Mol. Spectrosc. **156**, 383 (1992).

[20] Y. G. Smeyers, M. Villa, and M. L. Senent, J. Mol. Spectrosc. **191**, 232 (1998).

[21] M. Tsuboi, A. Y. Hirakawa, and K. Tamagake, Proc. Japan Acad. **42**, 795 (1966).

[22] L. Sztraka, Acta Chim. Hung. **6**, 865 (1987).

[23] N. Ohashi, K. Takagi, J. T. Hougen, W. B. Olson, and W. J. Lafferty, J. Mol. Spectrosc. **132**, 242 (1988).

[24] M. Tsuboi, A. Y. Hirakawa, T. Ino, T. Sasaki, and K. Tamagake, J. Chem. Phys. **41**, 2721 (1964).

[25] F. J. Lovas, J. Phys. Chem. Ref. Data **33**, 177 (2004).

[26] R. I. Thomphson, Astrophys. Lett. **16**, 3 (1975).

[27] D. A. Varshalovich and S. A. Levshakov, JETP Lett. **58**, 231 (1993).

[28] W. Ubachs, R. Buning, K. S. E. Eikema, and E. Reinhold, J. Mol. Spectrosc. **241**, 155 (2007).

[29] A. L. Malec, R. Buning, M. T. Murphy, N. Milutinovic, S. L. Ellison, J. X. Prochaska, L. Kaper, J. Tumlinson, R. F. Carswell, and W. Ubachs, MNRAS **403**, 1541 (2010).

[30] F. van Weerdenburg, M. T. Murphy, A. L. Malec, L. Kaper, and W. Ubachs, Phys. Rev. Lett. **106**, 180802 (2011).

[31] J. van Veldhoven, J. Küpper, H. L. Bethlem, B. Sartakov, A. J. A. van Roij, and G. Meijer, Eur. Phys. J. D **31**, 337 (2004).

[32] V. V. Flambaum and M. G. Kozlov, Phys. Rev. Lett. **98**, 240801 (2007).

[33] M. T. Murphy, V. V. Flambaum, S. Muller, and C. Henkel, Science **320**, 1611 (2008).

[34] N. Kanekar, Astroph. J. Lett. **728**, L12 (2011).

[35] S. P. Ellingsen, M. A. Voronkov, S. L. Breen, and J. E. J. Lovell, Astrophys. J. Lett. **747**, L7 (2012).

[36] S. Ellingsen, M. Voronkov, and S. Breen, Phys. Rev. Lett. **107**, 270801 (2011).

Supplementary Information for Sensitivity to a possible variation of the Proton-to-Electron Mass Ratio of Torsion-Wagging-Rotation Transitions in Methylamine (CH_3NH_2)

Vadim V. Ilyushin,[1] Paul Jansen,[2] Mikhail G. Kozlov,[3] Sergei A. Levshakov,[4] Isabelle Kleiner,[5] Wim Ubachs,[2] and Hendrick L. Bethlem[2]

[1]*Institute of Radio Astronomy of NASU, Chervonopraporna 4, 61002 Kharkov, Ukraine*
[2]*Institute for Lasers, Life and Biophotonics, VU University Amsterdam, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands*
[3]*Petersburg Nuclear Physics Institute, Gatchina 188300, Russia*
[4]*Ioffe Physical-Technical Institute, 194021 St. Petersburg, Russia*
[5]*Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), CNRS UMR 7583 et Universités Paris 7 et Paris Est, 61 avenue du Général de Gaulle, 94010 Créteil Cédex, France*

I. SCALING RELATIONS OF THE HIGHER ORDER MOLECULAR PARAMETERS

In the present work, we use the group-theoretical high-barrier tunneling formalism developed for methylamine by Ohashi and Hougen [1], which is capable of reproducing observations of the rotational spectrum of the ground vibrational state of CH_3NH_2 to within a few tens of kilohertz [2, 3]. Table I lists the molecular constants used in our calculations. It includes three types of parameters: 'non-tunneling' or pure rotational parameters; parameters associated with pure methyl torsion motion (odd numerical subscripts n); and parameters associated with the NH_2 wagging motion (even numerical subscripts n). The obtained μ-scaling relations for the different parameters of the high-barrier tunneling formalism of methylamine are listed in the rightmost column of Table I. In the main text we have discussed the scaling relations for the lowest order parameters. Here the scaling relations for the higher order tunneling parameters, and the problems encountered in determining these, are discussed. As detailed in the main text, we have used two different approaches:

(i) The first approach is based on the fact that the tunneling model essentially assumes that for each large-amplitude tunneling motion the system point travels along some path in coordinate space. In zeroth approximation, we may represent each large amplitude motion as a one-dimensional mathematical problem after parameterizing the potential along the path and the effective mass that moves along it.

(ii) In the second approach, we use the spectroscopic data of different isotopologues of methylamine to estimate the dependence of the tunneling constants.

A. f_2, f_3 terms and J and K dependences of the parameters

In determiniming the scaling relations for the J and K dependence of the different tunneling terms some ambiguities and discrepancies between the different approaches appear. Let us for example consider the K dependence of the h_{2v} splitting, i.e. the h_{2k} parameter. In the framework of our one dimensional model (see Eq. (3) of the main text), we can present the K dependence of the h_{2v} splitting as a $V_{6K}J_z^2\cos(6\tau)$ potential term, as a $F_K J_z^2 p_\tau^2$ kinetic term, or as a combination of these two. Numerical evaluation gives scaling factors of -5.9 for the potential term and -6.0 for the kinetic term, where we assume the same μ-dependence of the one-dimensional model parameters as was used for methanol [4, 5]. So, for the pure kinetic term we obtain that the K^2 dependence of the amino wagging splitting gives approximately an additional $\mu^{-1/2}$ factor in the scaling relations, whereas each additional J_z^2 factor (which brings us to h_{2KK} and so on) results in an additional μ^{-1} factor. This corresponds to $K_\mu^{h_{2k}} = K_\mu^{h_{2v}} - 1/2$ and to adding -1 with each additional power of K^2.

The problems arise when we consider the combination of the kinetic and potential terms, in particular when we consider terms that contain the difference between the two (it seems obvious that both types of corrections are in fact present, one should just look at a number of molecules with methyl top large amplitude torsion motion like, for example, methanol). If we consider the combination $F_K J_z^2 p_\tau^2 - V_{6K} J_z^2 \cos(6\tau)$ and fix the V_{6K}/F_K ratio at the level of V_6/F (taken from subsection IIIC), we obtain that the dependence of the amino wagging splitting has approximately an additional μ^{-1} factor in the scaling relations. But if we keep the V_{6K}/F_K ratio at the level of $\sim 1.25V_6/F$, then we obtain from numerical calculations a μ^0 factor in the scaling relations (implying that the h_{2k} parameter should scale as the h_{2v} parameter). Thus depending on the particular combination, we obtain rather different values for the scaling relations. The same situation is observed for the $J, K, \Delta K = 2$ dependences of both the h_{2v} and the h_{3v} parameters. It is clear that we get the maximum variation when the contributions of the kinetic and potential terms are comparable, since in this case we will get a resonance enhancement of the difference in scaling relations for potential and kinetic terms (which as can be seen above is of the order of 0.1).

Table I. Molecular parameters, P_s, of the ground torsional state of methylamine CH_3NH_2 [2], and their sensitivity to a variation of the proton-to-electron mass ratio μ defined as $K_\mu^{P_s} = \frac{\mu}{P_s}\frac{\partial P_s}{\partial \mu}$. All molecular parameters are in MHz, except ρ and ρ_K, which are dimensionless.

Rotation[a]			Inversion[b]			Torsion[c]		
	$K_\mu^{P_s}$			$K_\mu^{P_s}$			$K_\mu^{P_s}$	
$\bar{B}$	−1	22 169.36636(30)	h_{2v}	−5.5	−1 549.18621(77)	h_{3v}	−4.7	−2 493.5140(12)
$A-\bar{B}$	−1	80 986.3823(11)	h_{4v}	−8.2	2.73186(96)	h_{5v}	−8.8	2.88398(55)
$B-C$	−1	877.87717(53)	h_{2J}	−5.5	0.101759(11)	h_{3J}	−4.7	−0.052546(20)
D_J	−2	0.0394510(18)	h_{2K}	−5.5	1.73955(16)	h_{5J}	−8.8	0.0002282(55)
D_{JK}	−2	0.170986(15)	h_{4K}	−8.2	−0.004778(37)	h_{3K}	−4.7	1.16676(22)
D_K	−2	0.701044(24)	h_{2JJ}	−6.5	−0.000005466(88)	h_{5K}	−8.8	−0.002667(73)
δ_J	−2	0.00175673(17)	h_{2KK}	−6.5	−0.0009016(63)	h_{3JJ}	−5.7	−0.000017296(44)
δ_K	−2	−0.33772(13)	h_{2JK}	−6.5	−0.00015400(94)	h_{3KK}	−5.7	−0.0002995(42)
Φ_J	−3	−0.0000000485(16)	h_{2JKK}	−7.5	0.0000001923(56)	h_{3JJK}	−6.7	−0.00000004702(67)
Φ_{JK}	−3	0.000002442(50)	q_2	−5.5	21.54923(52)	f_3	−4.7	−0.173439(24)
Φ_{KJ}	−3	−0.00000855(10)	q_4	−8.2	−0.03071(20)	f_{3J}	−5.7	−0.00000261(13)
Φ_K	−3	0.00003322(29)	q_{2J}	−6.5	−0.0037368(45)	f_{3K}	−5.7	−0.0001359(32)
ϕ_K	−3	0.0002366(48)	q_{2K}	−6.5	−0.019676(43)	f_{3JK}	−6.7	−0.0000000646(27)
			q_{2JJ}	−7.5	0.000002098(62)	$f_3^{(2)}$	−5.7	−0.000003021(89)
			q_{2KK}	−7.5	0.00001023(54)	$f_{3J}^{(2)}$	−6.7	0.00000000220(13)
ρ	0	0.64976023(13)	f_2	−5.5	−0.096739(38)			
ρ_K	−1	−0.0000011601(77)	f_4	−8.2	0.0002153(39)			
			f_{2J}	−6.5	0.000004452(67)			
			f_{2K}	−6.5	0.001188(37)			
			f_{2KK}	−7.5	−0.000001600(47)			
			$f_2^{(2)}$	−6.5	−0.000002443(55)			
			r_2	−5.5	10.979(37)			
			r_{2K}	−6.5	−0.7206(73)			

[a] These parameters do not involve tunneling motions.
[b] These parameters arise from the NH_2 inversion tunneling motion.
[c] These parameters arise from the CH_3 torsional tunneling motions.

From the above discussion it is clear that, within our one-dimensional approach, we are not able to obtain unambiguous scaling relations for the J and K dependences of the tunneling splittings, since we do not know which particular combination of the kinetic and potential terms we should use. The only case where the choice of the term in a one-dimensional Hamiltonian seems straightforward is the J and K dependences of the q_2 parameter. We can represent the K dependence as $J_z^3 p_\tau$ and the J dependence as $J^2 J_z p_\tau$ terms (the q_2 term in one dimensional model is represented by $J_z p_\tau$). In this case each J_z^2 or J^2 factor gives an additional -1 in the K_μ scaling coefficient.

The second, isotopologue, approach does not save the situation since different correlation problems come in play. In addition to inherent correlation problems caused by nonorthogonality of the vibrational basis functions, we have the usual correlations between parameters when the same effect in the spectrum may be taken into account by different sets of Hamiltonian terms (a problem of the Hamiltonian reduction). Although, the basic set of parameters is the same in both the CH_3NH_2 and the CH_3ND_2 fit, there are some differences (note also that in the case of CH_3ND_2, we miss the 850 FIR transitions that are available for CH_3NH_2[2, 3]). For example the CH_3ND_2 fit did not require a r_2 term but did require a ρ_J term which is absent in the CH_3NH_2 set of parameters (and as was pointed out in Ref. [6] the centrifugal distortion corrections to ρ may be highly correlated with centrifugal distortion corrections to h_{nv} and q_n). These two sources of correlation may result in more or less significant distortions in the higher order terms. The most striking unexpected change is observed for the h_{2J} parameter which in the CH_3NH_2 fit has a different sign than in the CH_3ND_2 fit. Therefore, within the isotopologue approach, we may expect to obtain reasonable results for the scaling relations only for some largest high order terms like h_{2k} and h_{3k}. For the h_{2k} and h_{3k} parameters, we get K_μ values of -5.24 and -4.83, respectively, for the f_2 and f_3 terms we get K_μ-values of -5.47 and -4.46, repectively, and for the q_{2J} and q_{2K} terms, we get K_μ-values of -5.97 and -5.27, respectively. In view of the above mentioned inconsistency in the sign of h_{2J} parameter, which we attribute to correlation problems, we did not attempt to find a scaling for the h_{2J} and the h_{3J} parameters from the isotopologue scaling.

From the results above it is seen that the K_μ-coefficients of the h_{2k} and the h_{3k} parameters and the f_2 and the f_3 parameters are in reasonable proximity of the corresponding values of the h_{2v} and the h_{3v} parameters, respectively. So the isotopologue results may be interpreted in favor of using the same scaling factors for h_{2k}, f_2 and h_{2v} as well as for h_{3k}, f_3 and h_{3v}. An interesting argument in support of the same scaling ratios for the h_{nJ}, h_{nK}, f_n and h_{nv} parameters [7] originates from a generalized internal axis method for the high-barrier tunneling formalism developed for the water dimer [8–10] which was also applied to the methanol-water heterodimer [11]. This modification of the high-barrier tunneling formalism is based on the same assumptions as used in the case of methylamine but instead of canceling angular momentum conjugated to only one selected type of tunneling process, like in methylamine, it attempts to accomplish this cancellation for all tunneling processes in the molecule. It is shown that one type of contribution to the correction to the rotational parameters as a result of different tunneling motions, may be expressed as the splitting term h_{nv} multiplied by a small factor that depends on the 'axis switching' angle. The axis switching angle is introduced by the backward rotation required to cancel the angular momentum generated by the considered tunneling process (see for example Eq. (33) or Eq. (36) of Ref. [11]). The 'axis switching' angle is determined from a system of differential equations with coefficients that depend on the different ratios of moments of inertia and, therefore, it is independent of μ (the same is true for ρ in the case of methylamine). Therefore the μ-scaling of these corrections to the rotational constants (which, in the methylamine model, correspond to the h_{nJ}, h_{nK}, and f_n parameters) will be equal to the μ scaling of the h_{nv} terms. Unfortunately, without explicit application of this approach to methylamine (which is outside the scope of the present study), it is impossible to say whether these contributions to the J and K dependences will dominate or not. Nevertheless, it does not seem unreasonable to set the scaling relations for the h_{nJ}, h_{nK} and f_n parameters to be equal to the scaling relations of the main tunneling terms h_{nv}.

The problems discussed above demonstrate that at the present level of our understanding of the tunneling processes in methylamine, it is impossible to derive scaling relations for the higher order parameters at the same level of accuracy as achieved for the main tunneling terms. It is clear that scaling factors of the J and K dependences of the tunneling splittings should lie in the same range as the scaling factors of the main tunneling terms. Therefore, for the high order terms, we will abandon our attempts to find 'accurate' scaling relations that are supported by both applied methods and take the average of the outcome of the two methods. As discussed in the main text, the higher order tunneling parameters only marginally affect the K_μ coefficients of the considered transitions in methylamine.

So, finally we choose the following μ scaling scheme for the f_2, f_3 terms and the J and K dependences of the parameters: The f_n, h_{nK} and h_{nJ} parameters scale as h_{nv}. Each additional J_z^2 or J^2 factor gives an additional -1 factor in the scaling relation, corresponding to the addition of -1 to the respective K_μ. The $f_n^{(2)}$ parameters scale as $\mu^{-1} f_n$. Each J_z^2 or J^2 factor in the q_2 or r_2 series of parameters gives an additional -1 factor. We put an uncertainty of ±1 on the scaling relations of all these parameters.

B. Higher order expansion terms h_{4v} and h_{5v}.

In the interpretation of the high-barrier tunneling formalism given by Hougen and Ohashi [1], the h_{4v} and h_{5v} terms correspond to tunneling from framework 1 to the next neighbor framework (or potential well) in inversion and torsional motion, respectively. The physical interpretation of these terms is not entirely clear, but they must be included when the single-well wavefunctions used as the starting point of the tunneling model become so delocalized (or the measurement precision becomes so high) that next-nearest-neighbor wavefunctions must be considered to communicate directly with each other. This seems to favor the interpretation that these terms describe tunneling splittings governed by overlap integrals evaluated at twice the distance used for the nearest neighbor step, rather than splittings governed by two sequential nearest neighbor tunneling steps. In any case, since interpretation of these splittings in terms of one-dimensional models is less straightforward than for the h_{2v} and h_{3v} terms, we decided to use the K_μ-scaling factors obtained from the isotopologue approach based on CH_3NH_2 and CH_3ND_2 data. We obtained $K_\mu^{h_{4v}} = -8.23$ and $K_\mu^{h_{5v}} = -8.75$. An approximate semiclassical consideration of these splittings gives K_μ coefficients of the same order. From an extension of the treatment of the parameter correlations based on the two possible choices of ρ [6], we find that the q_4 parameter should scale in the same way as the h_{4v} parameter.

[1] N. Ohashi and J. T. Hougen, J. Mol. Spectrosc. **121**, 474 (1987).

[2] V. V. Ilyushin, E. A. Alekseev, S. F. Dyubko, R. A. Motiyenko, and J. T. Hougen, J. Mol. Spectrosc. **229**, 170 (2005).

[3] V. V. Ilyushin and F. J. Lovas, J. Phys. Chem. Rev. Data **36**, 1141 (2007).

[4] P. Jansen, L.-H. Xu, I. Kleiner, W. Ubachs, and H. L. Bethlem, Phys. Rev. Lett. **106**, 100801 (2011).

[5] P. Jansen, I. Kleiner, L.-H. Xu, W. Ubachs, and H. L. Bethlem, Phys. Rev. A **84**, 062505 (2011).

[6] N. Ohashi, K. Takagi, J. T. Hougen, W. B. Olson, and W. J. Lafferty, J. Mol. Spectrosc. **126**, 443 (1987).

[7] J. T. Hougen, Private Communication.

[8] J. T. Hougen, J. Mol. Spectrosc. **114**, 395 (1985).

[9] L. Coudert and J. Hougen, J. Mol. Spectrosc. **130**, 86 (1988).

[10] L. Coudert and J. Hougen, J. Mol. Spectrosc. **139**, 259 (1990).

[11] J. Hougen and N. Ohashi, J. Mol. Spectrosc. **159**, 363 (1993).