FY24 R&TD Innovative Spontaneous Concepts (ISC)

Spectroscopy of NH_2D and $^{15}NH_3$ near 10 µm for TLS in support of planetary missions

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Objectives: The objective was to characterize spectroscopic line parameters of NH_3 and NH_2D in the 1000 – 1020 cm^{-1} region, covering Tunable Laser Spectrometer (TLS) spectral range [1]. By analyzing a series of high-res spectra both from a high-purity NH_3 gas sample and from two sets of (NH_3:ND_3) mixtures, we aimed to retrieve line positions, intensities, Self- broadened collisional widths and frequency shifts, as well as their lower state energies for $^{14}NH_3$ and NH_2D. We also measured their collisional broadening by H_2, the dominant atmospheric constituent of Jovian planets. Results from this work would enable to probe atmospheric D/H ratio from NH_3 ispectra n a very narrow band at 10 µm.

Background: Ammonia (NH_3) is found ubiquitous in space, such as giant planets in our Solar system, molecular clouds, star-forming regions, proto-stellar disks, etc. Its minor isotopologue (NH_2D) exhibits complex and densely populated transitions in the infrared region, which can serve as excellent probe, enabling physical and chemical properties to be deduced in a relatively narrow spectral range. Spectroscopy of NH_3 and NH_2D, in particular, can be used to determine D/H ratio in the planetary atmospheres, which, in turn, provides useful constraints for planetary origin and atmospheric evolution. Infrared features are strongest in the ν_2 band near 10 µm, which is covered by Tunable Laser Spectrometer (TLS) [1], thus carrying the most useful spectroscopic features for planetary atmospheric remote sensing. However, no spectroscopic characterization has been established for NH_2D to date, primarily because of experimental difficulties in a laboratory. For instance, the super strong ν_2 band requires a very short gas cell (*e.g.*, 0.5 cm long) to avoid any saturation during data acquisition. For NH_2D, a pure gas sample is not commercially available, making it even more difficult to study in a laboratory. We have resolved these two challenging issues for this RTD-ISC task as described below.

Approach and Results: This project proceeded in four steps. (1) We analyzed a series of NH_3 spectra obtained using a 5 mm path long gas cell coupled to a Fourier-transform spectrometer (FTS) at JPL [Fig. 1]. Deuterated NH_3 samples were prepared on-site by mixing anhydrous NH_3(99.99+) and ND_3 (D atom 99%) in a prescribed manner. As expected, deuterated NH_3 isotopologs were generated through isotope-exchange reactions [2]. We finally performed the sample characterization of the (NH_3:ND_3) mixtures by comparing $^{14}NH_3$ line intensities with the public database [3] [Fig. 2], which has confirmed the relative $^{14}NH_3$ abundances that we derived based on the stochastic equilibrium. (2) We fitted all pure and deuterated NH_3 spectra simultaneously [Fig. 3a] to determine spectroscopic line parameters of NH_2D in the region for the first time. We noted, however, that most of the strong transitions (thus most useful to remote sensing) in our spectrum sets arose from both $^{14}NH_3$ and NH_2D only. (3) We also obtained two new spectra of the deuterated NH_3 sample broadened by H_2, the dominant atmospheric constituent of Jovian planets by using a 15.01 cm long gas cell (not presented). Note that a longer path cell required only small amount of NH_3 sample in which self-broadening becomes insignificant when compared to the H_2-broadening. Thus, we fit the two H_2-broadened deuterated NH_3 spectra [Fig. 3b] to retrieve H_2-broadened half widths and pressure-shifts parameters, both at room temperature. (4) We determined lower state energy (E") values of all the measured transitions through line-by-line matching referenced to NH_2D model calculations [4]. Finally, we compiled the retrieved line parameters of $^{14}NH_3$ and NH_2D as presented in Table 1.

Significance/Benefits to JPL and NASA: Accurate knowledge of D/H ratio provides one of critical inputs to constrain planetary atmospheric origin and evolution (e.g., atmospheric escape), original water content, and planet formation itself. We have identified the strongest NH_2D transitions in the 1000 – 1020 cm^{-1} region, showing that the TLS probe [1] would be able to capture both NH_3 and NH_2D transitions simultaneously. These NH_3 spectroscopy updates are readily applicable to any archived or potential future planetary missions (e.g., Saturn probe under New Frontier Program at JPL). This project also provided a proof-of-concept on how to characterize spectroscopy of all other deuterated NH_3, which will pave the road for JPL proposals to NASA-SMD/ROSES calls such as SSW, EW, and APRA as well as for a planned ROSES/PDART proposal to cover the entire 700 – 1200 cm^{-1} (8.3 – 14 µm) region, including that of $^{15}NH_3$ that had to be dropped in this R&D-ISC task due to a substantial funding cut.

References: [1] C.R. Webster et al. Space Science Reviews (2023) 219:78. [2] B-M Cheng et al. ApJ. 647: 1535 – 1542 (2006). [3] I.E. Gordon, et al. JQSRT, 277:107949 (2022); [4] Priv. Comm. to Shanshan Yu of Jet Propulsion Lab.

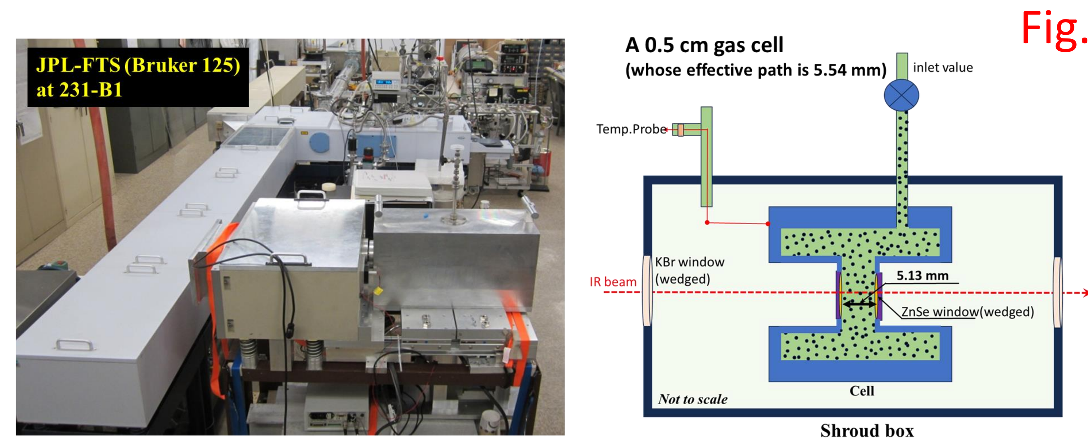

Fig. 1 A high-resolution Fourier transform spectrometer, JPL-FTS, and a schematic diagram of the 0.513 cm gas cell, whose effective path is measured to be 0.554 cm taking into account a triple pass component.

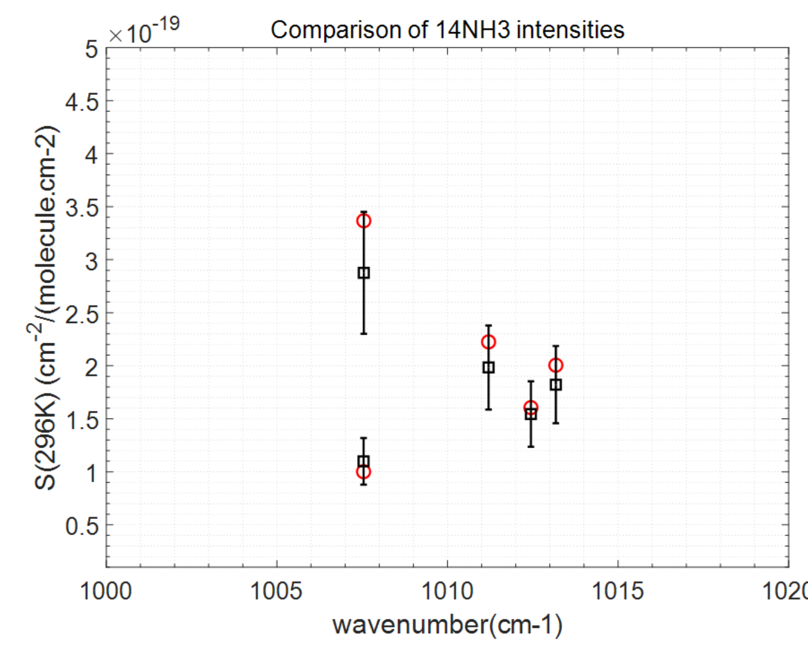

Fig. 2 Five $^{14}NH_3$ line intensities retrieved from this work are compared to HITRAN 2020 database [3]. Significant discrepancy (whose mean value is - 6%) is seen, but still agree within their uncertainties (10 – 20 %) listed in the HITRAN, thus, validating the estimates of individual isotopologs abundance for the sample mixtures..

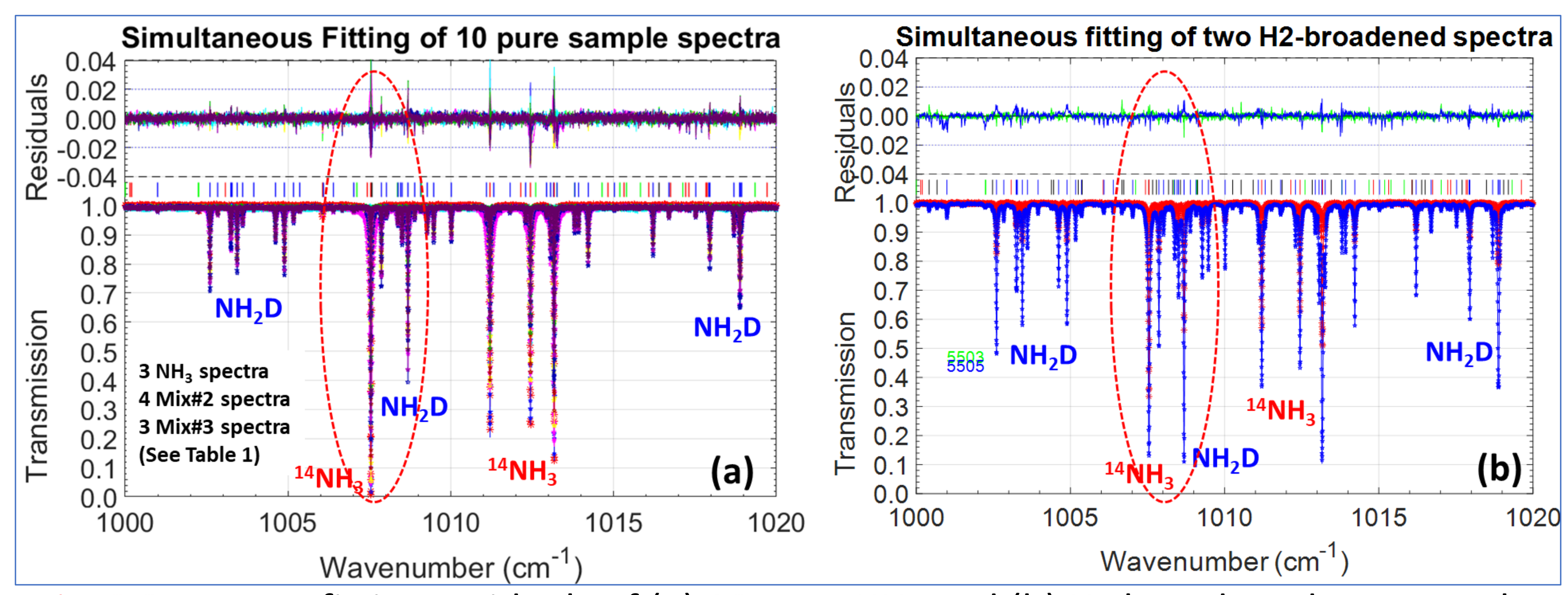

Fig. 3 Spectrum fitting residuals of (a) 10 pure NH_3 and (b) H_2-broadened spectra. The two strong NH_3 and NH_2D lines inside the dashed circle (in red) are the best promising transitions for TLS observations in study of D/H ratio. The short vertical color-coded lines at the top of the spectra indicate the position of the lines included in the fitting ($^{14}NH_3$ in red, $^{15}NH_3$ in green, $^{14}NH_2D$ in blue).

Table 1 An excerpt of the table of their spectroscopic line parameters in HITRAN format [3]. The lines in the highlighted box are those promising transitions for D/H observations by TLS [1].

mmi	pos (cm^{-1})	S100%	A	γ(H_2)	γ(slf)	E"(cm^{-1})	nT	δ(H_2)	fitfix
112	1002.254300	2.704E-19	0.000E+00	.09500	.323	19.4920	.75	.000000	110101
113	1002.602474	5.758E-20	0.000E+00	.07900	.317	272.8990	.75	.003368	001010
113	1003.239311	1.786E-20	0.000E+00	.07200	.273	337.7620	.75	.009806	000000
113	1003.260378	1.833E-20	0.000E+00	.07400	.275	337.7360	.75	.008909	000010
113	1003.438615	3.872E-20	0.000E+00	.07300	.283	383.7530	.75	-.001820	000000
113	1003.606508	1.200E-20	0.000E+00	.07400	.350	345.1720	.75	.000000	000000
113	1004.616623	2.612E-20	0.000E+00	.07500	.389	436.4690	.75	.003944	000000
113	1004.887276	3.963E-20	0.000E+00	.07400	.278	381.5670	.75	.004273	000010
112	1007.113500	1.874E-19	0.000E+00	.10100	.510	85.9760	.75	.000000	110111
111	1007.539958	1.001E-19	0.000E+00	.09000	.418	16.1730	.75	.000000	001010
111	1007.546209	3.367E-19	0.000E+00	.09300	.307	19.8899	.75	.005842	001010
113	1007.867990	4.880E-20	0.000E+00	.06800	.289	362.3130	.75	.002187	000010
112	1008.360500	1.469E-19	0.000E+00	.09500	.424	104.6560	.75	.000000	110111
113	1008.379389	1.761E-20	0.000E+00	.08800	.577	360.8820	.75	.005956	000010
113	1008.505480	3.202E-20	0.000E+00	.08600	.485	319.0710	.75	.000000	001010
113	1008.682410	6.722E-20	0.000E+00	.05900	.274	269.7410	.75	-.002987	000010
113	1008.684550	6.722E-20	0.000E+00	.05900	.274	269.7390	.75	.006169	001010
113	1009.274015	2.366E-20	0.000E+00	.07900	.481	403.5790	.75	.006153	000000
113	1009.473015	1.830E-20	0.000E+00	.07200	.270	302.4720	.75	.003642	000010
113	1010.015345	1.877E-20	0.000E+00	.07500	.276	301.7960	.75	.003285	001010
111	1011.202958	2.225E-19	0.000E+00	.09100	.551	86.6578	.75	.013954	001010
113	1012.297771	1.229E-20	0.000E+00	.08200	.490	319.6670	.75	.005356	001010
111	1012.444497	1.605E-19	0.000E+00	.08000	.420	105.1837	.75	.009262	010000
113	1013.060947	2.764E-20	0.000E+00	.06600	.296	477.6320	.75	.005651	000010
113	1013.156052	4.711E-20	0.000E+00	.03700	.258	381.5950	.75	.007691	001010
113	1013.156352	4.711E-20	0.000E+00	.08000	.258	381.5940	.75	.000000	000010
111	1013.174986	2.005E-19	0.000E+00	.07300	.335	116.2783	.75	.007209	000000
113	1013.261720	1.647E-20	0.000E+00	.07200	.350	282.6610	.75	.000000	000000
113	1013.806633	1.335E-20	0.000E+00	.08000	.282	417.0930	.75	.000000	000010
113	1013.921425	1.229E-20	0.000E+00	.07000	.253	416.9450	.75	.003179	001010
113	1014.221860	4.209E-20	0.000E+00	.07600	.355	350.9340	.75	.002736	000000
113	1016.209903	2.750E-20	0.000E+00	.07300	.288	472.2380	.75	.004281	001010
113	1017.954363	3.682E-20	0.000E+00	.07100	.301	457.6790	.75	-.001420	000000
113	1018.692522	1.429E-20	0.000E+00	.07300	.265	383.4340	.75	.000000	000000
113	1018.868302	5.385E-20	0.000E+00	.06400	.290	337.4390	.75	.000935	001010
113	1018.890562	5.382E-20	0.000E+00	.06900	.290	337.4130	.75	.000000	011011

Notes: mmi= 111,112,113 for $^{14}NH_3$,$^{15}NH_3$,$^{14}NH_{2D}$; S100% = Intensity @ 296K (cm/molecule) for 100%-enriched sample; **A** for a place holder, γ = half-width, E"=lower state energy(cm-1); nT = temp.dependence (assumed); δ =pressure-shift; fitfix flag = 0 (floated), 1(fixed) for pos., S, γ (H_2), γ(slf), δ(H_2) δ(slf), respectively.

Publication: Keeyoon Sung, Geoffrey Toon, Deacon Nemchick, Shanshan Yu, Timothy Crawford, D. Chris Benner, and Chris R. Webster. FT-IR measurements of NH_2D transitions for the TLS window characterization near 10 µm. *in prep. to be submitted to J. Quant. Spectrosc. Radiat. Transfer.*

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