Accurate Rotational Rest Frequencies for Ammonium Ion Isotopologues

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Abstract

We report rest frequencies for rotational transitions of the deuterated ammonium isotopologues NH_3D^+ , NH_2D_2^+ , and NHD_3^+ , measured in a cryogenic ion trap machine. For the symmetric tops NH_3D^+ and NHD_3^+ , one and three transitions are detected, respectively, and five transitions are detected for the asymmetric top NH_2D_2^+ . While the lowest frequency transition of NH_3D^+ was already known in the laboratory and space, this work enables the future radio astronomical detection of the two other isotopologues.

Key words: ISM: molecules – methods: laboratory: molecular – molecular data – techniques: spectroscopic

1. Introduction

Nitrogen is one of the most abundant elements in the local universe, and has a notably rich chemistry, with more than 70 nitrogen-containing molecules identified in space to date.³ Two of the most abundant nitrogen-bearing molecules in the interstellar medium (ISM) are N_2 and NH_3 , which are predicted to be present in many different media, from cold dark clouds (see, e.g., Nejad et al. 1990) or protostellar cores (see, e.g., Aikawa et al. 2008) to active galactic nuclei (see, e.g., Harada et al. 2010). N_2 , being a homonuclear diatomic molecule, cannot be observed through its (electric-dipole) rotation or vibration transitions. It can be observed, however, through electronic transitions in the far-ultraviolet, with only one direct observation reported by Knauth et al. (2004), or by its frequently used proxy, the diazenylium ion (N_2H^+). Ammonia, in turn, is the first polyatomic molecule identified in space (Cheung et al. 1968), and since then has been observed in many environments. To date, all deuterated isotopologues of ammonia, NH_2D , NHD_2 , and ND_3 , have been observed (see e.g., Harju et al. 2017 for a recent account), as well as $^{15}\text{NH}_3$ and $^{15}\text{NH}_2\text{D}$ (Gerin et al. 2009).

The astrophysical relevance of the ammonium ion, NH_4^+ , stems from its role as a gas-phase forebear of the ammonia molecule through its dissociative recombination. The full family of nitrogen hydrides is initiated by the reaction $\text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H}$ (Zymak et al. 2013). Subsequent exothermic H_2 abstraction reactions lead to the formation of NH_2^+ , NH_3^+ , and NH_4^+ , and their recombination with electrons form the neutral hydrides NH , NH_2 , and NH_3 . Ammonia is supposed to be mainly depleted onto grains at the temperatures of cold dark clouds ($T \sim 10$ K). On the other hand, the grains can free NH_3 molecules upon heating by shocks or in irradiated regions, increasing its gas-phase concentration and leading to appreciable quantities of NH_4^+ , formed by the proton transfer from H_3^+ to NH_3 . Actually, NH_3 has one of the highest proton affinities (PA) of simple interstellar molecules ($\text{PA}[\text{NH}_3] = 8.85$ eV), including H_2 (which has $\text{PA}[\text{H}_2] = 4.39$ eV), so NH_4^+ , once formed, remains stable against further collisions with H_2 .

NH_4^+ has tetrahedral symmetry without a permanent electric-dipole moment. Therefore, it is untraceable by radio astronomy

through its rotational transitions. On the other hand, the deuterated isotopologues NH_3D^+ , NH_2D_2^+ , and NHD_3^+ have sizable permanent electric-dipole moments (approximately 0.26 D, 0.29 D, and 0.24 D, respectively) due to the separation between the center of charge (which remains centered on the central N atom) and the center of mass (which is displaced towards the D atoms), thus making their detection feasible. Indeed, the detection of ammonium in space was claimed through the assignment of an emission line centered at 262,817 GHz (observed both in Orion IRC2 and in Barnard B1-bS) to the 1_0-0_0 transition of NH_3D^+ (Cernicharo et al. 2013). The laboratory rest frequency was derived from the analysis of the high-resolution infrared (IR) spectrum of the ν_4 band, originally made by Nakanaga & Amano (1986) and considerably improved by Doménech et al. (2013). The rest frequency was later confirmed, and its uncertainty was substantially decreased, by the direct measurement of the rotational transition by Stoffels et al. (2016).

Besides their importance as tracers of NH_4^+ , the deuterated isotopologues are also relevant regarding the subject of deuterium fractionation. In cold dark clouds, when CO freezes onto grains and its abundance falls below that of HD, deuteration of other species becomes efficient. This can be explained by the exothermicity (~ 230 K) of the reaction $\text{H}_3^+ + \text{HD} \rightarrow \text{H}_2\text{D}^+ + \text{H}_2$ and the subsequent deuteron transfer to other molecules. Similarly, the exothermic reactions of H_2D^+ and HD_2^+ with HD efficiently produce HD_2^+ and D_3^+ (Hugo et al. 2009) in case of extreme depletion, and the subsequent deuteron transfer to ammonia leads to the deuterated forms of NH_4^+ e.g., $\text{NH}_3 + \text{H}_2\text{D}^+ \rightarrow \text{NH}_3\text{D}^+ + \text{H}_2$. Furthermore, the zero-point energy differences of other reactions involving H or D atoms at temperatures of cold dark clouds ($T \sim 10$ K) also enhance deuteration (Millar 2003). For the case of nitrogen, the reaction $\text{N}^+ + \text{HD} \rightarrow \text{ND}^+ + \text{H}$ has a lower endothermicity than the corresponding reaction with H_2 mentioned above (Grozdanov et al. 2016), leading to an enrichment in deuterated ammonium and ammonia isotopologues. The detected abundances of deuterated variants of ammonia are orders of magnitude higher than what is expected based on the $[\text{D}]/[\text{H}]$ abundance ratio (2.35×10^{-5} in the local universe; Linsky et al. 2006). Detection of other deuterated ammonium isotopologues besides NH_3D^+ will clearly help to constrain and to understand the conditions of formation and distribution of ammonia molecules and, possibly, other nitrogen-containing prebiotic species.

³ CDMS 2018, <https://www.astro.uni-koeln.de/cdms/molecules>.

The only previous spectroscopic laboratory data on the doubly and triply deuterated species (NH_2D_2^+ and NHD_3^+) that we are aware of are the recent publication of the analysis of the ν_1 and ν_6 infrared bands of NH_2D_2^+ (Chang & Nesbitt 2018) and the communication of preliminary results on the analysis of the ν_1 band of NHD_3^+ (Chang & Nesbitt 2013), both recorded at high resolution in a supersonic slit-jet discharge with an infrared difference-frequency laser spectrometer. In this work, we present direct and accurate laboratory measurements of the lowest frequency rotational transitions of NH_3D^+ , NH_2D_2^+ , and NHD_3^+ . The fundamental rotational frequency for NH_3D^+ has already been published previously, and we only confirm its value, while our reported values for the other two isotopologues represent the first available sub-mm wave data.

2. Experimental Methods

The rotational transitions of the deuterated ammonium isotopologues have been measured in the Köln laboratories, exploiting the rotational state dependence of the attachment of He atoms to cations (Brünken et al. 2014, 2017; Doménech et al. 2017, 2018; Jusko et al. 2017). The experiment was performed in the 4 K trapping machine COLTRAP described by Asvany et al. (2010, 2014). The ions were generated in a storage ion source by bombarding the precursor gas mixture with electrons (energy 30–40 eV). For generating NH_3D^+ and NH_2D_2^+ , NH_3 (Messer, 99.8% purity) and a 1:5 mixture of D_2 (Linde, 99.8%) and He (Linde, 99.999%) were admitted to the ion source via two separate leakage valves. The approximate proportions were 1:1:5 for NH_3D^+ and 1:2:10 for NH_2D_2^+ . For NHD_3^+ , we applied a similar mixture using ND_3 (Campro Scientific, 99% atom D) and H_2 (Linde, 99.9999%). A pulse of several 10,000 mass-selected parent ions was injected into the 4 K cold 22-pole ion trap filled with about 10^{14} cm^{-3} He. During the trapping time of 750 ms, cation–helium complexes were formed by three-body collisions. The detection of the resonant absorption of the admitted continuous wave (sub) millimeter radiation by the trapped cold parent cations was achieved by observing the decrease of the number of cation–helium complexes formed. For example, for recording a rotational transition of NH_2D_2^+ , the NH_2D_2^+ –He complexes are counted (typical counts are on the order of 2000) as a function of the (sub)millimeter-wave frequency. The (sub) millimeter-wave radiation was supplied by a rubidium atomic clock–referenced synthesizer (Rohde & Schwarz SMF100A) driving a multiplier chain source (Virginia Diodes, Inc.), covering the range of 80–1100 GHz.

3. Results

We started our measurements by optimizing the experimental conditions using the known $1_0\text{--}0_0$ line of NH_3D^+ , which has been measured by Stoffels et al. (2016) with the same ion trap technique. We confirm their value for $1_0\text{--}0_0$, as well as the inability of the applied setups to detect the $2_0\text{--}1_0$ and $2_1\text{--}1_1$ transitions. All experimental values of this work are summarized in Table 1.

For NH_2D_2^+ , we based our search on the predictions from the high-resolution infrared vibration-rotation spectra of the ν_1 and ν_6 bands recently published by Chang & Nesbitt (2018). In total, we searched for eight rotational lines of NH_2D_2^+ of which five were detected. All measured and predicted transitions are included in Table 1. Figure 1 shows two example

Table 1
Frequencies of Pure Rotational Transitions (in MHz) of Deuterated Ammonium Isotopologues

NH_3D^+	$J'_K \leftarrow J''_K$	This Work	Former Work ^a
	$1_0 \leftarrow 0_0$	262816.8864(8)	262816.904(15)
NH_2D_2^+	$J'_{K'_a K'_c} \leftarrow J''_{K''_a K''_c}$	This Work	Former Prediction ^b
	$1_{10} \leftarrow 1_{01}$	42273.4715(47) ^c	42270(6)
	$1_{11} \leftarrow 0_{00}$	248918.2760(8)	248924(6)
	$2_{02} \leftarrow 1_{11}$	412755.5374(27)	
	$2_{12} \leftarrow 1_{01}$	455534.5852(16)	455540(12)
	$2_{21} \leftarrow 1_{10}$	540046.0112(75)	
	$2_{20} \leftarrow 1_{11}$	560809.9582(37)	
	$3_{03} \leftarrow 2_{12}$	632874.2(17) ^c	
	$3_{13} \leftarrow 2_{02}$	656593.10(82) ^c	
NHD_3^+	$J'_K \leftarrow J''_K$	This Work	
	$1_0 \leftarrow 0_0$	222228.9432(7)	
	$2_0 \leftarrow 1_0$	444415.7929(42)	
	$2_1 \leftarrow 1_1$	444421.2980(18)	

Notes. The final error is given in parentheses in units of the last digit.

^a Stoffels et al. (2016).

^b Chang & Nesbitt (2018).

^c Our prediction.

measurements for NH_2D_2^+ . All lines have been measured at least 7 times and fitted to Gaussian functions, from which line centers and widths were determined. The values quoted in Table 1 represent the combined mean and standard deviation of all measurements. During the measurements, care was taken to avoid power broadening. By this, the line widths are determined only by the Doppler broadening due to the kinetic temperature of the ions in the trap (nominal temperature of $T = 4$ K) and also by a small contribution from the unresolved hyperfine splitting due to the quadrupole moments of the ^{14}N and ^2H nuclei, both with spins of $I = 1$. Effectively, we measure line widths corresponding to $T = 10\text{--}20$ K for NH_2D_2^+ , depending on the observed line. The $1_0\text{--}0_0$ line of NH_3D^+ seems to be more affected by hyperfine splitting, with an effective temperature of $T \approx 30$ K.

For NHD_3^+ , our search was guided by mass-scaling the rotational constants from the other isotopologues, as well as by an estimation based on the available IR-derived rotational constants from the Nesbitt group (Chang & Nesbitt 2013). In contrast to NH_3D^+ , we were able to measure not only the fundamental $1_0\text{--}0_0$ for NHD_3^+ , but also detected the $2_0\text{--}1_0$ and $2_1\text{--}1_1$ transitions. The reason is a more advantageous partition function for NHD_3^+ , as well as more available millimeter-wave power at the lower transition frequencies of the heavier NHD_3^+ .

4. Spectroscopic Parameters

As accurate spectroscopic parameters and predictions for the ground state of NH_3D^+ were already given by Stoffels et al. (2016) and Doménech et al. (2013), we treat here only the isotopologues NH_2D_2^+ and NHD_3^+ . For NH_2D_2^+ , the measured frequencies of the pure rotational lines collected in Table 1 were fit together with the ground state combination differences derived from Chang & Nesbitt (2018) (two duplicated entries had to be trimmed) using the program PGOPHER (Western 2017), rendering the final set of parameters for the ground state given in Table 2. Both sets of data were weighted according

Figure 1. Example measurements of the $2_{12}-1_{01}$ and $1_{01}-0_{00}$ rotational transitions of NH_2D_2^+ , recorded as a depletion signal of the normalized NH_2D_2^+ -He counts. Gray dots are single measurements, the blue line is the average binned in 25 kHz steps, and the black trace is a Gaussian fit.

Table 2
Derived Spectroscopic Parameters (in MHz) from a Fit to
All Measured Transitions

NH_2D_2^+	Parameter	This Work	Former Work ^a
	A	145600.69(33)	145601.7(12)
	B	118963.31(77)	118966.3(12)
	C	103324.30(63)	103328.6(18)
	Δ_J	1.698(46)	2.10(9)
	Δ_{JK}	-0.85(24)	-1.9(4)
	Δ_K	3.08(24)	3.87(3)
	δ_J	0.371(15)	0.18(6)
	δ_K	0.01(20)	0.9(3)
NHD_3^+	Parameter	This Work	Former Work ^b
	B	111117.9794(6)	111120.9(8)
	D_J	1.7539(2)	2.01(7)
	D_{JK}	-1.3763(11)	-2.0(2)

Notes. Numbers in parentheses are one standard deviation in units of the last digit.

^a Chang & Nesbitt (2018).

^b Chang & Nesbitt (2013).

to their different uncertainties, in the kHz range for the present measurements, and ~ 7 MHz for the IR measurements, resulting in a weighted standard deviation of the fit $\sigma_w = 1.02$. The accuracy of the spectroscopic parameters of this work is marginally improved (a factor of $\sim 2-3$) with respect to the former work, since only five rotational lines could be recorded in high resolution but eight parameters are fit. It may be also noted that the δ_k parameter is not significantly different from zero in this fit.

For NHD_3^+ , we only have the three presently measured transition frequencies available; therefore, we cannot provide a least squares fit. Furthermore, since the transitions obey $\Delta K = 0$, we cannot determine C and D_K . With the three experimental frequencies, we have determined B , D_J , and D_{JK} , as shown in Table 2. Also listed in Table 2 are the values quoted by Chang & Nesbitt (2013). Our quoted errors are obtained by propagating the experimental uncertainties through the closed linear relations existing between the three observed frequencies and the three retrieved constants. We assumed that there is no correlation between the experimental frequencies, thus the uncertainties are just added in quadrature with the appropriate coefficients.

5. Conclusion and Outlook

We measured, with kHz-level accuracies, rotational transitions originating from the lowest energy levels of the deuterated ammonium isotopologues NH_3D^+ , NH_2D_2^+ , and NHD_3^+ . Prior to this work, NH_3D^+ was already identified in Orion IRC2 and Barnard B1b (Cernicharo et al. 2013). For the NH_2D_2^+ and NHD_3^+ isotopologues, these rest frequencies will facilitate the search for these ions in the ISM. Cold dark clouds that are highly depleted in C and O are the kind of sources where high-deuterium fractionation is expected. The cold protostellar core B1b is a source where the abundance of deuterated isotopologues of ammonia and the diazenylium ion (N_2H^+) is quite remarkable, as is the presence of other multiply deuterated species, like D_2CS (Marcelino et al. 2005) or D_2S (Vastel et al. 2003). The chemical model used in the interpretation of NH_3D^+ observations in B1b predicted that the abundance of NH_2D_2^+ could be just a factor of two lower

than that of NH_3D^+ . Therefore, one could expect the detection of more deuterated species of the ammonium ion in this or other cold dark clouds. We note, however, that the partition function of NH_2D_2^+ , being an asymmetric top, is more unfavorable, and, even at the low temperature of B1b ($T \sim 12$ K), spectral dilution is to be expected. The slightly higher electric-dipole moment (0.29 D versus 0.26 D) just marginally improves this situation. Although the necessary sensitivity for this detection seems demanding, the ever increasing capabilities of receivers and observatories will likely make it possible in the not-so-distant future. NHD_3^+ has a smaller abundance and dipole moment, but it has higher symmetry (it is a symmetric top, like NH_3D^+), and, therefore, a more favorable partition function, so it may also be soon within the reach of observational radio astronomy. In any case, the frequencies provided in this work will enable those detections.

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Software: PGOPHER (Western 2017).

Note Added in Proof. At the proof stage of this paper, we learned of the very recent publication of the infrared spectrum of the $\text{NHD}_3^+ \nu_1$ band (Chang et al. 2018). A combined analysis of the present rotational data together with the new available combination differences has been performed, allowing us to do a least squares fit. The new values thus derived for the ground state rotational constants of NHD_3^+ are (in MHz) $B = 111117.97939(48)$, $D_J = 1.75390(15)$, and $D_{JK} = -1.37627(95)$.

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