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Far-infrared spectra and ground state spectroscopic parameters of $^{15}\text{NH}_2\text{D}$ Adriana Predoi-Cross^a, Hoimonti Rosario^a, Gianfranco Di Lonardo^b, Luciano Fusina^b, Filippo Tamassia^{b,*}^a Department of Physics and Astronomy, University of Lethbridge, 4401 University Drive, Lethbridge, AB T1K 3M4, Canada^b Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, 40136 Bologna, Italy

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During the analysis of the rotation–inversion spectrum of $^{15}\text{NH}_3$ [1] a large number of extra lines were observed in the spectrum. Apart from the presence of the pure rotation lines of water which were used to calibrate the spectrum [2,3] and of the pure rotational spectrum of $^{15}\text{NH}_3$ in the $\nu_2 = 1$ state, we have observed a large number of additional lines without any obvious pattern. These lines were attributed to rotational transitions of a light asymmetric top molecule. Since the presence of lines belonging to partially deuterated water (HOD) was already observed in the spectra, the $^{15}\text{NH}_2\text{D}$ molecule was considered to be the most probable candidate for the unknown transitions. In 2008 Elkeurti et al. [4] reported on the inversion–rotation spectra of $^{15}\text{NH}_2\text{D}$ and $^{15}\text{NHD}_2$. For the former molecule, about 60 transitions were measured in the microwave (MW) region (18–64 GHz), with an accuracy estimated to be better than 50 kHz, whereas about 350 transitions were assigned in the far infrared region (FIR) between 22 and 110 cm^{-1} using a spectrum recorded at a resolution of 0.002 cm^{-1} . Two sets of rotational constants: one for the s , the other for the a inversion states, the inversion splitting and the Coriolis constant connecting them were determined. The centrifugal distortion constants up to second order, D and H , were evaluated, whereas the L parameters were kept fixed to the values obtained by Fusina et al. [5].

The spectra for the $^{15}\text{NH}_2\text{D}$ molecule were recorded at an unapodized resolution of 0.00096 cm^{-1} in the 65–360 cm^{-1} range at pressures of 0.27 Pa of $^{15}\text{NH}_3$, for 8 m path length, and 6.67 and

133.32 Pa of $^{15}\text{NH}_3$, respectively, for 72 m path length. The Bruker IFS 125 Fourier transform spectrometer located at the far-infrared beamline, Canadian Light Source, and the synchrotron radiation were used to record the spectra at 298 K using a multipass, coolable absorption cell of 2 m base. The cell had wedged polypropylene windows. The sample was supplied by Sigma–Aldrich with a purity of 98% $^{15}\text{NH}_3$ and was used without any further purification. More detailed information will be given in [1].

The $^{15}\text{NH}_2\text{D}$ molecule, having only one symmetry plane, belongs to the C_s group, but if one also takes into consideration the inversion motion, the permutation–inversion group that best describes the molecule is isomorphic to C_{2v} . The symmetry species of the rotation–inversion levels as a function of J , K_a , K_c and a or s symmetry of the $0(s)$ and $1(a)$ levels are reported in Table VI of [6]. The statistical weight of the A_1 and A_2 levels is 5 whereas that of the B_1 and B_2 levels is 15.

The permanent dipole moment lays in the symmetry plane of the molecule containing the a and c axis, the a component being smaller than the c one. The a -type selection rules give rise to the pure rotational spectrum in the $0(s)$ and $1(a)$ levels:

$$\Delta J = 0, \pm 1, \quad \Delta K_a \text{ even}, \quad \Delta K_c \text{ odd}, \quad s \leftrightarrow s, \quad a \leftrightarrow a,$$

whereas the c -type selection rules give rise to the rotation–inversion spectrum:

$$\Delta J = 0, \pm 1, \quad \Delta K_a \text{ odd}, \quad \Delta K_c \text{ even}, \quad s \leftrightarrow a$$

Fig. 1 shows a small portion of the FIR spectrum containing four a -type transitions of $^{15}\text{NH}_2\text{D}$, i.e. two doublets, $8_{1,8}$ – $7_{1,7}$ and $8_{0,8}$ – $7_{0,7}$ in the $0(s)$ and $1(a)$ states. Intensity alternation between the strong $B_1 \leftrightarrow B_2$ and the weak $A_1 \leftrightarrow A_2$ transitions is evident.

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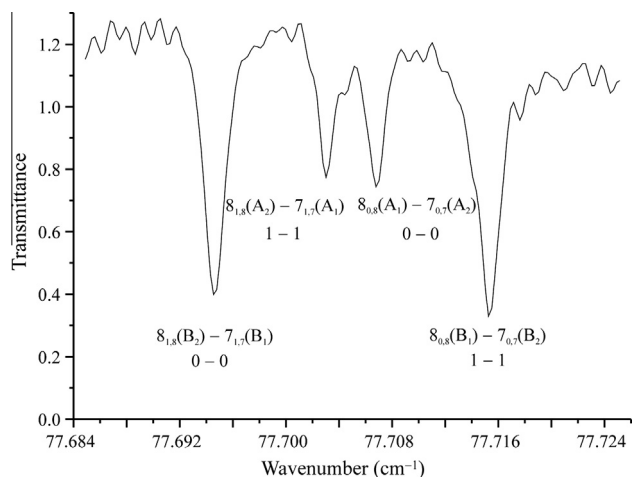


Fig. 1. Portion of the FIR spectrum containing α -type transitions of $^{15}\text{NH}_2\text{D}$. The levels involved are identified by $J_{Ka,Kc}$, symmetry, and the $0(s)$ and $1(a)$ vibrational inversion states. Intensity alternation between the strong $B_1 \leftrightarrow B_2$ and the weak $A_1 \leftrightarrow A_2$ transitions is evident.

The first stage of our analysis was simplified because the line positions could be reasonably predicted using the parameters in [4]. Successively, the dataset was extended to include transitions with higher J and K_a values, thus enabling the refinement of the parameters, which in turn improved the calculated (i.e. predicted) line positions. This procedure was repeated until all the lines of $^{15}\text{NH}_2\text{D}$ were identified in the spectra.

All the data were analyzed simultaneously on the basis of a Watson-type III' rotation-inversion S -reduced Hamiltonian which included vibration-rotation interaction terms, the same adopted in the analysis of the FIR spectrum of the $^{14}\text{NH}_2\text{D}$ and $^{14}\text{NHD}_2$ [5]. The dataset included the MW and FIR transitions up to 65.48 cm^{-1} as reported in [4] and the present assignments from 65.66 cm^{-1} to 324.53 cm^{-1} . The FIR data from 65.48 cm^{-1} to 108.46 cm^{-1} in [4] were not included because they are less precise and less numerous than the present measurements. In total the line positions of 1481 transitions, including the positions of 55 MW and 175 FIR lines taken from [4], were fitted to 49 parameters in a nonlinear least squares procedure. The maximum value of J and K_a for the present data is 20 and 17, respectively. The weight of each line position was set equal to the square of its reciprocal experimental uncertainty. An uncertainty of 0.05 MHz and 0.00025 cm^{-1} was given to the MW and FIR data, respectively, as quoted in [4], whereas the value of 0.0001 was given to our measurements. Twenty-two FIR transitions were excluded from the final cycle of the refinement since their observed-calculated values exceeded the chosen limit for rejection, which was set equal to 3 times their uncertainties. The parameters obtained from the fit are listed in Table 1. They include the inversion term value, the rotational and distortion constants up to the 8th power in the angular momentum but l_4 of the $\nu=0$ state, and the interaction constant F . The 10th order P parameters were refined but they resulted undetermined and were constrained to zero. All the parameters are statistically well determined and are in agreement with those reported previously (see Table 5 of [4]). However, the refinement of the L parameters, which were constrained to the $^{14}\text{NH}_2\text{D}$ values in [4] prevents a more detailed comparison. The constants in Table 1 have smaller errors with respect to the corresponding ones in [4] as expected from the analysis of more precise and more numerous data.

Table 1
Parameters for the ground state of $^{15}\text{NH}_2\text{D}$.^a S reduction, III' representation.

Parameter	$\nu=0$	$\nu=1$
E (MHz)	0.0	11487.00343(4805)
B_x (MHz)	289233.4399(6270)	289143.0027(6287)
B_y (MHz)	191518.11024(4852)	191487.04858(4741)
B_z (MHz)	140675.3177(6283)	140696.5433(6275)
D_J (kHz)	15843.7207(1886)	15664.3234(1776)
D_{JK} (kHz)	-23993.3753(3738)	-23624.2024(4661)
D_K (kHz)	10956.7344(3764)	10750.4742(4260)
d_1 (kHz)	-4202.5945(1196)	-4122.0861(1002)
d_2 (kHz)	136.85506(6858)	149.30457(6113)
H_J (Hz)	3716.005(1435)	3359.930(1179)
H_{JK} (Hz)	-8804.545(4765)	-8057.442(3908)
H_{KJ} (Hz)	9138.636(8418)	8452.870(7132)
H_K (Hz)	-3894.992(4566)	-3590.459(4417)
h_1 (Hz)	1938.429(1145)	1726.1447(8285)
h_2 (Hz)	466.1624(8024)	407.4273(5919)
h_3 (Hz)	37.9314(1787)	38.6395(1612)
l_J (Hz)	-1.281471(3284)	-0.887795(2643)
l_{JK} (Hz)	3.62044(1586)	2.69081(1469)
l_{JK} (Hz)	-6.21904(4228)	-4.98525(3822)
l_{KJ} (Hz)	5.69881(4605)	4.59295(4121)
l_K (Hz)	-1.89906(1871)	-1.48691(1609)
l_1 (Hz)	-0.899063(2935)	-0.654247(1791)
l_2 (Hz)	-0.358103(2318)	-0.266825(1394)
l_3 (Hz)	-0.0382488(7669)	-0.0335040(5545)
l_4 (Hz)	0.0 ^b	-0.0036802(1509)
F (MHz)	-5439.744(8558)	
$F_J = F_K$	0.0 ^b	
Number of fitted data	1459	
Standard deviation of obs. unit weight	1.2	

^a Standard uncertainties (1σ) in parentheses refer to the least significant digits.

^b Constrained.

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Appendix A. Supplementary material

Supplementary data for this article (Table A1) are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://library.osu.edu/sites/msa/jmsa_hp.htm). Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jms.2014.05.002>.

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