DETECTION OF THE AMMONIUM ION IN SPACE

J. Cernicharo1, B. Tercero2, A. Fuente2, J. L. Domenech3, M. Cueto3, E. Carrasco3, V. J. Herrero3, I. Tanarro3, N. Marcelino4, E. Roueff5, M. Gerin6, and J. Pearson7

1 Departament of Astrophysics, CAB, INTA-CSIC, Ctra Torrejón-Ajalvir Km 4, E-28850 Torrejón de Ardoz, Madrid, Spain; jcernicharo@cab.inta-csic.es
2 Observatorio Astronómico Nacional, Apdo. 112, E-28803 Alcalá de Henares, Spain
3 Instituto de Estructura de la Materia, IEM-CSIC, Serrano 123, E-28006 Madrid, Spain
4 NRAO, 520 Edgemont Road, Charlottesville, VA 22902, USA
5 Luth, Observatoire de Paris, CNRS UMR8102, Place J. Janssen F-92190 Meudon, France
6 LERMA, Observatoire de Paris, CNRS UMR8112 and Ecole Normale Superieure, 61 Avenue de l’Observatoire, F-75014 Paris, France
7 Jet Propulsion Laboratory, 4800 Oak Grove Drive, MC 168-314, Pasadena, CA 91109, USA

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ABSTRACT

We report on the detection of a narrow feature at 262816.73 MHz toward Orion and the cold prestellar core B1-bS which we attribute to the 1_0−0_0 line of the deuterated ammonium ion, NH_3D^+. The observations were performed with the IRAM 30 m radio telescope. The carrier has to be a light molecular species as it is the only feature detected over 3.6 GHz of bandwidth. The hyperfine structure is not resolved, indicating a very low value for the electric quadrupolar coupling constant of nitrogen which is expected for NH_3D^+ as the electric field over the N nucleus is practically zero. Moreover, the feature is right at the predicted frequency for the 1_0−0_0 transition of the ammonium ion, 262817 ± 6 MHz (3σ), using rotational constants derived from new infrared data obtained in our laboratory in Madrid. The estimated column density is (1.1 ± 0.2) × 10^{-13} cm^{-2}. Assuming a deuterium enhancement similar to that of NH_2D, we derive N(NH_3^+) ≃ 2.6 × 10^{-13} cm^{-2}, i.e., an abundance for ammonium of a few 10^{-11}. Key words: ISM: abundances – ISM: individual objects (B1-bS) – ISM: molecules – line: identification – molecular data

1. INTRODUCTION

Two of the major nitrogen-bearing molecules in the interstellar medium (ISM) are N_2 and NH_3, which are predicted to be present in many different media (see, e.g., Nejad et al. 1990; Aikawa et al. 2008; Harada et al. 2010). Whereas N_2 is expected to be largely in the gas phase, NH_3 should be mostly frozen onto the surface of dust grains for temperatures lower than 100 K. Dizayenyllium (N_2H^+) and ammonium (NH_3^+), the protonated ions of N_2 and NH_3, can also provide crucial information for the understanding of interstellar chemistry. The N_2H^+ ion is usually taken as a tracer for the apolar N_2 molecule, which is practically impossible to observe directly using conventional spectroscopic techniques. Detection of dizayenyllium has been reported from many different sources (Turner 1974; Green et al. 1974; Fuente et al. 1993; Daniel et al. 2007). The ion is assumed to be formed almost exclusively through the reaction of N_2 molecules with H_3^+ and to be destroyed mostly in collisions with electrons or with CO molecules. The existence of interstellar NH_3^+ is also predicted in various astrochemical models. In particular, in hot cores (Aikawa et al. 2011) and in other high-temperature environments like active galactic nuclei (Harada et al. 2010), grain evaporation leads to a large increase in the gas-phase concentration of NH_3. Ammonia has a high proton affinity and its protonated derivative, NH_3^+, is predicted to become one of the dominant ions (Aikawa et al. 2008, 2011). Ammonium is also the dominant ion in many cold laboratory plasmas containing hydrogen and nitrogen (Carrasco et al. 2011, 2013). However, the symmetric character of NH_3^+ precludes its observation through radioastronomic methods, and NH_3^+ has never been detected in the ISM. Therefore, the deuterated variant NH_3D^+, possessing a small permanent dipole moment, is more suitable for astronomical searches.

Deuterated ammonia NH_2D was detected in Orion by Rodriguez-Kuiper et al. (1978) and in SgrB2 by Turner et al. (1978). A detailed analysis of the NH_2D/NH_3 abundance ratio in Orion was first provided by Walmsley et al. (1987) who obtained a value of 0.003. Deuterated ammonia is produced through the dissociative recombination of NH_3D^+ with electrons. NHD_2 and ND_3 have also been detected toward a large variety of molecular clouds harboring a large range of kinetic temperatures (Saito et al. 2000; Roueff et al. 2000, 2005; Lis et al. 2002, 2006). Hence, the precursor molecule NH_3D^+, and even more deuterated isotopologues of the ammonium ion, could be present in hot and cold molecular clouds.

In this Letter we report on the first detection in space of the singly deuterated ammonium ion toward the sources Orion-IRc2 and the cold prestellar core B1-bS, a source where the whole family of ^15N and deuterated isotopologues of ammonia and NNH^+ have been detected (Lis et al. 2002, 2006; Saito et al. 2000; F. Daniel et al., in preparation).

2. OBSERVATIONS

The observations presented in this Letter were motivated by the analysis of the Orion line survey carried out with the 30 m IRAM telescope (Tercero et al. 2010, 2011). During the interpretation of the line survey we had to deal with more than 8000 unidentified features. Around 4400 of them have been successfully assigned to several isotopes of CH_3CH_2CN, CH_2CHCN, CH_3COCH, their vibrational levels and those of all abundant molecules, and to the recently detected methyl acetate and the gauche conformer of ethyl formate in this source (Demyk et al. 2007; Carvajal et al. 2009; Margulès...
et al. 2009, 2010; Tercero et al. 2010, 2011, 2012, 2013; Motiyenko et al. 2012; Daly et al. 2013; A. López et al., in preparation). Among the strongest unidentified features, we found one at 262816.7 MHz for \( v_{\text{LSR}} = 9 \) km s\(^{-1}\) (see Figure 1) that was very close to the predicted frequency for the \( J_K = 1_0 - 0_0 \) line of NH\(_3\)D\(^+\). This deuterated species of the ammonium ion was observed in the laboratory by Nakanaga & Amano (1986), through its \( v_4 \) vibrational mode from which rotational constants for the ground state were derived. The molecule was incorporated some time ago to the MADEX code (Cernicharo et al. 2012). The calculated frequency for the \( J_K = 1_0 - 0_0 \) transition of NH\(_3\)D\(^+\) from these rotational constants is 262807 MHz with a ±3σ uncertainty of ±9 MHz. The spectrum shown in Figure 1 shows a line 10 MHz away from the predicted one with a line width similar to those of the NH\(_3\)D\(^+\) lines observed in the same frequency survey. The observed feature, labeled U262816.7 in Figure 1, is practically free of blending from other species. None of the rotational transitions of the recently characterized isotopologues and vibrationally excited states of methyl/vinyl/ethyl cyanide, methyl formate, formamide, or from the abundant species found in Orion (Tercero et al. 2010) matches the frequency of U262816.7, except a possible very weak contribution from \( ^{13}\text{CH}_3\text{OCOH} \) in its first torsional state. Nevertheless, still having 3600 unidentified features in Orion, claiming a possible identification with NH\(_3\)D\(^+\) will be extremely risky and speculative without a more precise frequency measurement in the laboratory (see Section 4).

Prompted by the observed line in Orion, we started a search for a similar feature toward the cold prestellar cloud B1-bS. Complex organic molecules have been recently found in this cold core (Marcelino et al. 2009, 2010; Cernicharo et al. 2012). This source also shows an impressive enhancement in the deuteration of abundant molecules such as H\(_2\)CO, H\(_2\)CS, and NH\(_3\) (Lis et al. 2002, 2006; Marcelino et al. 2005; Saito et al. 2000). With a kinetic temperature of \( \approx 12 \) K, the expected density of lines at 262.8 GHz is rather low. Previous observations at 3 and 2 millimeter wavelengths indicate that only some diatomic and triatomic species will have significant emission at these high frequencies (Marcelino et al. 2005, 2009, 2010; Cernicharo et al. 2012).

The observations were performed at the IRAM 30 m telescope at Pico Veleta (Spain) using the 1 mm Eight Mixer Receivers (EMIR). The back end was a fast Fourier Transform Spectrometer with a spectral resolution of 50 kHz and 37275 channels. Two bands, 1.82 GHz wide each, were centered at 262.816 and 265.886 GHz. These two bands were observed simultaneously in the two orthogonal polarizations of the EMIR 230 GHz receiver. All the observations were performed using the Wobbler Switching mode which produces remarkably flat baselines. Pointing errors were always within 3′. The 30 m beam size at the observing frequency is 11′′. The spectra were calibrated in antenna temperature corrected for atmospheric attenuation using the ATM package (Cernicharo 1985; Pardo et al. 2001).

Two different runs have been used for the present observations. The first one in 2012 July allowed us to detect a feature at the same frequency of the line observed in Orion (262816.73 MHz). During this run, weather conditions were mostly average to moderate summer, with 3–10 mm of precipitable water vapor. Receiver temperatures were between 80–100 K and system temperatures always above 400 K. A second run in 2013 January provided much better weather conditions and sensitivities. The water vapor amount was 1–2 mm and system temperatures between 200 and 250 K. The final spectrum, with all the data averaged, has a sensitivity of 4.9 mK with 48.9 KHz of spectral resolution (3.7 mK after a box smoothing of two channels). The total observing time was 50.8 hr with an averaged system temperature of 249 K.

3. RESULTS

The resulting spectrum from the 30 m telescope observations is shown in Figure 2. The upper panel shows the data at the

![Figure 1](https://via.placeholder.com/150)

**Figure 1.** Observed spectrum toward Orion-IRc2 around the expected frequency of the \( J_K = 1_0 - 0_0 \) line of the deuterated ammonium ion. Identification of all other lines in this frequency range is indicated. The predicted frequency and its 3σ error bar are indicated at the bottom for the Nakanaga & Amano (1986) measurements and at the top for our new laboratory data (Domenech et al. 2013).

![Figure 2](https://via.placeholder.com/150)

**Figure 2.** Observed spectrum toward B1-bS (\( \alpha_{2000} = 03^h33^m21^s34, \delta_{2000} = 31°07′26″7 \)) at the expected frequency of NH\(_3\)D\(^+\) \( J_K = 1_0 - 0_0 \) transition. The upper panel contains the raw data resulting from a total integration time of 51 hr with a spectral resolution of 48.8 KHz (0.054 km s\(^{-1}\)). The bottom panel shows the same data smoothed to 98 KHz. For a LSR velocity of the source of 6.5 km s\(^{-1}\), the derived line frequency for the observed feature is 262816.73 ± 0.1 MHz.
original spectral resolution of 48.9 KHz. The lower panel shows
the same data smoothed to 97.8 KHz. A feature is observed
right at the expected frequency (see below) with a signal-
to-noise ratio of 4.5 and 6 in the upper and lower panels,
respectively. The line is narrow, having a width at half maximum
of 0.65 km s$^{-1}$. It appears as having a double peak that could
be due to the hyperfine structure but it is within the noise
of the data. Due to the central position of the nitrogen atom
in ammonium, the electric field on the nucleus is close to
zero. Hence, the quadrupolar coupling constant of the nitrogen
nucleus is probably negligible. The deuterium atom has a spin
of 1 and could introduce also some hyperfine splitting but the
Corresponding quadrupolar momentum is also expected to be
very low. The identification relies on the close match between the
frequency of the feature with that predicted from the rotational
constants derived with our new laboratory measurements (see
below). Moreover, this is the unique feature detected together
with the lines of CCH $N = 3–2$ over a bandwidth of 3.8 GHz.
Taking into account the low kinetic temperature of the cloud,
no candidates can be found in MADEX, the CDMS, or JPL
catalogs. Hence, the carrier has to be a light species and
no candidates can be found in MADEX, the CDMS, or JPL
Taking into account the low kinetic temperature of the cloud,
omography is well constrained and the abundance of NH$_3$ and its
related species is high.

4. NEW LABORATORY EXPERIMENTS

The density of lines in B1-bS is low at these high frequencies
and the agreement between the frequency of the observed feature
with the predictions of Nakanaga & Amano (1986) is very good.
However, a final assignment relies on the precise determination
from laboratory data of the rotational constants of NH$_3^+$.
We again measured the $v_4$ band of deuterated ammonium with better absolute frequency calibration and more
lines than those reported by Nakanaga & Amano (1986; 2×10$^{-4}$
versus 1×10$^{-3}$ cm$^{-1}$ and 76 versus 61 lines, respectively).
A detailed description of these experiments and calculations
are presented in the accompanying Letter (Domenech et al.
2013). The predicted frequency, calculated from the ground-
state rotational constants derived from a fit with the same
parameters as those of Nakanaga & Amano (1986), is 262817
± 6 MHz ($\pm 3 \sigma$). The difference with the observed frequency
is much less than $1 \sigma$ deviation. Hence, we are fully confident
that the detected feature in Orion and B1-bS corresponds to the
$1_0$–$0_0$ transition of NH$_3^+$.

5. GAS-PHASE CHEMICAL MODELING

The Orion data will be interpreted in a forthcoming paper.
In this work we will concentrate on the analysis of the B1-bS
data. Due to the low dipole moment of NH$_3^+$, $\mu = 0.26$ D,
the Einstein coefficient for spontaneous emission is $A_{ij} = 4.8 \times 10^{-6}$ s$^{-1}$ and the critical density to efficiently pump the $1_0$
rotational level is just of a few 10$^4$ cm$^{-3}$. Hence, we could
assume that the levels of NH$_3^+$ are thermalized at $T_K$
= 12 K (Marcelino et al. 2005; Cernicharo 2012); we derive for
the A species of NH$_3^+$ a column density of (5.5 ± 1.0) \times 10^{12}$
cm$^{-2}$. The total column density of deuterated ammonium
is, hence, $N$(NH$_3^+$) = (1.1 ± 0.2) \times 10^{12}$ cm$^{-2}$. The column
density of molecular hydrogen derived by Hirano et al. (1999) is
1.3 \times 10^{23}$ cm$^{-2}$. Therefore, the abundance of deuterated
ammonium is $\approx 8 \times 10^{-12}$. NH$_2$D has been observed by
Saito et al. (2000) who obtained a column density of (3.2 ± 1.2) \times 10^{14}$ cm$^{-2}$. Hence, the abundance ratio of deuterated
ammonia over the deuterated ammonium ion is $\approx 300$. Assuming
a deuteration enhancement similar to that observed for NH$_2$D
(Saito et al. 2000), the abundance of ammonium is $\approx 1.6 \times 10^{-10}$.

All deuterated isotopologues of ammonia have been detected
in B1-bS (Lis et al. 2002, 2006; Saito et al. 2000) and the
Corresponding gas-phase chemical models have been presented
by Roueff et al. (2005), who were able to obtain satisfactory
agreement between observations and gas-phase models in which
depletion effects of C and O on grains have been simulated.
In these models, ammonia formation results directly from
dissociative recombination of the deuterated ammonium ion
which preferentially gives the NH$_3$ + H product (Öjekull et al.
2004). As a consequence, these models suggest that ammonium
is present at a significative level in this environment and its
possible detection is a major witness of the occurrence of such
a gas-phase chemistry.

Nitrogen chemistry has received considerable recent interest
(Dislaire et al. 2012) with the reevaluation of the starting
step of gas-phase chemical reactions leading to ammonia via
the ammonium ion: N$^+$ + H$_2$ $\rightarrow$ NH$^+$ + H. This reaction
is known to have a slight endothermicity and its efficiency
is very much dependent on the para/ortho state of H$_2$, i.e.,
whether rotational state of H$_2$ is 0/1, respectively. Indeed,
based on low-temperature experiments (Marquette et al. 1985),
the endothermicity involved is 168.5 K with para-H$_2$ and 41.9 K
when H$_2$ is in its “normal” form (1/4 para + 3/4 ortho). These
values should be compared to the energy defect between the
corresponding $J = 0$ and $J = 1$ levels of H$_2$, which is 170.5 K.
Dislaire et al. (2012) have reevaluated the reaction rate constant
involved with the ortho form of H$_2$ with significant differences
compared to the previous estimate of Le Bourlot (1991). An
additional complexity, which is not yet fully understood, is
the occurrence of fine structure of N$^+$, whose levels are also split
by similar amounts. These effects are neglected up to now.

Interestingly enough, thanks to the lower zero-point vibrational
energy of HD, the reactions

$$N^+ + HD \rightarrow ND^+ + H,$$

$$N^+ + HD \rightarrow NH^+ + D$$

are found to have even smaller endothermicity. We derive a value
of 16.3 K for the production of ND$^+$ and 100 K for the channel
toward NH$^+$. Once NH$^+$ or ND$^+$ is produced, they react with H$_2$,
HD, and D$_2$ in a sequence of rapid exothermic reactions until the
formation of ammonium. Walsum and colleagues have been
the first to include both para and ortho forms of H$_2$, related
ions (H$_2^+$, H$_3^+$), and their multiply deuterated isotopologues for
completely depleted regions (Walsum et al. 2004; Flower et al.
2004, 2006a, 2006b), following an earlier suggestion of Pagani et al.
(1992). We have extended this approach to a full
chemical network including oxygen, carbon, sulfur, and nitrogen
(Pagani et al. 2011). For the purpose of the present Letter, we
have updated this chemical network with the recent findings on
nitrogen chemistry reported above on the one hand and included
also some recently determined neutral–neutral reaction rate
constants (Duranlott et al. 2012). As a result, the present model
contains 220 species (including ortho/para forms) of singly
fully deuterated substitutes and more than 4000 reactions.
We display in Figure 3 the corresponding time evolution of the
fractional abundances relative to molecular hydrogen
of NH$_4^+$ and NH$_3$D$^+$. The physical conditions correspond to those
supposed to hold in B1-bS: the proton density is taken as $2 \times 10^5$ cm$^{-3}$, a temperature $T = 12$ K is assumed, and the elemental abundances correspond to model 2 of Roueff et al. (2005). We see that the fractional abundances of NH$_4^+$ and NH$_3D^+$ peak are $\approx 10^{-10}$ (0.7 Myr) and $\approx 10^{-11}$ (1 Myr), respectively, which are consistent with the observational derivations. The abundance ratio $X$(NH$_4^+) / X$(NH$_3D^+$) is $\approx 10$. This value is similar to that found for NH$_3$/NH$_2$D by Saito et al. (2000). For $t = 1$ Myr this ratio is $\approx 2$.

Our chemical models predict that the abundance of NH$_2D^2$ could be a factor of two lower than that of NH$_3D^+$. Consequently, we could expect to detect more deuterated species of the ammonium ion in cold dark clouds. However, more accurate spectroscopic data are needed for NH$_2D^2$ and NH$_D^3$ in order to search for these species.

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REFERENCES

Aikawa, Y., Furuya, V., Wakelam, F., et al. 2011, in IAU Symp. 280, The Molecular Universe, ed. J. Cernicharo & R. Bachiller (Cambridge: Cambridge Univ. Press), 33