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Accurate prediction of the ammonia probes of a variable proton-to-electron mass ratio

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ABSTRACT

A comprehensive study of the mass sensitivity of the vibration–rotation–inversion transitions of ^{14}NH$_3$, ^{15}NH$_3$, ^{14}ND$_3$ and ^{15}ND$_3$ is carried out variationally using the TROVE approach. Variational calculations are robust and accurate, offering a new way to compute sensitivity coefficients. Particular attention is paid to the $\Delta k = \pm 3$ transitions between the accidentally coinciding rotation–inversion energy levels of the $\nu_2 = 0^+, 0^-, 1^+$ and 1^- states, and the inversion transitions in the $\nu_4 = 1$ state affected by the 'giant' l-type doubling effect. These transitions exhibit highly anomalous sensitivities, thus appearing as promising probes of a possible cosmological variation of the proton-to-electron mass ratio μ. Moreover, a simultaneous comparison of the calculated sensitivities reveals a sizeable isotopic dependence which could aid an exclusive ammonia detection.

Key words: molecular data – cosmological parameters – infrared: ISM – submillimetre: ISM.

1 INTRODUCTION

Molecular spectroscopy is a well-established discipline and the increasing precision of measurements has provided the capacity to test fundamental physics. Recently, a set of several 'forbidden' $\Delta k = \pm 3$ transitions between the rotation–inversion energy levels of ^{14}NH$_3$ in the ν_2 vibrational state were proposed as a promising tool to probe a possible space–time variation of the proton-to-electron mass ratio $\mu = m_p/m_e$ (Jansen, Bethlem & Ubachs 2014; Špirko 2014). The anomalous mass dependence of these transitions arises from accidental near-degeneracies of the involved energy levels. The sensitivity coefficient $T_{u,l}$, defined as

$$T_{u,l} = \frac{\mu}{E_u - E_l}\left(\frac{dE_u}{d\mu} - \frac{dE_l}{d\mu}\right), \qquad (1)$$

where E_u and E_l refer to the energy of the upper and lower state, respectively, allows one to quantify the effect that a possible variation of μ would have for a given transition. The larger the magnitude of $T_{u,l}$, the more favourable a transition is to test for a drifting μ.

The so-called ammonia method (Flambaum & Kozlov 2007), which was adapted from van Veldhoven et al. (2004), relies on the inversion transitions in the vibrational ground state of ^{14}NH$_3$. Constraints on a temporal variation of μ have been determined using this method from measurements of the object B0218+357 at redshift $z \sim 0.685$ (Flambaum & Kozlov 2007; Murphy et al. 2008; Kanekar 2011), and of the system PKS1830−211 at $z \sim 0.886$ (Henkel et al. 2009). A major source of systematic error when using the ammonia method is the comparison with rotational lines from other molecular species, particularly molecules that are non-nitrogen-bearing (see Murphy et al. 2008; Henkel et al. 2009; Kanekar 2011, for a more complete discussion). The most stringent limit using ammonia (Kanekar 2011) has since been improved upon with methanol absorption spectra observed in the lensing galaxy PKS1830−211 (Bagdonaite et al. 2013). Three different radio telescopes were used to measure 10 absorption lines with sensitivity coefficients ranging from $T = -1.0$ to -32.8.

Here we present a comprehensive study of the mass sensitivity of the vibration–rotation–inversion transitions of ^{14}NH$_3$, ^{15}NH$_3$, ^{14}ND$_3$ and ^{15}ND$_3$. A joint comparison of all relevant isotopic transitions could open the door to an all-ammonia detection, and potentially eliminate certain systematic errors that arise from using alternative reference molecules. We also note that the transitions of the ^{15}N isotopes are optically thin and free of the nuclear quadrupole structures, providing a simpler radiative and line-shape analysis. A rigorous evaluation of the sensitivity coefficients will hopefully offer new scope for the ammonia method, and guide future

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measurements that could be carried out for example at the Atacama Large Millimeter/submillimeter Array (ALMA).

2 METHODS

2.1 Background

The induced frequency shift of a probed transition is given as

$$\frac{\Delta\nu}{\nu_0} = T_{\mathrm{u},1}\frac{\Delta\mu}{\mu_0}, \qquad (2)$$

where $\Delta\nu = \nu_{\mathrm{obs}} - \nu_0$ is the change in the frequency and $\Delta\mu = \mu_{\mathrm{obs}} - \mu_0$ is the change in μ, both with respect to their accepted values ν_0 and μ_0. Using this relation one can easily show that the rotation–inversion transitions associated with the ν_2 vibrational state of ammonia may exhibit induced frequency shifts more than one order of magnitude larger than the pure inversion transitions in the vibrational ground state, which are currently used in the probing of μ both temporally (Flambaum & Kozlov 2007; Menten et al. 2008; Murphy et al. 2008; Henkel et al. 2009; Kanekar 2011) and spatially

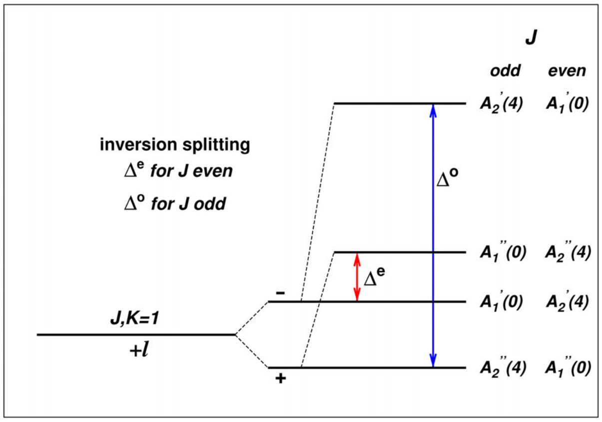

Figure 1. 'Reversal' of the inversion doublets in the $+l$ component of the ν_4 level by the 'giant' l-type doubling effect. Values in parentheses are the spin statistical weights.

Table 1. The rotation–inversion frequencies (ν), Einstein coefficients (A) and sensitivities (T) of ^{14}NH$_3$ and their ^{15}NH$_3$ counterparts in the ν_2 vibrational state.

Γ'	p'	J'	K'	v_2'	Γ''	p''	J''	K''	v_2''	ν/MHz	A/s^{-1}	T
						^{14}NH$_3$						
E''	s	2	1	1	E'	a	1	1	1	140 142^a	0.1474×10^{-4}	17.24(16.92^b)
A_2''	a	0	0	1	A_2'	s	1	0	1	466 244^c	0.1824×10^{-2}	−6.587(−6.409)
						^{15}NH$_3$						
E''	s	2	1	1	E'	a	1	1	1	175 053	0.2939×10^{-4}	13.33(13.28)
A_2''	a	0	0	1	A_2'	s	1	0	1	430 038	0.1425×10^{-2}	−6.894(−6.908)

Notes. ^{14}NH$_3$ – Einstein coefficients from Yurchenko et al. (2011b); ^{a}Astronomical observation from Mauersberger et al. (1988) and Schilke et al. (1990); ^{b}JBU sensitivity coefficient reaches a value of 18.8 (see Jansen et al. 2014); ^{c}Astronomical observation from Schilke et al. (1992); values in parentheses from Špirko (2014), obtained using the non-rigid inverter theory.
^{15}NH$_3$ – frequencies and Einstein coefficients from Urban et al. (1985) and Yurchenko (2015), respectively; values in parentheses obtained using the non-rigid inverter theory with the frequencies from Urban et al. (1985).

Table 2. The wavenumbers (ν), wavelengths (λ), Einstein coefficients (A) and sensitivities (T) for transitions between the ground and ν_2 vibrational state of ^{14}NH$_3$ and their ^{15}NH$_3$ counterparts.

Γ'	p'	J'	K'	v_2'	Γ''	p''	J''	K''	v_2''	ν/cm^{-1}	λ/μm	A/s^{-1}	T
							^{14}NH$_3$						
A_2'	s	6	6	1	A_2''	a	6	6	0	927.3230	10.7837	$0.1316 \times 10^{+2}$	−0.367(−0.356)
E'	s	2	2	1	E''	a	2	2	0	931.3333	10.7373	$0.1030 \times 10^{+2}$	−0.371(−0.366)
E''	s	2	1	1	E'	a	1	1	0	971.8821	10.2893	$0.5238 \times 10^{+1}$	−0.399(−0.394)
E''	s	1	1	1	E'	a	2	1	0	891.8820	11.2122	$0.6795 \times 10^{+1}$	−0.344(−0.339)
A_2'	s	1	0	1	A_2''	a	2	0	0	892.1567	11.2088	$0.9054 \times 10^{+1}$	−0.344(−0.339)
A_2''	s	3	3	1	A_2'	a	3	3	0	930.7571	10.7439	$0.1158 \times 10^{+2}$	−0.370(−0.366)
							^{15}NH$_3$						
A_2'	s	6	6	1	A_2''	a	6	6	0	923.4541	10.8289	$0.1290 \times 10^{+2}$	−0.365(−0.365)
E'	s	2	2	1	E''	a	2	2	0	927.4034	10.7828	$0.1010 \times 10^{+2}$	−0.373(−0.373)
E''	s	2	1	1	E'	a	1	1	0	967.8597	10.3321	$0.5133 \times 10^{+1}$	−0.400(−0.400)
E''	s	1	1	1	E'	a	2	1	0	888.0413	11.2607	$0.6664 \times 10^{+1}$	−0.345(−0.345)
A_2'	s	1	0	1	A_2''	a	2	0	0	888.3174	11.2572	$0.8878 \times 10^{+1}$	−0.346(−0.346)
A_2''	s	3	3	1	A_2'	a	3	3	0	926.8378	10.7894	$0.1135 \times 10^{+2}$	−0.372(−0.372)

Notes. ^{14}NH$_3$ – wavenumbers and Einstein coefficients from Urban et al. (1984a) and Yurchenko et al. (2011b), respectively; astronomical observations reported in Betz, McLaren & Spears (1979) and Evans, Lacy & Carr (1991); values in parentheses from Špirko (2014), obtained using the non-rigid inverter theory.
^{15}NH$_3$ – wavenumbers provided by Fusina, Di Lonardo & Predoi-Cross (in preparation), Einstein coefficients from Yurchenko (2015); values in parentheses obtained using the non-rigid inverter theory with the frequencies from Fusina, Di Lonardo & Predoi-Cross (in preparation).

(Molaro, Levshakov & Kozlov 2009; Levshakov et al. 2010a,b, 2013). Various ^{14}NH$_3$ ro-inversional transitions have already been observed extraterrestrially (Mauersberger, Henkel & Wilson 1988; Schilke et al. 1990, 1992), whilst others with notable sensitivities possess Einstein coefficients comparable to those of the observed transitions. It is legitimate then to expect their eventual extragalactic detection, and when combined with their enhanced sensitivity, there is scope for a major improvement of the current ammonia analyses.

Another promising anomaly exhibited by the spectra of ammonia is caused by the so-called giant l-type doubling, which leads to a 'reversal' of the inversion doublets in the $K = 1$ levels in the $+l$ component of the ν_4 states of ^{14}NH$_3$ and ^{15}NH$_3$. The inversion

Table 3. The vibration–rotation–inversion transitions associated with the $|a, J, K = 3, v_2 = 1\rangle - |s, J, K = 0, v_2 = 1\rangle$ resonances.

Γ'	p'	J'	K'	v_2'	Γ''	p''	J''	K''	v_2''	ν/MHz	A/s^{-1}	T	Obs. Ref.
								^{14}NH$_3$					
A_2'	a	3	3	1	A_2''	s	3	3	0	290 003 13.7	$0.1176 \times 10^{+2}$	−0.484(−0.484)	^{b}
A_2'	s	3	0	1	A_2''	s	3	3	0	289 974 30.0	0.2025×10^{0}	−0.405(−0.405)	^{b}
	a	3	3	1		s	3	0	1	2883.7		−790.6(−1001^{a})	^{b}
A_2'	a	3	3	1	A_2''	a	2	0	1	772 594.9	0.6018×10^{-4}	−0.868(−0.868)	^{c}
A_2'	s	3	0	1	A_2''	a	2	0	1	769 710.2	0.3471×10^{-2}	2.090(2.089)	^{c}
	a	3	3	1		s	3	0	1	2884.7		−790.3(−1001)	^{c}
A_2'	a	3	3	1	A_2''	s	3	3	1	1073 050.7	0.1634×10^{-1}	−3.350(−3.353)	^{c}
A_2'	s	3	0	1	A_2''	s	3	3	1	1070 166.6	0.2765×10^{-3}	−1.228(−1.229)	^{c}
	a	3	3	1		s	3	0	1	2884.1		−790.5(−1001)	^{c}
A_2'	a	5	3	1	A_2''	s	5	3	0	28 971 3 40.5	$0.4692 \times 10^{+1}$	−0.484(−0.484)	^{d}
A_2'	s	5	0	1	A_2''	s	5	3	0	29 050 552.5	0.2147×10^{-2}	−0.408(−0.408)	^{d}
	a	5	3	1		s	5	0	1	792 12.0		27.38(27.35)	^{d}
A_2'	a	5	3	1	A_2''	s	5	3	1	979 649.1	0.5141×10^{-2}	−3.425(−3.427)	^{d}
A_2'	s	5	0	1	A_2''	s	5	3	1	1058 861.1	0.3714×10^{-5}	−1.120(−1.120)	^{d}
	a	5	3	1		s	5	0	1	792 12.0		27.38(27.35)	^{d}
A_2'	a	5	3	1	A_2''	a	4	0	1	1956 241.1	0.4129×10^{-4}	−0.988(−0.988)	^{d}
A_2'	s	5	0	1	A_2''	a	4	0	1	2035 453.1	0.7023×10^{-1}	0.116(0.116)	^{d}
	a	5	3	1		s	5	0	1	79 212.0		27.38(29.35)	^{d}
A_2'	a	7	3	1	A_2''	s	7	3	0	28 934 0 99.5	$0.2399 \times 10^{+1}$	−0.480(−0.480)	^{d}
A_2'	s	7	0	1	A_2''	s	7	3	0	29 118 808.5	0.1095×10^{-3}	−0.416(−0.416)	^{d}
	a	7	3	1		s	7	0	1	184 709.0		9.561(9.582)	^{d}
A_2'	a	9	3	1	A_2''	s	9	3	0	28 892 0 89.9	$0.1444 \times 10^{+1}$	−0.475(−0.475)	^{d}
A_2'	s	9	0	1	A_2''	s	9	3	0	29 194 454.6	0.1029×10^{-3}	−0.425(−0.425)	^{d}
	a	9	3	1		s	9	0	1	302 364.7		4.350(4.363)	^{d}
								^{15}NH$_3$					
A_2'	a	3	3	1	A_2''	s	3	3	0	28 843 885.0	$0.1171 \times 10^{+2}$	−0.486(−0.486)	^{e}
A_2'	s	3	0	1	A_2''	s	3	3	0	28 872 669.9	0.2187×10^{-2}	−0.403(−0.403)	^{e}
	a	3	3	1		s	3	0	1	287 84.9		82.96(81.69)	^{e}
A_2'	a	3	3	1	A_2''	a	2	0	1	774 222.8	0.7160×10^{-6}	−0.999(−0.999)	^{f}
A_2'	s	3	0	1	A_2''	a	2	0	1	802 986.7	0.4035×10^{-2}	2.011(2.010)	^{f}
	a	3	3	1		s	3	0	1	28 763.9		83.02(81.69)	^{f}
A_2'	a	3	3	1	A_2''	s	3	3	1	1035 207.4	0.1491×10^{-1}	−3.473(−3.476)	^{f}
A_2'	s	3	0	1	A_2''	s	3	3	1	1063 971.3	0.3245×10^{-5}	−1.228(−1.135)	^{f}
	a	3	3	1		s	3	0	1	28 763.9		83.02(81.69)	^{f}
A_2'	a	5	3	1	A_2''	s	5	3	0	28 817 906.5	$0.4598 \times 10^{+1}$	−0.483(−0.483)	^{e}
A_2'	s	5	0	1	A_2''	s	5	3	0	28 927 141.3	0.7768×10^{-3}	−0.409(−0.409)	^{e}
	a	5	3	1		s	5	0	1	109 234.8		19.02(19.02)	^{e}
A_2'	a	5	3	1	A_2''	s	5	3	1	943 226.9	0.4588×10^{-2}	−3.453(−3.455)	^{f}
A_2'	s	5	0	1	A_2''	s	5	3	1	1052 459.7	0.1548×10^{-5}	−1.120(−1.121)	^{f}
	a	5	3	1		s	5	0	1	109 232.8		19.04(19.02)	^{f}
A_2'	a	5	3	1	A_2''	a	4	0	1	1955 711.7	0.1882×10^{-4}	−0.988(−0.988)	^{f}
A_2'	s	5	0	1	A_2''	a	4	0	1	2064 944.5	0.7369×10^{-1}	0.071(0.071)	^{f}
	a	5	3	1		s	5	0	1	109 232.8		19.05(19.02)	^{f}
A_2'	a	7	3	1	A_2''	s	7	3	0	28 784 706.6	$0.2399 \times 10^{+1}$	−0.479(−0.479)	^{e}
A_2'	s	7	0	1	A_2''	s	7	3	0	28 997 286.1	0.1095×10^{-3}	−0.418(−0.418)	^{e}
	a	7	3	1		s	7	0	1	212 579.5		7.898(7.073)	^{e}
A_2'	a	9	3	1	A_2''	s	9	3	0	28 747 714.9	$0.1444 \times 10^{+1}$	−0.479(−0.475)	^{e}
A_2'	s	9	0	1	A_2''	s	9	3	0	29 075 088.5	0.1029×10^{-3}	−0.418(−0.427)	^{e}
	a	9	3	1		s	9	0	1	327 373.6		3.782(3.782)	^{e}

Notes. ^{14}NH$_3$ – Einstein coefficients from Yurchenko et al. (2011b); ^{a}JBU sensitivity coefficient reaches a value of −938 (see Jansen et al. 2014); values in parentheses obtained using the non-rigid inverter theory with the calculated TROVE frequencies; ^{b}Fichoux et al. (1998); ^{c}Belov et al. (1980); ^{d}Urban et al. (1984a).

^{15}NH$_3$ – Einstein coefficients from Yurchenko (2015); values in parentheses obtained using the non-rigid inverter theory with the calculated TROVE frequencies; ^{e}Fusina, Di Lonardo & Predoi-Cross (in preparation); ^{f}Urban et al. (1985).

doublets are reversed because for $K = 1$, only one of the A_1 or A_2 sublevels is shifted by the Coriolis interactions, and only the A_2 states have non-zero spin statistical weights (see Fig. 1 and Špirko, Stone & Papoušek 1976). So far these transitions have not been detected extraterrestrially. This is to be expected since the physical temperatures prevailing in the interstellar medium are too low to provide significant population of the aforementioned states. However, they could be effectively populated by exoergic chemical formation processes, resulting in the detection of highly excited states (Mills & Morris 2013; Lis et al. 2014). Interestingly, the 'highest energy' $(J, K) = (18, 18)$ line of ^{14}NH$_3$ observed towards the galactic centre star-forming region Sgr B2 corresponds to the state lying 3130 K above the ground vibrational state (Wilson, Henkel & Huettemeister 2006).

The most common approach to computing sensitivity coefficients for a molecular system makes use of an effective Hamiltonian model, and determining how the parameters of this model depend on μ (Jansen et al. 2011a,b; Kozlov, Porsev & Reimers 2011; Levshakov, Kozlov & Reimers 2011; Ilyushin et al. 2012; Ilyushin 2014; Viatkina & Kozlov 2014). For ammonia, the semiclassical Wentzel–Kramers–Brillouin (WKB) approximation has been used to obtain a general relationship to estimate the sensitivity of pure inversion frequencies in the ground vibrational state for ^{14}NH$_3$ (Flambaum & Kozlov 2007), ^{15}NH$_3$ (Bethlem et al. 2008), ^{14}ND$_3$ (Flambaum & Kozlov 2007) and ^{15}ND$_3$ (van Veldhoven et al. 2004), whilst rotation–inversion transitions have been considered for the partly deuterated species ^{14}NH$_2$D and ^{14}ND$_2$H by Kozlov, Lapinov & Levshakov (2010).

The vibration–rotation–inversion transitions of ^{14}NH$_3$ were investigated by Špirko (2014), but theoretical calculations of the sensitivities using perturbation theory may not be entirely robust since the nominator and denominator in equation (1) contain differences of large numbers. We thus find it worthwhile not only to check the literature data for ^{14}NH$_3$ by means of highly accurate

Table 4. Inversion frequencies (ν), Einstein coefficients (A), and sensitivities (T) of ^{14}NH$_3$ and their ^{15}NH$_3$ counterparts in the ground vibrational state.

J	K	ν/MHz	A/s^{-1}	T	J	K	ν/MHz	A/s^{-1}	T
				^{14}NH$_3$					
1	1	23 694.3	0.1657×10^{-6}	−4.310(−4.365)	4	3	22 688.3	0.1311×10^{-6}	−4.289(−4.514)
2	1	23 098.8	0.5123×10^{-7}	−4.297(−4.413)	4	4	24 139.4	0.2797×10^{-6}	−4.317(−4.471)
2	2	23 722.5	0.2216×10^{-6}	−4.311(−4.385)	5	1	19 838.3	0.6540×10^{-8}	−4.220(−4.700)
3	2	22 834.2	0.9902×10^{-7}	−4.288(−4.464)	5	2	20 371.5	0.2828×10^{-7}	−4.231(−4.546)
3	3	23 870.1	0.2538×10^{-6}	−4.312(−4.419)	5	3	21 285.3	0.7239×10^{-7}	−4.257(−4.634)
4	1	21 134.3	0.1182×10^{-7}	−4.249(−4.568)	5	4	22 653.0	0.1546×10^{-6}	−4.282(−4.592)
4	2	21 703.4	0.5114×10^{-7}	−4.262(−4.545)	5	5	24 533.0	0.3053×10^{-6}	−4.327(−4.509)
				^{15}NH$_3$					
1	1	22 624.9	0.1464×10^{-6}	−4.352(−4.333)	4	3	21 637.9	0.1149×10^{-6}	−4.330(−4.309)
2	1	22 044.2	0.4521×10^{-7}	−4.341(−4.321)	4	4	23 046.0	0.2469×10^{-6}	−4.360(−4.341)
2	2	226 349.8	0.1958×10^{-6}	−4.349(−4.330)	5	1	18 871.5	0.5729×10^{-8}	−4.264(−4.239)
3	2	21 783.9	0.8730×10^{-7}	−4.333(−4.312)	5	2	19 387.4	0.2480×10^{-7}	−4.278(−4.254)
3	3	22 789.4	0.2241×10^{-6}	−4.356(−4.337)	5	3	20 272.1	0.6358×10^{-7}	−4.299(−4.276)
4	1	20 131.4	0.1039×10^{-7}	−4.293(−4.270)	5	4	21 597.9	0.1360×10^{-6}	−4.330(−4.309)
4	2	20 682.8	0.4498×10^{-7}	−4.306(−4.284)	5	5	23 422.0	0.2695×10^{-6}	−4.366(−4.347)

Notes. ^{14}NH$_3$ – frequencies and Einstein coefficients from Lovas et al. (2009) and Yurchenko et al. (2011b), respectively; values in parentheses from Špirko (2014), obtained using the non-rigid inverter theory.
^{15}NH$_3$ – frequencies and Einstein coefficients from Urban et al. (1985) and Yurchenko (2015), respectively; values in parentheses obtained using the non-rigid inverter theory with the frequencies from Urban et al. (1985).

Table 5. The rotation–inversion frequencies (ν), Einstein coefficients (A) and sensitivities (T) of ^{14}NH$_3$ and their ^{15}NH$_3$ counterparts in the ground vibrational state.

Γ'	p'	J'	K'	v_2'	Γ''	p''	J''	K''	v_2''	ν/MHz	A/s^{-1}	T
							^{14}NH$_3$					
A_2'	s	1	0	0	A_2''	a	0	0	0	572 498	0.1561×10^{-2}	−0.860(−0.862)
A_2''	a	2	0	0	A_2'	s	1	0	0	1214 859	0.1791×10^{-1}	−1.060(−1.063)
E'	a	2	1	0	E''	s	1	1	0	1215 245	0.1344×10^{-1}	−1.061(−1.064)
							^{15}NH$_3$					
A_2'	s	1	0	0	A_2''	a	0	0	0	572 112	0.1557×10^{-2}	−0.865(−0.866)
A_2''	a	2	0	0	A_2'	s	1	0	0	1210 889	0.1774×10^{-1}	−1.058(−1.058)
E'	a	2	1	0	E''	s	1	1	0	1211 277	0.1331×10^{-1}	−1.059(−1.059)

Notes. ^{14}NH$_3$ – frequencies and Einstein coefficients from Persson et al. (2010) and Yurchenko et al. (2011b), respectively; values given in parentheses from Špirko (2014), obtained using the non-rigid inverter theory.
^{15}NH$_3$ – frequencies and Einstein coefficients from Urban et al. (1985) and Yurchenko (2015), respectively; values in parentheses obtained using the non-rigid inverter theory with the frequencies from Urban et al. (1985).

variational calculations, but to extend the treatment to ^{15}NH$_3$, ^{14}ND$_3$ and ^{15}ND$_3$, which are equally valid probes of μ. It is also straightforward to incorporate the so far unprobed ν_4 states into the present study.

The advantage of our variational approach is that along with sensitivity coefficients, reliable theoretical transition frequencies can be generated if no experimental data is available, and for all selected transitions, Einstein *A* coefficients can be calculated to guide future observations.

2.2 Variational calculations

The variational nuclear motion program TROVE (Yurchenko, Thiel & Jensen 2007) has provided highly accurate theoretical frequency, intensity and thermodynamic data for both ^{14}NH$_3$ and ^{15}NH$_3$ (Yurchenko et al. 2009, 2011a; Yachmenev et al. 2010; Yurchenko, Barber & Tennyson 2011b; Sousa-Silva et al. 2014; Yurchenko 2015). We use the potential energy surface and computational setup as described in Yurchenko et al. (2011b) and Yurchenko (2015), which can naturally be extended to treat ^{14}ND$_3$ and ^{15}ND$_3$. Here we only discuss the calculation of sensitivity coefficients, for the method used to compute transition frequencies and Einstein *A* coefficients we refer the reader to Yurchenko et al. (2009).

We rely on the assumption that the baryonic matter may be treated equally (Dent 2007), i.e. μ is assumed to be proportional to the molecular mass. It is then sufficient to perform a series of calculations employing suitably scaled values for the mass of ammonia. We choose the scaling coefficient $f_m = \{0.9996, 0.9998, 1.0000, 1.0002, 1.0004\}$ such that the scaled mass, $m'_{\mathrm{NH}_3} = f_m \times m_{\mathrm{NH}_3}$. The mass dependence of any energy level can be found by using finite differences for (a) the $f_m = \{0.9998, 1.0002\}$, and (b) the $f_m = \{0.9996, 1.0004\}$ calculated energies. Both (a) and (b) should yield identical results, with the latter values used to verify the former. Numerical values for the derivatives $\mathrm{d}E/\mathrm{d}\mu$ are easily determined and then used in equation (1), along with accurate experimental values for the transition frequencies, to calculate sensitivity coefficients. Calculations with $f_m = 1.0000$ provide theoretical frequency data and Einstein *A* coefficients.

The variational approach is powerful in that it allows a comprehensive treatment of a molecule to be undertaken. All possible transitions and their mass dependence can be calculated. This permits a simple exploration of the sensitivities for any molecule, provided the necessary steps have been taken to perform accurate variational calculations in the first place. As a cross-check, we also employ the non-rigid inverter theory (Špirko et al. 1976; Špirko 1983) to compute sensitivity coefficients as was done by Špirko (2014). In the following we evaluate both approaches. Note that the standard

Table 6. Inversion frequencies (ν), Einstein coefficients (*A*), and sensitivities (*T*) of ^{14}NH$_3$ and ^{15}NH$_3$ in the ν_4 vibrational state.

J	K	l	ν/MHz	A/s^{-1}	T	J	K	l	ν/MHz	A/s^{-1}	T
						^{14}NH$_3$					
1	1	−1	32 400	0.4243×10^{-6}	−4.268	4	3	1	57 132	0.1968×10^{-5}	1.561
1	1	1	57 843	0.2411×10^{-5}	−2.234	4	2	−1	47 526	0.5467×10^{-6}	−1.550
2	2	−1	32 111	0.5514×10^{-6}	−4.250	4	2	1	46 515	0.4020×10^{-6}	−0.247
2	2	1	40 189	0.1056×10^{-5}	−2.381	4	1	−1	57 681	0.2548×10^{-6}	−0.220
2	1	−1	36 797	0.2085×10^{-6}	−3.133	4	1	1	145 888[a]	0.3787×10^{-5}	−0.962
2	1	1	20 655	0.3743×10^{-7}	2.720	5	5	−1	32 037	0.6848×10^{-6}	−4.264
3	3	−1	31 893	0.6081×10^{-6}	−4.259	5	5	1	68 699	0.6198×10^{-5}	4.672
3	3	1	46 679	0.1863×10^{-5}	−0.667	5	4	−1	39 071	0.8020×10^{-6}	−2.832
3	2	−1	37 500	0.4424×10^{-6}	−2.961	5	4	1	73 534	0.4807×10^{-5}	4.480
3	2	1	44 963	0.6906×10^{-6}	−1.023	5	3	−1	48 346	0.8610×10^{-6}	−1.506
3	1	−1	44 755	0.1908×10^{-6}	−1.687	5	3	1	64 906	0.1799×10^{-5}	3.044
3	1	1	177 783[a]	0.1087×10^{-4}	−0.482	5	2	−1	58 699	0.6967×10^{-6}	−0.181
4	4	−1	31 884	0.6482×10^{-6}	−4.258	5	2	1	44 876	0.2025×10^{-6}	0.239
4	4	1	55 765	0.3325×10^{-5}	1.668	5	1	1	78 141[a]	0.4324×10^{-6}	0.990
4	3	−1	38 460	0.6451×10^{-6}	−2.855	5	1	−1	380 542[a]	0.4015×10^{-4}	−0.178
						^{15}NH$_3$					
1	1	−1	31 108	0.3758×10^{-6}	−4.291	4	3	1	51 989	0.1501×10^{-5}	0.684
1	1	1	55 582	0.2142×10^{-5}	−2.410	4	2	−1	44 599	0.4524×10^{-6}	−1.765
2	2	−1	30 825	0.4880×10^{-6}	−4.271	4	2	1	43 225	0.3278×10^{-6}	−0.728
2	2	1	37 900	0.8883×10^{-6}	−2.722	4	1	−1	53 406	0.2029×10^{-6}	−0.558
2	1	−1	34 950	0.1788×10^{-6}	−3.273	4	1	1	146 961[a]	0.3870×10^{-5}	−0.983
2	1	1	21 904	0.4450×10^{-7}	2.351	5	5	−1	30 732	0.6050×10^{-6}	−4.280
3	3	−1	30 606	0.5377×10^{-6}	−4.281	5	5	1	61 128[a]	0.4341×10^{-5}	2.771
3	3	1	43 275	0.1492×10^{-5}	−1.358	5	4	−1	37 071	0.6856×10^{-6}	−2.937
3	2	−1	35 551	0.3772×10^{-6}	−3.082	5	4	1	65 945[a]	0.3431×10^{-5}	3.150
3	2	1	41 928	0.5649×10^{-6}	−1.494	5	3	−1	45 373	0.7129×10^{-6}	−1.689
3	1	−1	41 947	0.1574×10^{-6}	−1.941	5	3	1	59 236[a]	0.1351×10^{-5}	2.151
3	1	1	171 460[a]	0.9842×10^{-5}	−0.731	5	2	−1	54 322	0.5536×10^{-6}	−0.440
4	4	−1	30 591	0.5729×10^{-6}	−4.281	5	2	1	42 037[a]	0.1659×10^{-6}	−0.242
4	4	1	50 530	0.2502×10^{-5}	0.452	5	1	−1	71 752[a]	0.3362×10^{-6}	0.639
4	3	−1	36 472	0.5506×10^{-6}	−2.978	5	1	1	369 287[a]	0.3728×10^{-4}	−0.379

Notes. Frequencies from Cohen & Poynter (1974) and Cohen (1980); [a]TROVE calculated value.

Table 7. Inversion frequencies (ν), Einstein coefficients (A), and sensitivities (T) of ^{14}ND$_3$ and ^{15}ND$_3$ in the ground vibrational state.

J	K	ν/MHz	A/s^{-1}	T	J	K	ν/MHz	A/s^{-1}	T
				^{14}ND$_3$					
1	1	1589.006	0.5764×10^{-10}	−5.541(−5.528)	4	3	1558.600	0.4897×10^{-10}	−5.533(−5.520)
2	1	1568.357	0.1849×10^{-10}	−5.556(−5.542)	4	−3	1558.178	0.4893×10^{-10}	−5.534(−5.521)
2	2	1591.695	0.7721×10^{-10}	−5.543(−5.530)	4	4	1612.997	0.9623×10^{-10}	−5.536(−5.525)
3	1	1537.915	0.8725×10^{-11}	−5.526(−5.511)	5	1	1450.435^{a}	0.2937×10^{-11}	−5.511(−5.493)
3	2	1560.774	0.3644×10^{-10}	−5.537(−5.523)	5	2	1471.785	0.1226×10^{-10}	−5.504(−5.487)
3	3	1599.645	0.8810×10^{-10}	−5.571(−5.559)	5	3	1507.525	0.2960×10^{-10}	−5.553(−5.537)
3	−3	1599.704	0.8811×10^{-10}	−5.571(−5.559)	5	−3	1509.218	0.2969×10^{-10}	−5.499(−5.484)
4	1	1498.270	0.4848×10^{-11}	−5.503(−5.487)	5	4	1561.146	0.5827×10^{-10}	−5.524(−5.511)
4	2	1520.537	0.2025×10^{-10}	−5.493(−5.478)	5	5	1631.784	0.1036×10^{-9}	−5.561(−5.551)
				^{15}ND$_3$					
1	1	1430.340	0.4227×10^{-10}	−5.600(−5.577)	4	3	1401.312	0.3578×10^{-10}	−5.600(−5.577)
2	1	1410.980	0.1354×10^{-10}	−5.613(−5.589)	4	−3	1400.878	0.3575×10^{-10}	−5.602(−5.578)
2	2	1432.641	0.5661×10^{-10}	−5.604(−5.581)	4	2	1366.027	0.1476×10^{-10}	−5.586(−5.561)
3	1	1382.510	0.5374×10^{-11}	−5.585(−5.560)	5	1	1300.841^{a}	0.2130×10^{-11}	−5.562(−5.534)
3	2	1403.684	0.2665×10^{-10}	−5.566(−5.542)	5	2	1320.460^{a}	0.8907×10^{-11}	−5.575(−5.547)
3	3	1439.719	0.5458×10^{-10}	−5.601(−5.579)	5	3	1353.451	0.2153×10^{-10}	−5.585(−5.559)
3	−3	1439.783	0.6459×10^{-10}	−5.601(−5.579)	5	−3	1355.161	0.2162×10^{-10}	−5.551(−5.526)
4	1	1345.533^{a}	0.3530×10^{-11}	−5.564(−5.538)	5	4	1403.179	0.4254×10^{-10}	−5.606(−5.583)
4	2	1366.027	0.1476×10^{-10}	−5.586(−5.561)	5	5	1468.666	0.7595×10^{-10}	−5.639(−5.619)

Notes. Unless stated otherwise, ^{14}ND$_3$ and ^{15}ND$_3$ frequencies from Fusina & Murzin (1994) and Fusina et al. (1991), respectively; values in parentheses obtained using the non-rigid inverter theory with the calculated TROVE frequencies; the $K = -3$ values refer to transitions between levels with spin statistical weight =10 (A_1', A_1'' species), the $K = 3$ values refer to transitions between levels with spin statistical weight =1 (A_2', A_2'') species); ^{a}Urban et al. (1984b).

Table 8. The rotation–inversion frequencies (ν), Einstein coefficients (A) and sensitivities (T) of ^{14}ND$_3$ and ^{15}ND$_3$ in the ground vibrational state.

Γ'	p'	J'	K'	v_2'	Γ''	p''	J''	K''	v_2''	ν/MHz	A/s^{-1}	T
							^{14}ND$_3$					
A_1''	a	1	0	0	A_1'	s	0	0	0	309 909^{a}	0.2530×10^{-3}	−1.022
A_2''	a	2	0	0	A_2'	s	1	0	0	618 075^{a}	0.2409×10^{-2}	−1.009
E'	a	2	1	0	E''	s	1	1	0	618 124^{a}	0.1807×10^{-2}	−1.009
A_2'	s	1	0	0	A_2''	a	0	0	0	306 737^{a}	0.2450×10^{-3}	−0.973
A_1'	s	2	0	0	A_1''	a	1	0	0	614 933^{a}	0.2371×10^{-2}	−0.985
E''	s	2	1	0	E'	a	1	1	0	614 968^{a}	0.1778×10^{-2}	−0.985
A_1''	a	3	0	0	A_1'	s	2	0	0	925 947	0.8681×10^{-2}	−1.005
E'	a	3	1	0	E''	s	2	1	0	926 018	0.7717×10^{-2}	−1.005
E''	a	3	2	0	E'	s	2	2	0	926 228	0.4824×10^{-2}	−1.005
A_2'	s	3	0	0	A_2''	a	2	0	0	922 857	0.8591×10^{-2}	−0.989
E''	s	3	1	0	E'	a	2	1	0	922 911	0.7637×10^{-2}	−0.989
E'	s	3	2	0	E''	a	2	2	0	923 076	0.4773×10^{-2}	−0.999
							^{15}ND$_3$					
A_1''	a	1	0	0	A_1'	s	0	0	0	308 606^{a}	0.2499×10^{-3}	−1.020
A_2''	a	2	0	0	A_2'	s	1	0	0	615 628^{a}	0.2381×10^{-2}	−1.008
E'	a	2	1	0	E''	s	1	1	0	615 677^{a}	0.1785×10^{-2}	−1.009
A_2'	s	1	0	0	A_2''	a	0	0	0	305 750^{a}	0.2427×10^{-3}	−0.975
A_1'	s	2	0	0	A_1''	a	1	0	0	612 801^{a}	0.2346×10^{-2}	−0.987
E''	s	2	1	0	E'	a	1	1	0	612 836^{a}	0.1760×10^{-2}	−0.987
A_1''	a	3	0	0	A_1'	s	2	0	0	922 356	0.8582×10^{-2}	−1.004
E'	a	3	1	0	E''	s	2	1	0	922 426	0.7628×10^{-2}	−1.004
E''	a	3	2	0	E'	s	2	2	0	922 636	0.4768×10^{-2}	−1.004
A_2'	s	3	0	0	A_2''	a	2	0	0	919 577	0.8501×10^{-2}	−0.990
E''	s	3	1	0	E'	a	2	1	0	919 632	0.7556×10^{-2}	−0.990
E'	s	3	2	0	E''	a	2	2	0	919 800	0.4723×10^{-2}	−0.990

Notes. Unless stated otherwise, frequencies from Urban et al. (1984b); ^{a}Helminger & Gordy (1969) and Helminger, De Lucia & Gordy (1971).

Herzberg convention (Herzberg 1945) is used to label the vibrational states of ammonia with the normal mode quantum numbers v_1, v_2, v_3, v_4, l_3 and l_4. The ν_2 state corresponds to the singly excited inversion mode $v_2 = 1$, whilst ν_4 is the singly excited asymmetric bending mode $v_4 = |l_4| = 1$ (see Down et al. 2013 for more details).

3 RESULTS AND DISCUSSION

The variationally calculated sensitivities for ^{14}NH$_3$ and ^{15}NH$_3$ are listed in Tables 1–5. The results are consistent with previous perturbative values (Špirko 2014) obtained using the non-rigid inverter theory approach (Špirko et al. 1976; Špirko 1983), and 'Born–Oppenheimer' estimates from Jansen et al. (2014, subsequently referred to as JBU). For transitions involving the ν_2 vibrational states shown in Tables 1–3, the agreement is near quantitative with the exception of the 'forbidden' combination difference $|a, J = 3, K = 3, v_2 = 1\rangle - |s, J = 3, K = 0, v_2 = 1\rangle$. The profoundly different sensitivities for these transitions when going from ^{14}NH$_3$ to ^{15}NH$_3$ is of particular interest. A possible variation of μ requires the measurement of at least two transitions with differing sensitivities. In the case of $|a, J = 3, K = 3, v_2 = 1\rangle - |s, J = 3, K = 0, v_2 = 1\rangle$, both isotopologues possess a large value of T. Importantly though they are of opposite sign, thus enabling a conclusive detection with regard to these particular transitions. An all-ammonia observation of a drifting μ would circumvent some of the intrinsic difficulties that appear when using other reference molecules (Murphy et al. 2008; Henkel et al. 2009; Kanekar 2011), which may not necessarily reside at the same location in space.

The inversion frequencies in the ground vibrational state, Table 4, have comparable sensitivities for both ^{14}NH$_3$ and ^{15}NH$_3$, and this

Table 9. The rotation–inversion frequencies (ν), Einstein coefficients (A) and sensitivities (T) of ^{14}ND$_3$ and ^{15}ND$_3$ in the ν_2 vibrational state.

Γ'	p'	J'	K'	v_2'	Γ''	p''	J''	K''	v_2''	ν/MHz	A/s^{-1}	T
								^{14}ND$_3$				
A_1''	a	1	0	1	A_1'	s	0	0	1	412 847	0.4983×10^{-3}	−2.030
A_2''	a	2	0	1	A_2'	s	1	0	1	718 585	0.3131×10^{-2}	−1.585
E'	a	2	1	1	E''	s	1	1	1	719 092	0.2352×10^{-2}	−1.588
A_2'	s	1	0	1	A_2''	a	0	0	1	200 763	0.5423×10^{-4}	1.119
A_1'	s	2	0	1	A_1''	a	1	0	1	508 364	0.1082×10^{-2}	−0.170
E''	s	2	1	1	E'	a	1	1	1	507 940	0.8088×10^{-3}	−0.166
A_1''	a	3	0	1	A_1'	s	2	0	1	1023 449	0.9673×10^{-2}	−1.404
E'	a	3	1	1	E''	s	2	1	1	1023 971	0.8608×10^{-2}	−1.405
E''	a	3	2	1	E'	s	2	2	1	1025 546	0.5399×10^{-2}	−1.411
A_2'	s	3	0	1	A_2''	a	2	0	1	816 294	0.4830×10^{-2}	−0.491
E''	s	3	1	1	E'	a	2	1	1	815 898	0.4286×10^{-2}	−0.488
E'	s	3	2	1	E''	a	2	2	1	814 696	0.2663×10^{-2}	−0.480
A_2''	a	4	0	1	A_2'	s	3	0	1	1327 334	0.2188×10^{-1}	−1.304
E'	a	4	1	1	E''	s	3	1	1	1327 865	0.2053×10^{-1}	−1.305
E''	a	4	2	1	E'	s	3	2	1	1329 473	0.1647×10^{-1}	−1.309
A_2'	a	4	3	1	A_2''	s	3	3	1	1332 194	0.9646×10^{-2}	−1.317
A_1'	a	4	-3	1	A_1''	s	3	-3	1	1332 194	0.9646×10^{-2}	−1.317
A_1'	s	4	0	1	A_1''	a	3	0	1	1124 392	0.1315×10^{-1}	−0.637
E''	s	4	1	1	E'	a	3	1	1	1124 025	0.1231×10^{-1}	−0.636
E'	s	4	2	1	E''	a	3	2	1	1122 914	0.9805×10^{-2}	−0.630
A_2''	s	4	3	1	A_2'	a	3	3	1	1121 023	0.5679×10^{-2}	−0.621
A_1''	s	4	-3	1	A_1'	a	3	-3	1	1121 023	0.5679×10^{-2}	−0.621
A_1''	a	5	0	1	A_1'	s	4	0	1	1630 141	0.4149×10^{-1}	−1.239
E'	a	5	1	1	E''	s	4	1	1	1630 681	0.3986×10^{-1}	−1.240
E''	a	5	2	1	E'	s	4	2	1	1632 314	0.3494×10^{-1}	−1.243
A_2'	a	5	3	1	A_2''	s	4	3	1	1635 074	0.2671×10^{-1}	−1.249
A_1'	a	5	-3	1	A_1''	s	4	-3	1	1635 075	0.2671×10^{-1}	−1.249
E''	a	5	4	1	E'	s	4	4	1	1639 027	0.1509×10^{-1}	−1.258
A_2'	s	5	0	1	A_2''	a	4	0	1	1432 485	0.2790×10^{-1}	−0.722
E''	s	5	1	1	E'	a	4	1	1	1432 151	0.2676×10^{-1}	−0.721
E'	s	5	2	1	E''	a	4	2	1	1431 137	0.2333×10^{-1}	−0.717
A_2''	s	5	3	1	A_2'	a	4	3	1	1429 410	0.1768×10^{-1}	−0.710
A_1''	s	5	-3	1	A_1'	a	4	-3	1	1429 409	0.1768×10^{-1}	−0.710
E'	s	5	4	1	E''	a	4	4	1	1426 908	0.9864×10^{-2}	−0.700
								^{15}ND$_3$				
A_1''	a	1	0	1	A_1'	s	0	0	1	402 779	0.4636×10^{-3}	−1.979
A_2''	a	2	0	1	A_2'	s	1	0	1	707 552	0.2995×10^{-2}	−1.551
E'	a	2	1	1	E''	s	1	1	1	708 033	0.2250×10^{-2}	−1.554
A_2'	s	1	0	1	A_2''	a	0	0	1	208 813	0.6139×10^{-4}	0.891
A_1'	s	2	0	1	A_1''	a	1	0	1	515 358	0.1131×10^{-2}	−0.241
E''	s	2	1	1	E'	a	1	1	1	514 961	0.8458×10^{-3}	−0.237

Notes. Frequencies from Urban et al. (1984b).

also holds true for the ro-inversional transitions shown in Table 5, demonstrating the validity of ^{15}NH$_3$ as a probe of μ. The sensitivity coefficients of the ν_4 transitions shown in Table 6, although promising, do not acquire the impressive magnitudes of their ν_2 counterparts. However, the appearance of positive and negative values could be of real use in constraining μ.

Because of the substantial differences in size of the inversion splittings, the mass sensitivity of the ^{14}ND$_3$ and ^{15}ND$_3$ transitions exhibit centrifugal distortion and Coriolis interaction dependence significantly different from that exhibited by ^{14}NH$_3$ and ^{15}NH$_3$ (see Tables 7–10 and Fig. 2). The effects of these interactions are non-negligible and must be included in any critical analysis. As only a small fraction of the total presence of ammonia in the interstellar medium is heavy ammonia, a detection of ‘higher energy’ transitions is rather improbable. All the ammonia isotopomers appear as suitable targets for terrestrial studies however, such as those reported by van Veldhoven et al. (2004), Bethlem et al. (2008) and Quintero-Perez et al. (2014).

It is expected that any variation in the fundamental constants will be confirmed, or refuted, over a series of independent measurements on a variety of molecular absorbers. As a relevant astrophysical molecule, and with certain inversion transitions already detected extraterrestrially (Mauersberger, Wilson & Henkel 1986; Johnston et al. 1989; Schilke, Walmsley & Mauersberger 1991), ^{15}NH$_3$ has potential to aid this search along with the already established probes of ^{14}NH$_3$. For the deuterated species ^{14}ND$_3$ and ^{15}ND$_3$, it is perhaps more likely that their use will be restricted to precision measurements in the laboratory, despite possessing larger sensitivity coefficients for the pure inversion frequencies in the ground vibrational state.

4 CONCLUSION

A comprehensive study of the vibration–rotation–inversion transitions of all stable, symmetric top isotopomers of ammonia has been performed. The variational method offers a new and robust approach to computing sensitivity coefficients. The calculated mass sensitivities provide perspectives for the further development of the ammonia method, used in the probing of the cosmological variability of the proton-to-electron mass ratio. Most notably the reliance

Table 10. The wavenumbers (ν), wavelengths (λ), Einstein coefficients (A) and sensitivities (T) for transitions between the ground and ν_2 vibrational state of ^{14}ND$_3$ and ^{15}ND$_3$.

Γ'	p'	J'	K'	v_2'	Γ''	p''	J''	K''	v_2''	ν/cm^{-1}	λ/μm	A/s^{-1}	T
							^{14}ND$_3$						
A_1''	a	1	0	1	A_1'	s	0	0	0	759.3704	13.1688	$0.1955 \times 10^{+1}$	−0.475
A_2''	a	2	0	1	A_2'	s	1	0	0	769.5283	12.9950	$0.2444 \times 10^{+1}$	−0.482
E'	a	2	1	1	E''	s	1	1	0	769.5306	12.9949	$0.1834 \times 10^{+1}$	−0.482
A_2'	s	1	0	1	A_2''	a	0	0	0	755.7906	13.2312	$0.1948 \times 10^{+1}$	−0.454
A_1'	s	2	0	1	A_1''	a	1	0	0	765.9901	13.0550	$0.2434 \times 10^{+1}$	−0.461
E''	s	2	1	1	E'	a	1	1	0	765.9767	13.0552	$0.1827 \times 10^{+1}$	−0.461
E'	a	1	1	1	E''	s	1	1	0	749.0866	13.3496	$0.2810 \times 10^{+1}$	−0.468
E'	a	2	1	1	E''	s	2	1	0	748.9645	13.3518	0.9344×10^{0}	−0.468
E''	a	2	2	1	E'	s	2	2	0	748.9671	13.3517	$0.3744 \times 10^{+1}$	−0.468
E''	s	1	1	1	E'	a	1	1	0	745.4912	13.4140	$0.2798 \times 10^{+1}$	−0.446
E''	s	2	1	1	E'	a	2	1	0	745.4112	13.4154	0.9305×10^{0}	−0.446
E'	s	2	2	1	E''	a	2	2	0	745.3664	13.4162	$0.3729 \times 10^{+1}$	−0.446
A_2''	a	0	0	1	A_2'	s	1	0	0	738.8622	13.5343	$0.5381 \times 10^{+1}$	−0.461
A_1''	a	1	0	1	A_1'	s	2	0	0	728.5209	13.7264	$0.3427 \times 10^{+1}$	−0.453
E'	a	1	1	1	E''	s	2	1	0	728.5205	13.7264	$0.2572 \times 10^{+1}$	−0.453
A_1'	s	0	0	1	A_1''	a	1	0	0	735.2618	13.6006	$0.5358 \times 10^{+1}$	−0.439
A_2'	s	1	0	1	A_2''	a	2	0	0	724.9421	13.7942	$0.3412 \times 10^{+1}$	−0.431
E''	s	1	1	1	E'	a	2	1	0	724.9258	13.7945	$0.2560 \times 10^{+1}$	−0.431
							^{15}ND$_3$						
A_1''	a	1	0	1	A_1'	s	0	0	0	752.9702	13.2807	$0.1888 \times 10^{+1}$	−0.475
A_2''	a	2	0	1	A_2'	s	1	0	0	763.1000	13.1044	$0.2359 \times 10^{+1}$	−0.482
E'	a	2	1	1	E''	s	1	1	0	763.0998	13.1044	$0.1770 \times 10^{+1}$	−0.482
A_2'	s	1	0	1	A_2''	a	0	0	0	749.6973	13.3387	$0.1881 \times 10^{+1}$	−0.455
A_1'	s	2	0	1	A_1''	a	1	0	0	759.8667	13.1602	$0.2351 \times 10^{+1}$	−0.463
E''	s	2	1	1	E'	a	1	1	0	759.8517	13.1605	$0.1764 \times 10^{+1}$	−0.462
E'	a	1	1	1	E''	s	1	1	0	742.7222	13.4640	$0.2713 \times 10^{+1}$	−0.468
E'	a	2	1	1	E''	s	2	1	0	742.6101	13.4660	0.9023×10^{0}	−0.468
E''	a	2	2	1	E'	s	2	2	0	742.6053	13.4661	$0.3616 \times 10^{+1}$	−0.468
E''	s	1	1	1	E'	a	1	1	0	739.4346	13.5238	$0.2702 \times 10^{+1}$	−0.448
E''	s	2	1	1	E'	a	2	1	0	739.3626	13.5252	0.8988×10^{0}	−0.448
E'	s	2	2	1	E''	a	2	2	0	739.3131	13.5261	$0.3602 \times 10^{+1}$	−0.447
A_2''	a	0	0	1	A_2'	s	1	0	0	732.5333	13.6513	$0.5197 \times 10^{+1}$	−0.461
A_1''	a	1	0	1	A_1'	s	2	0	0	722.2354	13.8459	$0.3311 \times 10^{+1}$	−0.452
E'	a	1	1	1	E''	s	2	1	0	722.2324	13.8460	$0.2484 \times 10^{+1}$	−0.453
A_1'	s	0	0	1	A_1''	a	1	0	0	729.2409	13.7129	$0.5176 \times 10^{+1}$	−0.440
A_2'	s	1	0	1	A_2''	a	2	0	0	718.9634	13.9089	$0.3296 \times 10^{+1}$	−0.432
E''	s	1	1	1	E'	a	2	1	0	718.9456	13.9093	$0.2474 \times 10^{+1}$	−0.432

Notes. Wavenumbers from Urban et al. (1984b).

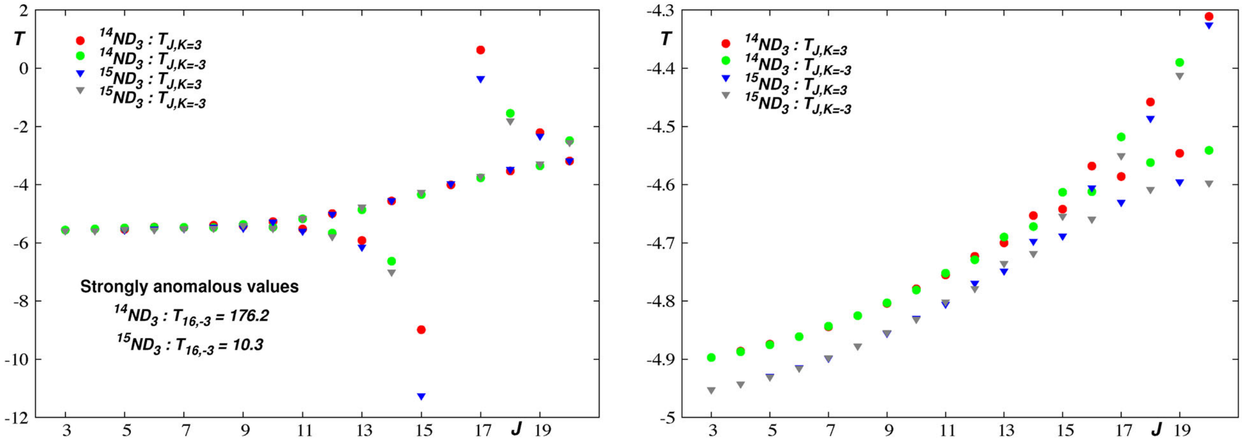

Figure 2. The sensitivities, T, of the inversion transitions of the (J, $K = \pm3$) rotational states of $^{14}ND_3$ and $^{15}ND_3$ in the ground (left-hand panel) and ν_2 (right-hand panel) vibrational states.

on other reference molecular species, which is the main source of systematic error, can be avoided. Although ammonia is not a primordial molecule and cannot be studied at extremal redshifts such as H_2^+, D_2^+ and He_2^+ for instance (Augustovičová et al. 2014), it can be detected in a wide variety of regions (Ho & Townes 1983), and at redshifts which dramatically enhance spectral shifts (see Riechers et al. 2013 and also equation 1 of Špirko 2014). The accuracy of the predicted sensitivities seems to fulfil the requirements needed for a reliable analysis of spectral data obtained at 'rotational' resolution. To go beyond this limit, one should account for the hyperfine interactions and this requires a correct description of the 'hyperfine' effects, which in turn should respect both the centrifugal distortion and Coriolis interaction (Fowler & Špirko 1990). A study along these lines is in progress in our laboratory. We also note that the ammonia rovibrational dynamics show the same characteristics as those of other inverting molecules, notably the hydronium cation (see Kozlov et al. 2011), thus calling for a rigorous investigation into such systems.

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