Electronic Supplementary Material
to the paper
Promoting and inhibiting tunneling via nuclear motions

Attila G. Császár and Tibor Furtenbacher
Institute of Chemistry, Loránd Eötvös University, H-1117 Budapest, Pázmány sétány 1/A, Hungary and MTA-ELTE Complex Chemical Systems Research Group, H-1518 Budapest 112, P.O. Box 32, Hungary

Table S1: Spin statistical weights and symmetry characteristics ($\Gamma_{\rm rve}$) of the rovibrational states of $^{14}NH_3$ based on the D_{3h}(M) molecular symmetry (MS) group
Related text: The existence of nuclear spin states which do not have the allowed symmetry for combination with a particular rovibronic state introduces the concept of 'missing' levels (irreducible representations with zero statistical weights, see Table S1). Such rovibronic levels correspond to eigenvalues of the usually employed rovibronic Hamiltonians, but no transitions will originate from or end on them because of symmetry restrictions.

Table S2: List of MARVEL energy levels of NH_3 [1] relabelled during the present study
Related text: There is a significant number of energy levels presented in Ref. [1] which had to be relabelled during the present study (see Table S2). For most of these energy levels the sign of either l_3 or l_4 had to be changed.

Table S3: List of MARVEL energy levels of NH_3 [1] deleted during the present study and the deleted transitions determining them
Related text: A few transitions had to be deleted from the MARVEL input of Ref. [1] and thus the MARVEL energy levels only they determine disappear after the new analysis. The deleted energy levels are listed in Table S3, grouped by vibrational quantum numbers. Thus, only the "rotation-inversion" labels [J K i], along with simplified vibrational labels, are provided to denote the energy levels. For the most part, energies of the remaining rovibrational levels changed only insignificantly, well within their uncertainties provided in Ref. [1]. Nevertheless, due to changes in the uncertainties of some of the related transitions, significantly different energy values have been obtained for the following two levels: (0 0 0 0 0 0 8 8 1) and (1 0 0 0 0 0 9 8 0), where the notation refers to that introduced in Ref. [1].

Table 1: Spin statistical weights and symmetry characteristics ($\Gamma_{\rm rve}$) of the rovibrational states of $^{14}NH_3$ based on the D_{3h}(M) molecular symmetry (MS) group.[a]

$\Gamma_{\rm rve}$	Statistical weight
A_1'	0
A_2'	12
E'	6
A_1''	0
A_2''	12
E''	6

[a] Levels of species $A_2^\dagger := \{A_2', A_2''\}$ belong to ortho-$^{14}NH_3$, levels of species $E^\dagger := \{E', E''\}$ belong to para-$^{14}NH_3$ (by definition, ortho levels should have the higher spin statistical weights [2]), while levels of species $A_1^\dagger := \{A_1', A_1''\}$ are so-called 'missing' levels. When the symmetry species are denoted according to the S_3^* permutation-inversion group, the superscripts of $\Gamma_{\rm rve}$ change according to $' = +$ and $'' = -$.

Table 2: List of MARVEL energy levels of NH_3 [1] relabelled during the present study.[a]

VBO	energy level
GS	[19 3 0] $\Longleftrightarrow$ [19 3 1]
ν_3	(0 0 1 0 1 0 9 5 0) $\Longleftrightarrow$ (0 0 1 0 1 0 9 5 1)
ν_4	(0 0 0 1 0 −1 10 0 0) $\Longrightarrow$ (0 0 0 1 0 1 10 0 0), (0 0 0 1 0 −1 10 0 1) $\Longrightarrow$ (0 0 0 1 0 1 10 0 1), (0 0 0 1 0 1 12 2 0) $\Longrightarrow$ (0 0 0 1 0 −1 12 2 0), (0 0 0 1 0 1 13 2 1) $\Longrightarrow$ (0 0 0 1 0 −1 13 2 1), (0 0 0 1 0 1 13 6 0) $\Longleftrightarrow$ (0 0 0 1 0 −1 13 6 0), (0 0 0 1 0 1 13 6 1) $\Longleftrightarrow$ (0 0 0 1 0 −1 13 6 1), (0 0 0 1 0 −1 13 7 1) $\Longleftrightarrow$ (0 0 0 1 0 1 13 7 1), (0 0 0 1 0 −1 9 2 0) $\Longleftrightarrow$ (0 0 0 1 0 1 9 2 0), (0 0 0 1 0 −1 9 2 1) $\Longleftrightarrow$ (0 0 0 1 0 1 9 2 1), (0 0 0 1 0 −1 10 2 1) $\Longrightarrow$ (0 0 0 1 0 1 10 2 1), (0 0 0 1 0 −1 11 2 0) $\Longleftrightarrow$ (0 0 0 1 0 1 11 2 0), (0 0 0 1 0 −1 11 2 1) $\Longleftrightarrow$ (0 0 0 1 0 1 11 2 1), (0 0 0 1 0 −1 12 2 0) $\Longrightarrow$ (0 0 0 1 0 1 12 2 0), (0 0 0 1 0 −1 12 2 1) $\Longleftrightarrow$ (0 0 0 1 0 1 12 2 1), (0 0 0 1 0 −1 13 2 0) $\Longleftrightarrow$ (0 0 0 1 0 1 13 2 0), (0 0 0 1 0 −1 13 2 1) $\Longrightarrow$ (0 0 0 1 0 1 13 2 1), (0 0 0 1 0 −1 14 2 0) $\Longleftrightarrow$ (0 0 0 1 0 1 14 2 0), (0 0 0 1 0 −1 14 2 1) $\Longleftrightarrow$ (0 0 0 1 0 1 14 2 1), (0 0 0 1 0 −1 15 2 0) $\Longleftrightarrow$ (0 0 0 1 0 1 15 20), (0 0 0 1 0 −1 15 2 1) $\Longleftrightarrow$ (0 0 0 1 0 1 15 21), (0 0 0 1 0 −1 13 4 1) $\Longleftrightarrow$ (0 0 0 1 0 1 13 4 1), (0 0 0 1 0 −1 15 4 1) $\Longleftrightarrow$ (0 0 0 1 0 1 15 4 1), (0 0 0 1 0 −1 15 5 1) $\Longleftrightarrow$ (0 0 0 1 0 1 15 5 1), (0 0 0 1 0 −1 16 5 1) $\Longleftrightarrow$ (0 0 0 1 0 1 16 5 1)
$\nu_2+\nu_3$	(0 1 1 0 1 0 0 0 1) $\Longleftrightarrow$ (0 1 1 0 1 0 0 0 0), (0 1 1 0 1070 1) $\Longleftrightarrow$ (0 1 1 0 1 0 7 0 0), (0 1 1 0 1 0 8 0 1) $\Longleftrightarrow$ (0 1 1 0 1 0 8 0 0), (0 1 1 0 1 0 9 0 1) $\Longleftrightarrow$ (0 1 1 0 1 0 9 0 0), (0 1 1 0 1 0 1 0 1) $\Longleftrightarrow$ (0 1 1 0 1 0 1 0 0), (0 1 1 0 1 0 2 0 1) $\Longleftrightarrow$ (011 0 1 0 2 0 0), (0 1 1 0 1 0 8 3 0) $\Longleftrightarrow$ (011 0 1 0 8 3 1), (0 1 1 0 1 0 9 3 0) $\Longleftrightarrow$ (0 110 1 0 9 3 1), (0 1 1 0 1 0 9 6 0) $\Longleftrightarrow$ (0 1 1 0 1 0 9 6 1), (0 1 1 0 −1 0 6 1 0) $\Longleftrightarrow$ (0 1 1 0 −1 0 6 1 1), (0 1 1 0 −1 0 3 3 0) $\Longleftrightarrow$ (0 1 1 0 −1 0 3 3 1), (0 1 1 0 −1 0 4 3 0) $\Longleftrightarrow$ (0 1 1 0 −1 0 4 3 1), (0 1 1 0 −1 0 6 3 0) $\Longleftrightarrow$ (0 1 1 0 −1 0 6 3 1, (0 1 1 0 −1 0 7 3 0) $\Longleftrightarrow$ (0 1 1 0 −1 0 7 3 1, (0 1 1 0 −1 0 8 3 0) $\Longleftrightarrow$ (0 1 1 0 −1 0 8 3 1, (0 1 1 0 −1 0 9 3 0) $\Longleftrightarrow$ (0 1 1 0 −1 0 9 3 1, (0 1 1 0 −1 0 4 4 0) $\Longleftrightarrow$ (0 1 1 0 −1 0 4 4 1, (0 1 1 0 −1 0 6 4 0) $\Longleftrightarrow$ (0 1 1 0 −1 0 6 4 1, (0 1 1 0 −1 0 5 5 0) $\Longleftrightarrow$ (0 1 1 0 −1 0 5 5 1, (0 1 1 0 −1 0 6 5 0) $\Longleftrightarrow$ (0 1 1 0 −1 0 6 5 1), (0 1 1 0 −1 0 7 5 0) $\Longleftrightarrow$ (0 1 1 0 −1 0 7 5 1), (0 1 1 0 −1 0 7 6 0) $\Longleftrightarrow$ (0 1 1 0 −1 0 7 6 1), (0 1 1 0 −1 0 9 6 0) $\Longleftrightarrow$ (0 1 1 0 −1 0 9 6 1), (01 1 0 −1 0 7 7 0) $\Longleftrightarrow$ (0 1 1 0 −1 0 7 7 1), (01 1 0 −1 0 8 7 0) $\Longleftrightarrow$ (0 1 1 0 −1 0 8 7 1), (01 1 0 −1 0 8 8 0) $\Longleftrightarrow$ (0 1 1 0 −1 0 8 8 1)
$\nu_2+\nu_4$	(0 1 0 1 0 1 3 2 0) $\Longleftrightarrow$ (0 1 0 1 0 −1 3 2 0), (0 1 0 1 0 1 4 2 0) $\Longleftrightarrow$ (0 1 0 1 0 −1 4 2 0), (0 1 01 0 1 5 5 0) $\Longleftrightarrow$ (0 1 0 1 0 −1 5 5 0), (0 1 01 0 1 4 3 0) $\Longleftrightarrow$ (0 1 0 1 0 −1 4 3 0)

[a] VBO = vibrational band origin. GS = gropund state. See the text for a detailed description of the rovibrational labels provided in parentheses and brackets. For MARVEL energy levels where the sign of either l_3 or l_4 had to be changed is indicated by "$\Longrightarrow$". Cases where labels of two MARVEL energy levels had to be exchanged are indicated by "$\Longleftrightarrow$".

Table 3: List of MARVEL energy levels of NH_3 [1] deleted during the present study and the deleted transitions determining them[a]

VBO	energy level	source
ν_1	[10 1 1]	99KlBrTaKo_RA [3]: .15, .81
	[10 2 1]	99KlBrTaKo_RA [3]: .82
	[10 3 1]	99KlBrTaKo_RA [3]: .149
	[10 5 0]	99KlBrTaKo [3]: .117, .146
	[10 6 1]	99KlBrTaKo_RA [3]: .47, .78
	[10 7 1]	99KlBrTaKo_RA [3]: .93, .111, .139, .142
ν_2	[4 0 0]	85UrMiRa [4]: .314
$2\nu_2$	[16 14 1]	11ZoShOvPo [5]: .2064, .2903, .4506
ν_4^{+1}	[10 0 1]	84UrCuNaPa [6]: .288, .370, .435; 00CoKlTaBr [7]: .578, .1118; 92SaEnHiPo [8]: .463; 11ZoShOvPo [5]: .671, .751, .4122, .4495
	[11 3 0]	11ZoShOvPo [5]: .306, .794, .1816, .4292
	[12 2 1]	11ZoShOvPo [5]: .5060, .5086
	[12 3 0]	00CoKlTaBr [7]: .1130; 11ZoShOvPo [5]: .24, .2166, .3873, .207
	[13 1 0]	11ZoShOvPo [5]: .1120, .4898
	[13 2 0]	11ZoShOvPo [5]: .1038, .2445, .3815, .5347
	[13 3 0]	11ZoShOvPo [5]: .1612, .3801
	[13 4 1]	11ZoShOvPo [5]: .1725, .3575, .3747
	[14 1 1]	11ZoShOvPo [5]: .4817
	[14 2 0]	11ZoShOvPo [5]: .4664
	[14 2 1]	11ZoShOvPo [5]: .47, .4544
	[15 2 0]	11ZoShOvPo [5]: .1591, .3385
	[15 2 1]	11ZoShOvPo [5]: .4063, .4179
	[15 4 1]	11ZoShOvPo [5]: .1609, .1670, .2375, .2410, .2927
	[15 5 1]	11ZoShOvPo [5]: .2110, .4044, .4195
	[16 4 1]	11ZoShOvPo [5]: .1781. .3691
	[16 5 1]	11ZoShOvPo [5]: .2406, .3365, .4036
	[17 7 1]	11ZoShOvPo [5]: .2253, .2443
ν_4^{-1}	[12 2 1]	11ZoShOvPo [5]: .238, .418, .1958, .2070, .3876
	[13 2 0]	11ZoShOvPo [5]: .2012, .2074
	[14 1 1]	11ZoShOvPo [5]: .3366, .4156
	[14 2 0]	11ZoShOvPo [5]: .1588, .3735; 13DoHiYuTe [9]: .810, .971
	[14 2 1]	11ZoShOvPo [5]: .1952, .3413
	[15 1 1]	11ZoShOvPo [5]: .3988, .5004
	[15 2 0]	11ZoShOvPo [5]: .1591, .3385
	[15 2 1]	11ZoShOvPo [5]: .621
	[15 4 1]	11ZoShOvPo [5]: .1782, .4116
	[15 5 1]	11ZoShOvPo [5]: .3240
	[16 5 1]	11ZoShOvPo [5]: .623, .2777
	[17 7 1]	11ZoShOvPo [5]: .3563
$\nu_1 + \nu_3^{+1}$	[6 3 0]	93LuHeNi [10]: .340
$\nu_2 + \nu_3^{-1}$	[7 1 0]	89UrTuRaGu [11]: .542
	[8 6 1]	89UrTuRaGu [11]: .301
$2\nu_4^{+2}$	[7 7 0]	99KlBrTaKo [3]: .311, .752
	[7 7 1]	99KlBrTaKo [3]: .312; 01CoTaKlBr [12]: .587
$2\nu_4^0$	[7 7 1]	99KlBrTaKo [3]: .427; 89GuAbTuRa [13]: .769
	[7 7 0]	99KlBrTaKo [3]: .27, .411; 01CoTaKlBr [12]: .642; 11ZoShOvPo [5]: .1115, .2418, .2447
	[7 6 1]	99KlBrTaKo [3]: .460, .839
	[7 6 0]	99KlBrTaKo [3]: .37, .447, .832, .554; 01CoTaKlBr [12]: .656, .781
	[7 5 1]	13DoHiYuTe [9]: .2023
	[7 5 0]	99KlBrTaKo [3]: .43, .472, .842; 01CoTaKlBr [12]: .793
	[7 4 1]	99KlBrTaKo [3]: .63, .516, .862; 11ZoShOvPo [5]: .2036
	[7 4 0]	99KlBrTaKo [3]: .50, .365, .488, .819, .849; 01CoTaKlBr [12]: .809; 11ZoShOvPo [5]: .815, .1804, .2035
	[7 3 1]	99KlBrTaKo [3]: .26, .67, .341, .521, .794, .868; 11ZoShOvPo [5]: .612, .1784, .2821, .2858, .3299
	[7 3 0]	99KlBrTaKo [3]: .59, .500, .774, .857, .976; 01CoTaKlBr [12]: .817, .823; 11ZoShOvPo [5]: .467, .683, .685, .1319, .2224, .2494
	[7 2 0]	99KlBrTaKo_RA [3]: .4, .61
	[7 1 1]	99KlBrTaKo_RA [3]: .5, .7, .24, .32, .35, .41, .62, .63; 11ZoShOvPo [5]: .1810
	[7 1 0]	99KlBrTaKo [3]: .45, .163, .482, .614, .845; 13DoHiYuTe [9]: .310 and .1680; 11ZoShOvPo [5]: .3065
	[7 0 0]	99KlBrTaKo [3]: .49, .110, .563, .847; 01CoTaKlBr [12]: .804

[a] The tags given here for the sources correspond to those employed in Ref. [1]. Since we could not decide whether for $2\nu_4^0$ the s, the a, or both of the energy levels are likely to be incorrect, we deleted the full set indicated in this table.

[1] A. R. Al Derzi, T. Furtenbacher, J. Tennyson, S. N. Yurchenko, A. G. Császár, MARVEL analysis of the measured high-resolution spectra of $^{14}NH_3$, J. Quant. Spectrosc. Rad. Transfer 116 (2015) 117–130.

[2] P. R. Bunker, P. Jensen, Molecular Symmetry and Spectroscopy, NRC Research, 1998.

[3] I. Kleiner, L. R. Brown, G. Tarrago, Q.-L. Kou, N. Picqué, G. Guelachvili, V. Dana, J.-Y. Mandin, Positions and intensities in the $2\nu_4/\nu_1/\nu_3$ vibrational system of $^{14}NH_3$ near 3 μm, J. Mol. Spectrosc. 193 (1999) 46–71.

[4] Š. Urban, P. Misra, K. Narahari Rao, The $\nu_1 + \nu_2$ and $\nu_1 + \nu_2 - \nu_2$ bands of $^{14}NH_3$ and $^{15}NH_3$, J. Mol. Spectrosc. 114 (1985) 377–394.

[5] N. F. Zobov, S. V. Shirin, R. I. Ovsyannikov, O. L. Polyansky, S. N. Yurchenko, R. J. Barber, J. Tennyson, R. J. Hargreaves, P. F. Bernath, Analysis of high temperature ammonia spectra from 780 to 2100 cm^{-1}, J. Mol. Spectrosc. 269 (2011) 104–108.

[6] Š. Urban, R. D'Cunha, K. Narahari Rao, D. Papoušek, The $\Delta k = \pm 2$ "forbidden band" and inversion-rotation energy levels of ammonia, Can. J. Phys. 62 (1984) 1775–1791.

[7] C. Cottaz, I. Kleiner, G. Tarrago, L. R. Brown, J. S. Margolis, R. L. Poynter, H. M. Pickett, T. Fouchet, P. Drossart, E. Lellouch, Line positions and intensities in the $2\nu_2/\nu_4$ vibrational system of $^{14}NH_3$ near 57 μm, J. Mol. Spectrosc. 203 (2000) 285–309.

[8] H. Sasada, Y. Endo, E. Hirota, R. L. Poynter, J. S. Margolis, Microwave and Fourier-transform infrared spectroscopy of the $v_4 = 1$ and $v_2 = 2$ states of NH_3, J. Mol. Spectrosc. 151 (1992) 33–53.

[9] M. J. Down, C. Hill, S. N. Yurchenko, J. Tennyson, L. R. Brown, I. Kleiner, Re-analysis of ammonia spectra: Updating the HITRAN $^{14}NH_3$ database, J. Quant. Spectrosc. Radiat. Transfer 130 (2013) 260–272.

[10] L. Lundsberg-Nielsen, F. Hegelund, F. M. Nicolaisen, Analysis of the high-resolution spectrum of ammonia ($^{14}NH_3$) in the near-infrared region, 6400–6900 cm^{-1}, J. Mol. Spectrosc. 162 (1993) 230–245.

[11] Š. Urban, N. Tu, K. Narahari Rao, G. Guelachvili, Analysis of high-resolution Fourier transform spectra of $^{14}NH_3$ at 2.3 μm, J. Mol. Spectrosc. 133 (1989) 312–330.

[12] C. Cottaz, G. Tarrago, I. Kleiner, L. R. Brown, Assignments and intensities of $^{14}NH_3$ hot bands in the 5- to 8-μm ($3\nu_2 - \nu_2$, $\nu_2 + \nu_4 - \nu_2$) and 4-μm ($4\nu_2 - \nu_2$, $\nu_1 - \nu_2$, $\nu_3 - \nu_2$ and $2\nu_4 - \nu_2$) regions, J. Mol. Spectrosc. 209 (2001) 30–49.

[13] G. Guelachvili, A. H. Abdullah, N. Tu, K. Narahari Rao, Š. Urban, D. Papoušek, Analysis of high-resolution Fourier-transform spectra of $^{14}NH_3$ at 3.0 μm, J. Mol. Spectrosc. 133 (1989) 345–364.