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# Deuterium hyperfine splittings in the rotational spectrum of NH<sub>2</sub>D as revealed by Lamb-dip spectroscopy

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## Abstract

In the context of radio-astronomical observations, laboratory experiments constitute a cornerstone in the interpretation of rich line surveys due to the concomitant presence of numerous emitting molecules. Here, we report the investigation of three different rotational transitions of monodeuterated ammonia (NH<sub>2</sub>D), a species of astrophysical interest, for which the contribution of the deuterium nuclear spin to the rotational spectrum has been resolved for the first time in the millimeter- and submillimeter-wave domain. The effect of hyperfine interactions on the rotational spectrum has been unveiled by a combined theoretical and experimental approach.

Quantum-chemical calculations based on coupled-cluster theory have been employed to evaluate the hyperfine parameters of nitrogen, hydrogen, and deuterium in NH<sub>2</sub>D. Subsequently, the Lamb-dip technique has been used to investigate the rotational spectrum of NH<sub>2</sub>D at high-resolution. In detail, three low-*J* transitions have been recorded at 86, 110, and 333 GHz with a frequency-modulation millimeter-/submillimeter-wave spectrometer. From the line profile analysis of the recorded spectra, the main terms responsible for the rotational hyperfine structure have been determined with good accuracy.

Our work allows a comprehensive analysis of the rotational features of NH<sub>2</sub>D in radioastronomical spectra and a more accurate evaluation of its column density, especially in non-turbulent regions showing narrow linewidths.

*Keywords:* Lamb-dip technique, Hyperfine structure, Quantum-chemical calculations, Ammonia, Interstellar medium, Deuterium fractionation

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## 1. Introduction

Ammonia (NH<sub>3</sub>) has been one of the first molecules observed in the interstellar medium (ISM) [1]: its detection contributed to the birth of astrochemistry as we know it today. Since then, the number of interstellar molecules has been increasing continuously. The current census accounts for more than 200 different species discovered in the ISM and circumstellar shells, and most of them have been detected thanks to their rotational features [2]. To contribute to new detections as well as to accurately derive molecular abundances, laboratory efforts dedicated to the study of molecules of astrophysical interest are fundamental. Besides the fascination of a new molecule identified in the ISM, astrochemical observations are crucial to constrain chemical models in astronomy. Deuterium fractionation processes, for instance, are of great importance in tracing evolutionary stages during the formation of a Sun-like star [3]. Deuterated ammonia is known to be relatively abundant in the ISM. NH<sub>2</sub>D transitions have been first observed towards the Orion nebula [4] and the giant molecular cloud Sagittarius B2 [5]. Later, NH<sub>2</sub>D has been observed in prestellar cores, low- and high-mass star-forming regions, hot core, cold molecular clouds, and many other objects [6, 7, 8, 9].

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15 Two rotational transitions in the 3 mm band are usually used to detect NH<sub>2</sub>D and to derive the deuterium  
 16 fractionation (D/H) of ammonia. These lines correspond to the  $J_{K_a, K_c} = 1_{1,1} - 1_{0,1}$  transitions of *ortho*-  
 17 (at 86 GHz) and *para*-NH<sub>2</sub>D (at 110 GHz). Typically, the observed linewidths are sufficiently narrow to  
 18 resolve the hyperfine structure caused by the nitrogen quadrupole coupling, and thus to properly estimate  
 19 the column density of NH<sub>2</sub>D. However, recent observations of monodeuterated ammonia with the IRAM  
 20 30m and APEX telescopes have pointed out that the hyperfine splittings due to deuterium may affect the  
 21 analysis of NH<sub>2</sub>D features and, consequently, its column density [10]. Indeed, the discrepancies between  
 22 observed and expected linewidths of the  $1_{1,1} - 1_{0,1}$  and  $1_{0,1} - 0_{0,0}$  transitions in the starless core H-MM1  
 23 could only be explained with the inclusion of the deuterium hyperfine structure. Unfortunately, to date,  
 24 laboratory studies of NH<sub>2</sub>D have never taken into account the effect of deuterium hyperfine interactions for  
 25 those transitions.

26 The investigation of the microwave spectrum of monodeuterated ammonia started in the 50s and 60s with  
 27 Stark effect [11] and maser spectroscopy measurements [12, 13], but the first thorough analysis of the  
 28 rotation-inversion spectrum of NH<sub>2</sub>D was carried out in the following decade by De Lucia & Helminger [14],  
 29 who recorded several transitions in the millimeter- and submillimeter-wave domains. The analysis of the  
 30 NH<sub>2</sub>D spectrum has been subsequently extended by the observation of nitrogen quadrupole resolved [15, 16]  
 31 and higher- $J$  transitions [15, 17].

32 Here, we report the Lamb-dip spectra of three NH<sub>2</sub>D transitions observed at millimeter-/submillimeter-  
 33 wavelengths, for which deuterium hyperfine splittings have been resolved for the first time. The experimental  
 34 work has been supported by state-of-the-art quantum-chemical calculations, which were used to evaluate  
 35 the nuclear quadrupole coupling (NQC), spin-rotation (SR), and dipolar spin-spin (SS) tensors of NH<sub>2</sub>D.

36 The structure of this paper is organized as follows. First, the complexity of the NH<sub>2</sub>D spectrum is presented  
 37 and the Hamiltonian described (§2). Second, the computational details employed in the evaluation of the  
 38 hyperfine parameters are reported (§3). Then, the experimental details are given together with the main  
 39 results (§4) and, finally, concluding remarks –with some emphasis on the astrophysical implications of this  
 40 work– are reported (§5).

## 41 2. Spectral analysis

42 Monodeuterated ammonia, NH<sub>2</sub>D, is an asymmetric-top rotor, which –like its parent species NH<sub>3</sub>– tunnels  
 43 between two equivalent configurations passing through a planar transition state: its molecular symmetry  
 44 group is the  $C_{2v}(M)$  (see Figure 1). The main effect of this inversion motion is the splitting of each  
 45  $J_{K_a, K_c}$  rotational level into two sub-levels, one symmetric ( $s, A_1$ ) and the other anti-symmetric ( $a, B_1$ ) with  
 46 respect to inversion, the energy splitting for the  $0_{0,0}$  levels being  $\Delta E = 12.169438(5)$  GHz. The permanent  
 47 dipole moment in NH<sub>2</sub>D ( $\mu = 1.474$  D) is distributed along two components,  $\mu_a = -0.18$  D ( $A_1$  symmetry)  
 48 and  $\mu_c = 1.463$  D ( $B_1$ ) [15]. Therefore,  $a$ -type transitions are pure rotational, whereas  $\mu_c$ -allowed transitions  
 49 connect inversion states of different symmetry.

50 The hyperfine structure of the NH<sub>2</sub>D rotational spectrum is the result of several interactions. In the present  
 51 case, all nuclei (<sup>14</sup>N, D and H) have non-zero nuclear spin ( $I$ ) and thus contribute to the hyperfine structure.  
 52 The presence of two equivalent hydrogen nuclei leads to the existence of *ortho* and *para* species, and the  
 53 total nuclear spin,  $I_{\text{H,tot}} = I_{\text{H}_1} + I_{\text{H}_2}$ , needs to be considered. The *ortho* species corresponds to  $I_{\text{H,tot}} =$   
 54 1, with three spin functions of  $A_1$  symmetry, whereas the *para* form is characterized by  $I_{\text{H,tot}} = 0$ , with  
 55 one spin function of  $B_2$  symmetry. In addition, the symmetry of the asymmetric-top states, denoted by the  
 56 parity of  $K_a$  and  $K_c$ , is:  $A_1$  for even, even ( $ee$ ),  $A_2$  for  $eo$ ,  $B_1$  for  $oo$ , and  $B_2$  for  $oe$ . In conclusion, since the  
 57 total wavefunction has to be of  $B$  symmetry, namely antisymmetric with respect to the exchange of the two  
 58 H nuclei, the *ortho* form has rotation-inversion states of the type ( $s, oo$ ), ( $s, oe$ ), ( $a, ee$ ), and ( $a, eo$ ), while  
 59 for the *para* form holds ( $s, ee$ ), ( $s, eo$ ), ( $a, oo$ ), and ( $a, oe$ ). Thus *ortho* and *para* species have similar spectra,  
 60 with the former stronger because of spin statistics.

61 Having  $I = 1$ , nitrogen and deuterium are quadrupolar nuclei, and thus the hyperfine interactions involved  
 62 are the quadrupole coupling and the spin-rotation interaction. For hydrogen, the nuclear spin is  $I_{\text{H}}=1/2$ ,  
 63 and thus only the spin-rotation interaction occurs. In addition, the dipolar spin-spin couplings between the  
 64 possible nuclear spin pairs, namely N-D, N-H, H-H and D-H, should be considered.

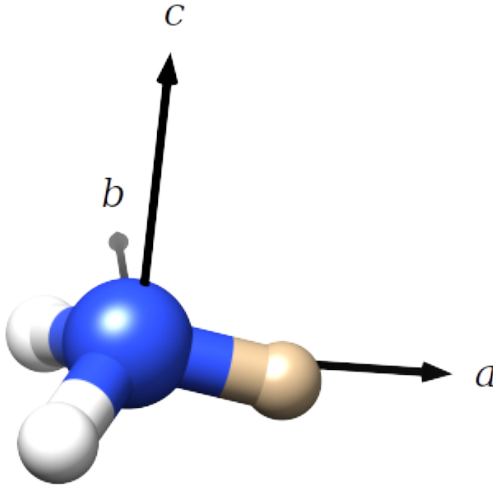


Figure 1: Monodeuterated ammonia  $\text{NH}_2\text{D}$  in its principal inertia system. The hydrogen atoms are depicted in white, while deuterium is in tan.

65 The Hamiltonian used in the analysis of the retrieved hyperfine component frequencies consists of four  
 66 different contributions:

$$\mathbf{H} = \mathbf{H}_{\text{ROT}} + \mathbf{H}_{\text{NQC}} + \mathbf{H}_{\text{SR}} + \mathbf{H}_{\text{SS}}, \quad (1)$$

67 where  $\mathbf{H}_{\text{ROT}}$  is the rotational part of the Hamiltonian operator [18].  $\mathbf{H}_{\text{NQC}}$  describes the nuclear quadrupole  
 68 couplings,  $\mathbf{H}_{\text{SR}}$  is the Hamiltonian describing the spin-rotation interactions, and  $\mathbf{H}_{\text{SS}}$  describes the spin-spin  
 69 couplings due to direct dipolar interactions.

70 The angular momentum coupling scheme adopted is:

$$\mathbf{F}_1 = \mathbf{J} + \mathbf{I}_N, \quad \mathbf{F}_2 = \mathbf{F}_1 + \mathbf{I}_D, \quad \mathbf{F} = \mathbf{F}_2 + \mathbf{I}_{\text{H,tot}}. \quad (2)$$

### 71 3. Computational details

72 For the accurate computation of hyperfine parameters, quantum-chemical calculations are based on the  
 73 coupled-cluster (CC) theory [19] for the treatment of the electron correlation. The CC singles and doubles  
 74 (CCSD) approach augmented by a perturbative treatment of triple excitations (CCSD(T)) [20] has been  
 75 used in conjunction with a hierarchic series of correlation consistent basis sets (the aug-cc-pCV $n$ Z, with  $n =$   
 76 D-6, basis sets [21, 22, 23, 24, 25]) in order to exploit the extrapolation to the complete basis set (CBS) limit.  
 77 To further improve the accuracy of the computed hyperfine parameters, the contributions due to the full  
 78 treatment of triple and quadruple excitations have also been considered. While the CCSD(T) computations  
 79 have been performed using the CFOUR program package [26], the CC singles, doubles and triples, CCSDT  
 80 [27, 28], and CC with singles, doubles, triples, quadruples, CCSDTQ [29], calculations have been carried  
 81 out using the MRCC program [30] interfaced to the CFOUR package. In detail, the composite scheme  
 82 employed, which involves only computations with all electron correlated (all), can be summarized as follows:

$$p_{\text{best}} = p^\infty(\text{HF} - \text{SCF}) + \Delta p^\infty(\text{CCSD(T)}) + \Delta p(\text{fT}) + \Delta p(\text{fQ}), \quad (3)$$

83 where  $p$  denotes a generic hyperfine parameter. The CBS limit has been obtained by means of a two-  
 84 step procedure by extrapolating separately the Hartree-Fock self-consistent-field (HF-SCF) part with the  
 85 exponential expression by Feller [31], applied to the aug-cc-pCV $n$ Z basis sets with  $n = Q, 5,$  and 6, and  
 86 the CCSD(T) correlation contribution with the  $n^{-3}$  extrapolation scheme [32], with the  $n=5$  and 6 sets  
 87 chosen for the purpose. Corrections due to a full treatment of triples (fT) and to quadruples (fQ) have been

88 evaluated as differences between CCSDT and CCSD(T) and between CCSDTQ and CCSDT calculations,  
 89 respectively. The aug-cc-pCVTZ basis set has been used for the fT term, whereas aug-cc-pCVDZ has been  
 90 employed for the fQ correction.

91 Computations of hyperfine parameters have been carried out at the equilibrium geometry obtained by resort-  
 92 ing to the so-called composite “gradient” scheme [33, 34]. The equilibrium structure has been determined  
 93 by minimizing the following energy gradient:

$$\frac{dE_{\text{best}}}{dx} = \frac{dE^\infty(\text{HF} - \text{SCF})}{dx} + \frac{d\Delta E^\infty(\text{CCSD(T)})}{dx} + \frac{d\Delta E(\text{core})}{dx} + \frac{d\Delta E(\text{fT})}{dx} + \frac{d\Delta E(\text{fQ})}{dx}. \quad (4)$$

94 The extrapolation to the CBS limit is analogous to that performed in Eq. (3), with different basis sets  
 95 employed, i.e., the cc-pVnZ family with  $n=Q, 5, 6$  have been chosen for the HF-SCF extrapolation as  
 96 well  $n=5$  and  $6$  for the CCSD(T) valence correlation energy. The third term on the right-hand side of the  
 97 equation above allows for incorporating the core-correlation effects as difference of all-electron and frozen-core  
 98 CCSD(T) calculations using the cc-pCV5Z set. The last two terms are the fT and fQ contributions, which  
 99 –as done for the extrapolation to the CBS limit– have been evaluated within the frozen-core approximation  
 100 using the cc-pVTZ and cc-pVDZ basis sets, respectively.

101 For a quantitative prediction of the hyperfine parameters, the equilibrium values need to be augmented  
 102 by vibrational corrections. For the evaluation of the latter, the approach employed is based on second-  
 103 order vibrational perturbation theory (VPT2) [35]. The VPT2 approach is described in detail in Ref. [36]  
 104 and is well-tested for the computation of vibrational corrections to hyperfine parameters (see, for example,  
 105 Refs. [37, 38, 39, 40, 41, 42]). Vibrational corrections have been computed at the CCSD(T)/aug-cc-pCVQZ  
 106 level with all electrons correlated. Subsequently, these corrections have been added to the best-estimated  
 107 equilibrium results to derive values that can be directly compared to experiment or can be used to guide  
 108 the spectral analysis and the fitting procedure.

109 The main focus of the present calculations is on the determination of the NQC, SR, and SS interaction con-  
 110 stants. While we refer interested readers to, e.g., Ref. [43] for a detailed account on how hyperfine parameters  
 111 can be obtained by means of quantum-chemical computations, in the following, we briefly summarize the rel-  
 112 evant information. For quadrupolar nuclei ( $^{14}\text{N}$  and  $\text{D}$  in the present case), the nuclear quadrupole-coupling  
 113 constants  $\chi_{ij}$  have been obtained by the following expression:

$$\chi_{ij} = eQq_{ij}, \quad (5)$$

114 where  $i$  and  $j$  refer to the inertial axes.  $eQ$  is the quadrupole moment (20.44(3) mbarn for  $^{14}\text{N}$  and  
 115 2.860(15) mbarn for  $\text{D}$  [44]), and  $q_{ij}$  represents the  $ij$ -th element of the electric-field gradient tensor [18, 43].  
 116 The latter is the quantity that needs to be quantum-chemically computed. As a first-order property, its  
 117 computation has been accomplished in a straightforward manner by means of analytic-gradient techniques  
 118 [45].

119 While a detailed account on quantum-chemical calculations of the nuclear SR tensors  $\mathbf{C}$  can be found in  
 120 Refs. [46, 47], here, we limit ourselves to note that the electronic contribution of  $\mathbf{C}$  is evaluated as the second  
 121 derivative of the electronic energy with respect to the rotational angular momentum and the nuclear spin  
 122 [46, 48, 47] in conjunction with perturbation-dependent basis functions [46] (also referred to as rotational  
 123 London orbitals) to improve the basis-set convergence. The nuclear contribution, instead, only depends on  
 124 the molecular geometry (see, e.g., Ref. [49] and references therein), and the same applies to the dipolar  
 125 spin-spin coupling tensor  $\mathbf{D}$ , for which expressions can be found, for instance, in Refs. [18, 43, 50].

126 The computed values of all NQC, SR, and SS interaction constants are listed in Table 1.

## 127 4. Experiment and Results

128 Spectral recordings were performed with a frequency-modulation (FM) submillimeter spectrometer, em-  
 129 ployed in the past for the study of other deuterated species [51, 52, 53, 54] and Lamb-dip measurements  
 130 (see, e.g., Refs. [40, 41, 55, 56]). A Gunn diode (J.E. Carlstrom Co) emitting in the 80–115 GHz range  
 131 is used as radiation source; spectral coverage of the  $1_{0,1} - 0_{0,0}$  transition around 333 GHz is obtained by

Table 1: Computed nuclear quadrupole, spin-rotation, and dipolar spin-spin coupling constants of NH<sub>2</sub>D.

Parameter	Atom	Unit	Value
$\chi_{aa}$	(N)	MHz	1.8986
$\chi_{cc}$	(N)	MHz	-3.9555
$\chi_{ac}$	(N)	MHz	0.9390
$C_{aa}$	(N)	kHz	6.967
$C_{bb}$	(N)	kHz	4.426
$C_{cc}$	(N)	kHz	5.067
$\chi_{aa}$	(D)	MHz	0.2405
$\chi_{cc}$	(D)	MHz	-0.1293
$\chi_{ac}$	(D)	MHz	-0.1110
$C_{aa}$	(D)	kHz	-0.1252
$C_{bb}$	(D)	kHz	-3.154
$C_{cc}$	(D)	kHz	-2.389
$C_{aa}$	(H)	kHz	25.599
$C_{bb}$	(H)	kHz	6.936
$C_{cc}$	(H)	kHz	13.165
$D_{aa}$	(N-D)	kHz	1.093
$D_{cc}$	(N-D)	kHz	1.290
$D_{aa}$	(N-H)	kHz	3.470
$D_{cc}$	(N-H)	kHz	-7.852
$D_{aa}$	(D-H)	kHz	4.075
$D_{cc}$	(D-H)	kHz	1.078
$D_{aa}$	(H-H)	kHz	28.080
$D_{cc}$	(H-H)	kHz	-56.160

**Notes:** Equilibrium values obtained using Eq. (3) augmented by vibrational corrections at the all-CCSD(T)/aug-cc-pCVQZ level. The nuclear quadrupole ( $\chi_{ii}$ ) and dipolar spin-spin coupling ( $D_{ii}$ ) tensors have zero trace; thus, only two of the three diagonal components are given.

132 coupling the Gunn diode to a passive frequency multiplier (Virginia Diodes, WR3.4x3). A 75 MHz sine-wave  
133 modulated wave is used as reference signal in a Phase-Lock Loop (PLL) through which the Gunn's radiation  
134 is locked to one harmonic of a digital synthesizer (HP8672A, 2–18 GHz). Frequency accuracy is achieved by  
135 locking the radio-frequency synthesizers to a 5 MHz rubidium atomic clock. An indium antimonide (InSb)  
136 hot-electron bolometer cooled down to liquid-helium temperature (QMC Instr. Ltd. type QFI/2) is used as  
137 detector. The detector output is then demodulated at twice the modulation frequency  $f$  through an analog  
138 lock-in amplifier, so that the second derivative of the actual absorption spectrum is recorded. An additional  
139 signal-to-noise (S/N) improvement is achieved by filtering the signal into an Ohmic RC circuit. The lock-in  
140 signal is finally analog-to-digital converted and sent to a computer.

141 The optical elements of the spectrometer were appropriately set up in a double-pass configuration to perform  
142 Lamb-dip measurements [57], as previously done for the parent species NH<sub>3</sub> [55]. A wire grid polarizer was  
143 placed in front of the high-density polyethylene window of the absorption cell at 45° along the path of the  
144 incoming radiation, while a roof-top mirror was placed at the end of the cell in order to reflect back the

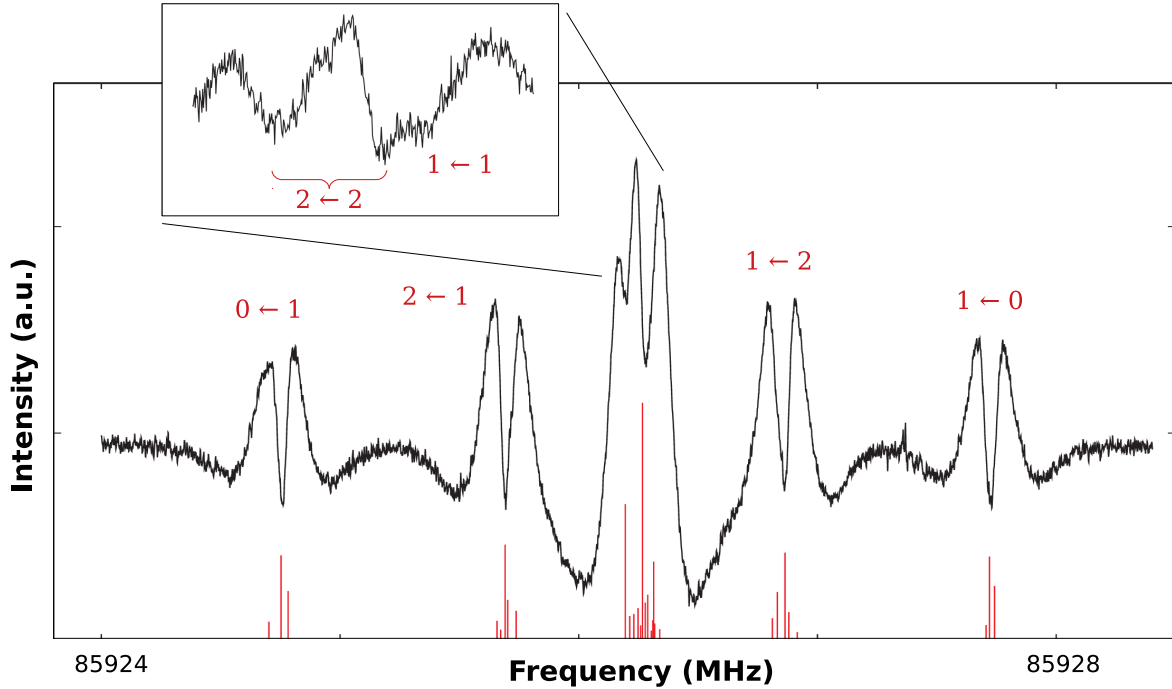


Figure 2: Lamb-dip spectrum of the *ortho*-NH<sub>2</sub>D  $1_{1,1} - 1_{0,1}$  transition showing nitrogen and deuterium hyperfine structure. The numbers above each hfs components refer to the  $F_1' \leftarrow F_1$  quantum numbers. The magnified window shows the splittings due to deuterium quadrupolar interaction, as unveiled at higher-resolution experimental conditions. Red sticks represent the position and the intensity of each transition as predicted from our best spectroscopic parameters.

145 incoming radiation with its polarization rotated by 90°. The back beam is then reflected by the polarizer  
 146 into the detector off-axes of 90°.

147 In addition to the double-pass arrangement, Lamb-dip measurements require a low-pressure regime, low  $f$   
 148 and modulation-depth values, and enough source power to partially saturate the transition. To record the  
 149 spectra, monodeuterated ammonia was formed *in situ*, by flowing a small amount of NH<sub>3</sub> (< 0.5 mTorr) in  
 150 the absorption cell where deuterium (D<sub>2</sub>) had been previously discharged for some minutes. A frequency  
 151 modulation of 1 kHz and modulation-depth values between 8 and 24 kHz were used to record the spectra.

152 These experimental conditions allowed to reveal both nitrogen and deuterium hyperfine splittings for three  
 153 different rotational transitions of NH<sub>2</sub>D. Figures 2 and 3 show the  $J_{Ka, Kc} = 1_{1,1} - 1_{0,1}$  transitions of  
 154 *ortho*- and *para*-NH<sub>2</sub>D, respectively. Because of nitrogen quadrupolar interactions, each transition appears  
 155 as a well-resolved quintet, with splittings of order of few hundreds kHz. On the other hand, deuterium  
 156 quadrupole splittings are less pronounced, i.e., at least one order of magnitude smaller. Nonetheless, the  
 157 deuterium hyperfine structure could be partially resolved, as shown in the magnified boxes of Figures 2 and  
 158 3.

159 Figure 4 illustrates the  $J_{Ka, Kc} = 1_{0,1} - 0_{0,0}$  transition of NH<sub>2</sub>D, which has been exclusively recorded for  
 160 the *ortho* state (the same transition for the *para* state is weaker for spin-statistics reasons and could not be  
 161 saturated in our experimental conditions). The transition appears as a well-resolved triplet, because only  
 162 the  $F_1 = 1$  level can exist for the lower state. The deuterium hyperfine structure is also less complicated and  
 163 has been partly resolved for the middle component of the triplet. Moreover, two crossover resonances (also  
 164 denoted as ghost transitions), marked with green asterisks, are evident in the spectrum of Figure 4. These  
 165 dips are due to the saturation of overlapping Gaussian profiles of two transitions with a common energy level.  
 166 Since they occur midway between the “interacting” transition frequencies, they offer additional information  
 167 for data analysis.

168 To analyze the recorded spectra, first of all, the hyperfine structure of the NH<sub>2</sub>D rotational spectrum



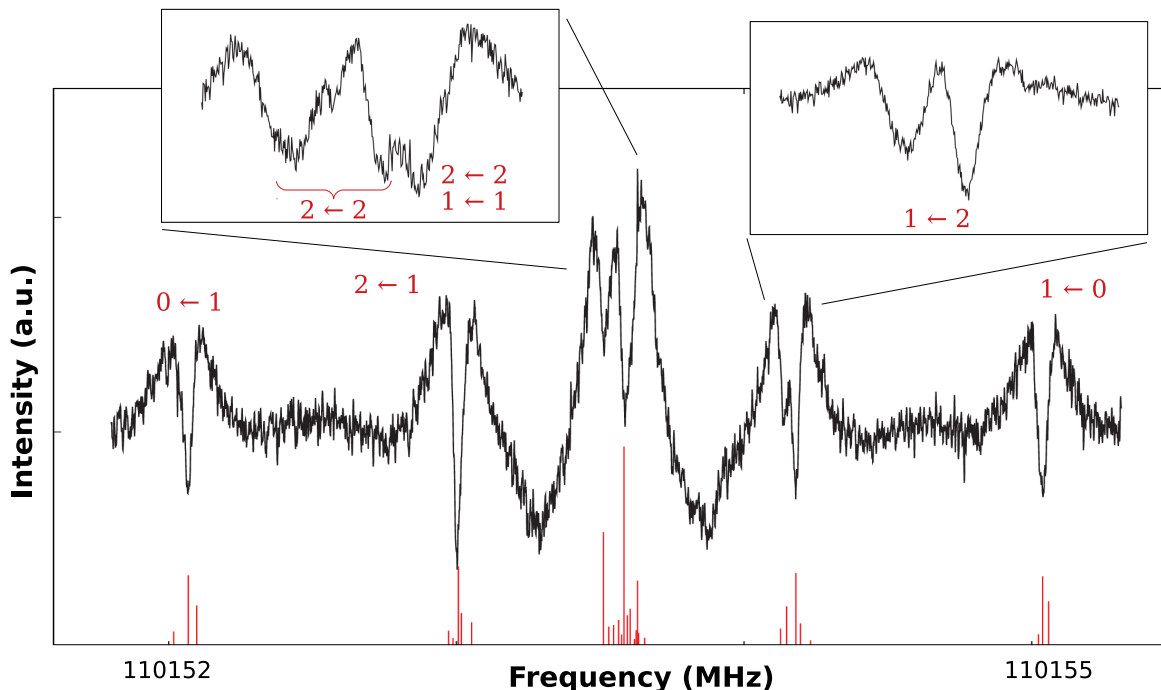


Figure 3: Lamb-dip spectrum of the *para*-NH<sub>2</sub>D  $1_{1,1} - 1_{0,1}$  transition showing nitrogen and deuterium hyperfine structure. The numbers above each hfs components refer to the  $F_1' \leftarrow F_1$  quantum numbers. The magnified windows show the splittings due to deuterium quadrupolar interaction, as unveiled in higher-resolution experimental conditions. Red sticks represent the position and the intensity of each transition as predicted from our best spectroscopic parameters.

169 was predicted using the computed hyperfine constants (as explained in §3) together with experimental  
 170 spectroscopic parameters ( $A$ ,  $B$ ,  $C$ , and so on) from previous works [15, 17]. The computed hyperfine  
 171 constants turned out to be rather good and allowed us to easily assign each dip to the correct hyperfine  
 172 component (or group of components). Then, the rest frequency of each line has been retrieved by modelling  
 173 the recorded absorption profile using the proFFiT line analysis code [58].

174 Eventually, the newly observed transition frequencies of NH<sub>2</sub>D (including ghost features) have been fitted  
 175 along with literature data to the Hamiltonian of Equation (1). The least-squares procedure, in which each  
 176 datum has been weighted proportionally to the inverse square of its uncertainty, has been performed with  
 177 the SPFIT suite of program [59]. As far as the centrifugal analysis of NH<sub>2</sub>D is concerned, most of the  
 178 spectroscopic parameters have been determined with an accuracy comparable to that of previous works  
 179 [15, 17]; for this reason, they are not reported here. Indeed, the focus and the major accomplishment of this  
 180 work are the accurate determination of the diagonal NQC constants,  $\chi_{ii}$ , and the  $C_{cc}$  SR constant of nitrogen  
 181 and deuterium nuclei, which are collected in Table 2. The  $\chi_{ii}$  terms of the hyperfine Hamiltonian are the  
 182 main responsible of the actual splittings observed in the recorded spectra, which are typically revealed only  
 183 in low- $J$  transitions. Spin-rotation and spin-spin coupling interactions, instead, produce a shift in the energy  
 184 levels that is difficult to determine without a larger set of hyperfine-resolved data. In our analysis, most SR  
 185 constants and all the SS parameters have been kept fixed at the computed values of Table 1.

186 The new experimental transition frequencies are listed in Table 3 together with their residual errors from  
 187 the global fit.

## 188 5. Conclusions

189 The hyperfine structure of the rotational spectrum of NH<sub>2</sub>D has been investigated by combining high-level  
 190 quantum-chemical calculations and high-resolution rotational spectroscopy. This work was motivated by

Table 2: Nitrogen and deuterium hyperfine constants determined for NH<sub>2</sub>D.

Parameter	Unit	Atom	This work	Ref. [10]	Computed
$\chi_{aa}$	MHz	(N)	1.9145(14)	1.906(84)	1.8986
$\chi_{cc}$	MHz	(N)	-3.9470(12)	-3.95(13)	-3.9555
$C_{cc}$	kHz	(N)	4.94(13)		5.067
$\chi_{aa}$	MHz	(D)	0.2229(67)	0.275 <sup>(a)</sup>	0.2405
$\chi_{cc}$	MHz	(D)	-0.1348(16)	-0.160(2)	-0.1293
$C_{cc}$	kHz	(D)	-2.266(97)		-2.389

**Notes:** Numbers in parenthesis are standard errors and apply to the last significant digits. (a) Fixed in the analysis.

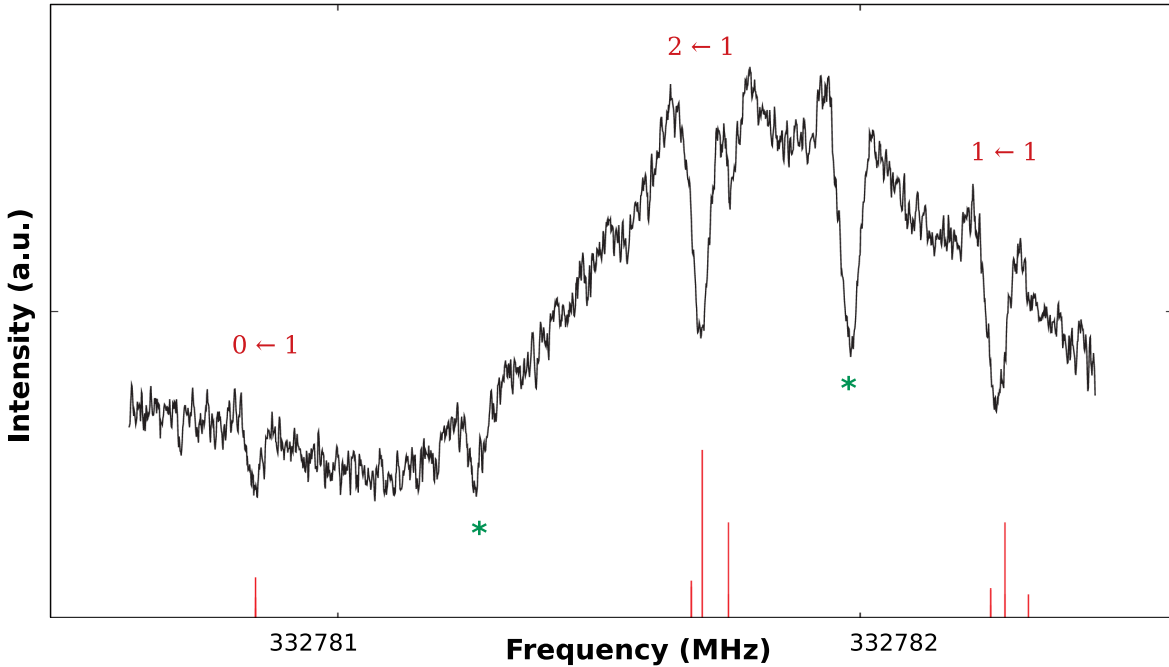


Figure 4: Lamb-dip spectrum of the *ortho*-NH<sub>2</sub>D  $1_{0,1} - 0_{0,0}$  transition showing nitrogen and deuterium hyperfine structure. The numbers above each hfs components refer to the  $F'_1 \leftarrow F_1$  quantum numbers, while ghost transitions are marked with green asterisks. Red sticks represent the position and the intensity of each transition as predicted from our best spectroscopic parameters.

191 the recent astronomical observation of NH<sub>2</sub>D toward the dense core H-MM1 in Ophiuchus [10], where the  
 192 rotational features show line-widths due to non-thermal motions that are sufficiently narrow to be affected  
 193 by the small broadening caused by deuterium hyperfine splittings.

194 An highly accurate composite scheme has been employed to compute nitrogen, hydrogen, and deuterium  
 195 hyperfine parameters, namely the NQC, SR, and SS interaction constants. Subsequently, three NH<sub>2</sub>D  
 196 rotational transitions have been recorded using the Lamb-dip technique, thus allowing not only the resolution  
 197 of the nitrogen hyperfine structure, but also splittings due to deuterium. From the analysis of the newly  
 198 observed transition frequencies, reliable values for the diagonal NQC constants and some SR parameters  
 199 of both N and D have been derived. As can be seen from Table 2, the accuracy of  $\chi_{aa}(\text{N})$  and  $\chi_{cc}(\text{N})$

Table 3: Measured hyperfine component frequencies of NH<sub>2</sub>D.

Upper state					Lower state					Frequency (MHz)	Obs.-Calc. <sup>(b)</sup> (MHz)
$J'$	$K'_a$	$K'_c$	$F'_1$	$F'_2$ <sup>(a)</sup>	$J$	$K_a$	$K_c$	$F_1$	$F_2$ <sup>(a)</sup>		
o-NH <sub>2</sub> D											
1	1	1	0		1	0	1	1		85924.756	-0.001
1	1	1	2		1	0	1	1		85925.695	0.001
1	1	1	2	2	1	0	1	2	2	85926.197	-0.006
1	1	1	2	3	1	0	1	2	3	} 85926.271	-0.003
1	1	1	2	2	1	0	1	2	1		
1	1	1	1		1	0	1	1		} 85926.298	-0.004
1	1	1	2	1	1	0	1	2	1		
1	1	1	1		1	0	1	2		85926.862	-0.005
1	1	1	1		1	0	1	0		85927.725	0.005
p-NH <sub>2</sub> D											
1	1	1	0		1	0	1	1		110152.066	-0.002
1	1	1	2		1	0	1	1		110153.003	-0.002
1	1	1	2	2	1	0	1	2	2	110153.517	0.003
1	1	1	2	3	1	0	1	2	3	} 110153.581	-0.005
1	1	1	2	2	1	0	1	2	1		
1	1	1	1		1	0	1	1		} 110153.604	-0.009
1	1	1	2	1	1	0	1	2	1		
1	1	1	1	2	1	0	1	2	2	} 110154.136	-0.001
1	1	1	1	1	1	0	1	2	2		
1	1	1	1	2	1	0	1	2	3	} 110154.177	0.001
1	1	1	1	0	1	0	1	2	1		
1	1	1	1		1	0	1	0		110155.038	0.004
o-NH <sub>2</sub> D											
1	0	1	0		0	0	0	1		332780.840	-0.003
1	0	1	2	1	0	0	0	1	0	} 332781.695	0.004
1	0	1	2	1	0	0	0	1	1		
1	0	1	2	1	0	0	0	1	2	} 332781.752	0.002
1	0	1	2	3	0	0	0	1	2		
1	0	1	2	2	0	0	0	1	1	} 332781.752	0.002
1	0	1	2	2	0	0	0	1	2		
1	0	1	1		0	0	0	1		332782.261	-0.006

**Notes:** Braces denote group of transitions observed as a single line. (a) Omitted when the deuterium hyperfine structure is unresolved. (b) In case of blended transitions, the deviation is computed from their intensity-averaged frequency.

200 has been improved with respect to Ref. [10] by more than one order of magnitude. Moreover,  $\chi_{aa}(\text{D})$  and  
201  $\chi_{cc}(\text{D})$  have been simultaneously determined for the first time, with  $\chi_{cc}(\text{D})$  being previously derived only  
202 from unresolved astronomical spectra [10]. A good agreement between experimental and theoretical values  
203 has also to be pointed out.

204 Even though deuterium hyperfine splittings are quite small and often negligible, it has been shown by

205 astronomical observations that neglecting them in the line-profile analysis can lead to an overestimation of  
206 the  $\text{NH}_2\text{D}$  column density by about 50% [10]. A similar effect is possibly exhibited by other deuterium-  
207 bearing species, such as multiply-deuterated ammonia  $\text{NHD}_2$  and  $\text{ND}_3$ , which suffer from the same lack of  
208 laboratory data. While a more extended investigation of the rotational spectra of ammonia isotopologues is  
209 in progress in our laboratory, the new set of spectroscopic constants determined in this work offers a reliable  
210 line-catalog (taking into account both N and D hf splittings) that can be used to guide future astronomical  
211 observations of  $\text{NH}_2\text{D}$ .

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