

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)

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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 determining the scaling relations for the J and K dependence of the different tunneling terms some ambiguities and discrepancies between the different ap-

proaches 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	-0.000000485(16)	h_{2JKK}	-7.5	0.000001923(56)	h_{3JJK}	-6.7	-0.0000004702(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 , respectively, 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.

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