



A hollow-cathode THz spectrometer for the study of astrophysical ions and radicals: Benchmarking with N_2H^+ and extended measurements for N_2D^+



Nadine Wehres, Trevor N.K. Cross, Mary L. Rad, Luyao Zou, Anne Carroll, Susanna L. Widicus Weaver*

Department of Chemistry, Emory University, 1515 Dickey Drive, Atlanta, GA, USA

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ABSTRACT

Here we present the first results from a DC-discharge hollow-cathode spectrometer developed for the detection of transient species of astrophysical interest in the THz spectral regime. The new instrument was benchmarked using rotational spectral lines of N_2H^+ and N_2D^+ . The known rotational lines of N_2H^+ were used to optimize ion formation conditions in the discharge. We then used the known spectral lines at frequencies below 700 GHz to further optimize the production efficiency of N_2D^+ , and extended spectral measurements for this ion up to ~ 1 THz. This resulted in the detection of four additional N_2D^+ rotational lines that have not been previously measured experimentally. We have used the observed line positions for N_2D^+ to refine the molecular parameters and extend a more accurate spectral prediction above 1 THz. In addition to being excellent target molecules for benchmarking our spectrometer, N_2D^+ and N_2H^+ are commonly used as tracers of isotopic fractionation in dense interstellar clouds. Therefore, these new measurements are important for guiding astronomical observations using the high frequency bands of the new Atacama Large Millimeter Array (ALMA) and other far-IR observatories.

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1. Introduction

Unstable molecular species such as radicals and ions are important intermediates that drive the chemistry of the interstellar medium (ISM; see [1] for a review). However, laboratory experiments to characterize these unstable molecules are challenging. Production efficiencies for radicals and ions from plasma discharges are very low, and the products are inherently reactive and unstable. Previous laboratory studies have shown that hollow-cathode discharges are particularly efficient at producing protonated molecular ions as compared to other plasma discharge techniques [2]. Given the high abundance of hydrogen in interstellar environments, and hence the fundamental role of protonated molecular ions in the chemistry of interstellar clouds, laboratory studies of such species are crucial for guiding astrochemical investigations. In particular, far-infrared or THz spectrometers dedicated to the study of molecular ions are needed to support observatories such as the Atacama Large Millimeter Array (ALMA), Herschel Space Observatory, and Stratospheric Observatory for Infrared Astronomy (SOFIA). Motivated by this need, we present here a hollow-cathode spectrometer that operates in the THz spectral

regime. We benchmarked this spectrometer using the rotational lines of N_2H^+ (diazenylium) and its deuterated isotopologue N_2D^+ , two molecular ions that are particularly important in the chemistry of dense interstellar clouds.

Small protonated species such as N_2H^+ are important in astrophysics because they can be used to trace their neutral counterparts (i.e. N_2), which are not easily detectable because they lack a permanent dipole moment. Because of their chemical simplicity and their relatively high abundance, these ions are also widely used to trace isotopic fractionation in cold dense cores [3–5]. N_2H^+ and its isotopologues are particularly important because other tracers such as HCO^+ and DCO^+ freeze out at earlier times, leaving N_2H^+ and its isotopologues as the only viable tracers of gas-phase chemistry. As the deuterium fractionation increases with decreasing temperatures, N_2H^+ and N_2D^+ are also often used to trace gas kinematics, as well as the physical and chemical conditions towards CO-depleted dense cloud cores [6–9]. We began with these two ions as our molecular targets because of their importance in astrochemistry, and because of their relatively straightforward production in a laboratory setting as compared with larger molecular systems.

N_2H^+ was first detected observationally in the ISM by Turner [10] in 1974. The unidentified line, or “U”-line, showed hyperfine splitting, and the carrier species was assumed to be a molecule

* Corresponding author.

with a total nuclear spin of 1, therefore likely containing nitrogen. Based on ab initio calculations, Green et al. [11] suggested N_2H^+ as the carrier of this “U”-line. A follow-up observational study with higher resolution then unambiguously confirmed the identification of N_2H^+ as the carrier of this line [12]. Subsequently, the first laboratory spectra of the $J'-J'' = 1-0$ transition of N_2H^+ and N_2D^+ were measured [13]. This high-resolution experiment allowed for the observation of the three hyperfine components of the N_2H^+ line. Since this original laboratory work, many experiments [14–20] have been dedicated to obtain the high-resolution laboratory spectrum of N_2H^+ , for which the pure rotational spectrum has now been measured up to 2 THz. Furthermore, excited vibrational states of both N_2H^+ and N_2D^+ have been reported in recent studies [19]. The ^{15}N containing isotopologues of N_2H^+ and N_2D^+ were also recently studied [21]. The most recent laboratory study by Cazzoli et al. [20] lists the hyperfine splittings for N_2H^+ up to the $J'-J'' = 4-3$ transition. This study includes the most recent ground state spectroscopic parameters of N_2H^+ based on the observed hyperfine splitting.

The spectrum for N_2D^+ has not been fully characterized yet, but has been experimentally measured for the lower-lying rotational lines up to the $J'-J'' = 9-8$ rotational transition at 693.806 GHz [15,18,19]. The hyperfine splitting was studied in a combined observational and laboratory study [18] leading to the determination of the rotational and distortion constants, as well as quadrupole coupling constants and spin-rotational constants. Measurements of higher rotational lines for N_2D^+ above 700 GHz have not been reported in the literature.

Here we present the design of our hollow-cathode instrument dedicated for the study of transient species of astrophysical interest, and benchmarking trials performed using the N_2H^+ and N_2D^+ molecular ions. We present the experimental details, the spectrometer benchmarking tests using known lines of N_2H^+ and N_2D^+ , new measurements of N_2D^+ lines above 700 GHz, and the associated refined spectral fit and prediction for N_2D^+ . We also include an outlook on the capabilities of the new spectrometer, and discuss its application to and relevance for measurements supporting far-infrared observatories.

2. Experimental

The experiment utilizes a DC-discharge hollow-cathode coupled with a direct absorption THz spectrometer. The hollow-cathode is based on the designs of Amano and coworkers [2], and the THz

spectrometer is based on our previous experiments [22,23]. A schematic diagram of the instrument is shown in Fig. 1. The instrument consists of a 1.4 m long copper tube that is 5 cm in diameter. The copper tube is housed in a ~ 2 m long PVC tube with an inner diameter of ~ 9 cm. The PVC tube is sealed on both ends with Teflon windows that allow for transmission of the THz radiation. The cathode is held in place within the PVC tube by Teflon spacers.

The copper tube is grounded and wrapped by a copper coil that can be used for cooling the cathode during operation; the copper coil is soldered to the cathode using silver solder. In the experiments presented here, liquid nitrogen (Nexair) was used as the coolant. The stainless steel anode is inserted into the spectrometer through a Teflon housing, suspended above a hole in the center of the copper cathode, and connected to a high voltage power supply (Spellman SL2000). The anode is cooled by recirculating ethylene glycol at a temperature of -14 °C (259 K) employing a recirculating chiller (Super RMT Lauda Brinkmann, model RM6).

Gas flow into the cathode was controlled using MKS mass-flow controllers. A 50/50 gas mixture containing N_2 (NexAir, ultrahigh purity) and either H_2 (NexAir, ultrahigh purity) or D_2 (Cambridge Isotopes Laboratories, 99.8% D_2 , 0.2% HD) was seeded in Argon buffer gas (NexAir, ultrahigh purity) and injected at end of the cell near the radiation source. A combined rotary vane and roots blower pumping system with an effective pumping speed at the cell of ≈ 250 L s^{-1} was used to maintain a pressure of ~ 50 mTorr during operation. The partial pressures of the gases were optimized for highest signal intensity of the N_2H^+ signal, and held constant at about 5 mTorr for H_2 (or D_2) and N_2 , and at about 40 mTorr for Argon that was used as buffer gas. It was found that increasing the ratio of N_2 and H_2 (D_2) with respect to Argon did not increase the signal intensity of N_2H^+ (or N_2D^+). Argon was crucial to ensure stability of the discharge as well as production of N_2H^+ . Highest signal intensity was measured at a constant current of 375 mA and 270 V discharge conditions. No N_2H^+ was detected when water or ethylene glycol was used to cool the cathode instead of liquid nitrogen.

The millimeter/submillimeter signal was generated by multiplication of the output signal from an analog signal generator (Agilent Technologies, E8257D PSG, with options 1EA, UNU, 550, and UNT). The output signal was frequency modulated at 15 kHz and then multiplied to the appropriate frequency range using a frequency multiplier chain (AMC-S268, Virginia Diodes, Inc.). This multiplier chain has several sets of multipliers and power amplifiers, enabling almost full frequency coverage from 50 to 1000 GHz. The specific components used in the experiments

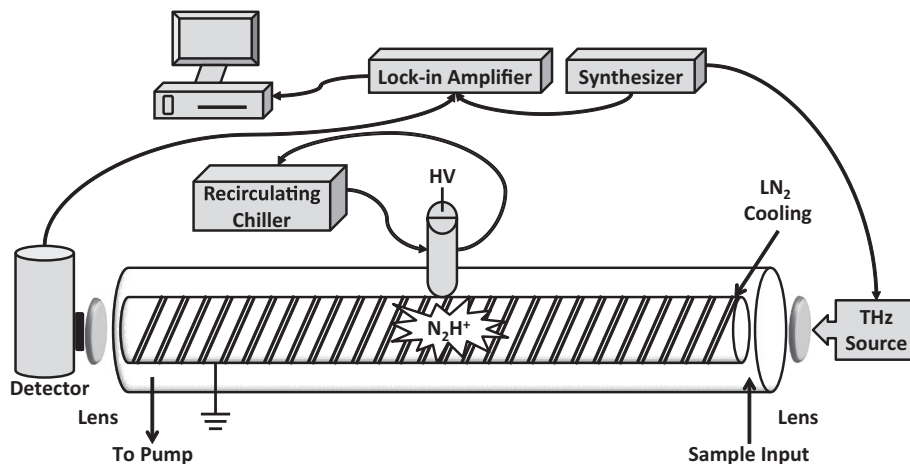


Fig. 1. Schematic diagram of the experimental setup employing a DC-discharge hollow-cathode instrument combined with a THz direct absorption spectrometer.

described here required an initial frequency from the signal generator between 23.3 and 37 GHz. This frequency was used as input into a WR10 \times 3 tripler (AMC-S268, Virginia Diodes, Inc.), which was connected to the appropriate multipliers in order to obtain output ranges of 270–460 GHz, 430–700 GHz, 650–800 GHz, and 700–1000 GHz. Some frequencies above 1 THz were also accessible, despite being outside of the specified operating range of the multipliers. The output radiation from the tripler was focused into the cathode using appropriate Teflon lenses (Edmund Optics). After a single pass through the hollow-cathode instrument, the radiation was focused with another Teflon lens and detected using a hot electron Bolometer (QMC Ltd., QFI/XBI). The output signal was processed using a lock-in amplifier (Stanford Research Systems, Model SR 830 DSP) which was locked to the modulation frequency of the input radiation

(15 kHz) using a 2f detection scheme. The output of the lock-in amplifier was recorded as a function of frequency by a custom computer-aided scanning routine. The spectral resolution was limited to 60 kHz by the step size used in the spectral acquisition; uncertainties in line center frequencies were determined through Gaussian fitting of the observed lines. Line widths ranged from 300 kHz on the lower end of the scanning range, to 2 MHz at frequencies near 1 THz. Most spectra were acquired with no averaging; the spectra for the new lines of N_2D^+ recorded at higher frequencies were acquired with 2 averages and a longer lock-in time constant to further decrease the noise level. It was experimentally verified that the time constant of the lock-in did not induce a shift in the frequencies of the observed lines based on the direction of the frequency sweep during spectral acquisition.

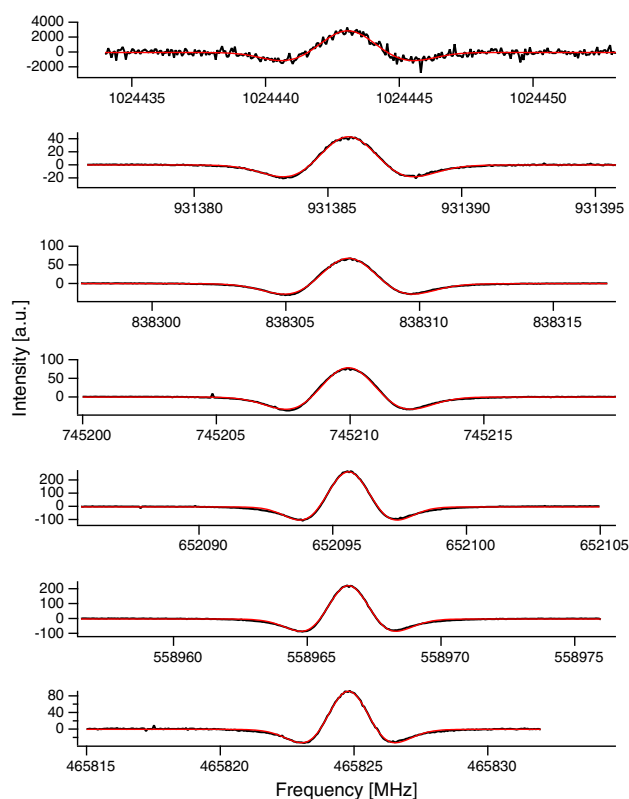


Fig. 2. Known transitions of N_2H^+ based on [19], used to benchmark the hollow-cathode instrument. The experimental spectra are shown in black, and the best-fit second derivative Gaussian lineshapes used to determine the center frequency of each line are shown in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

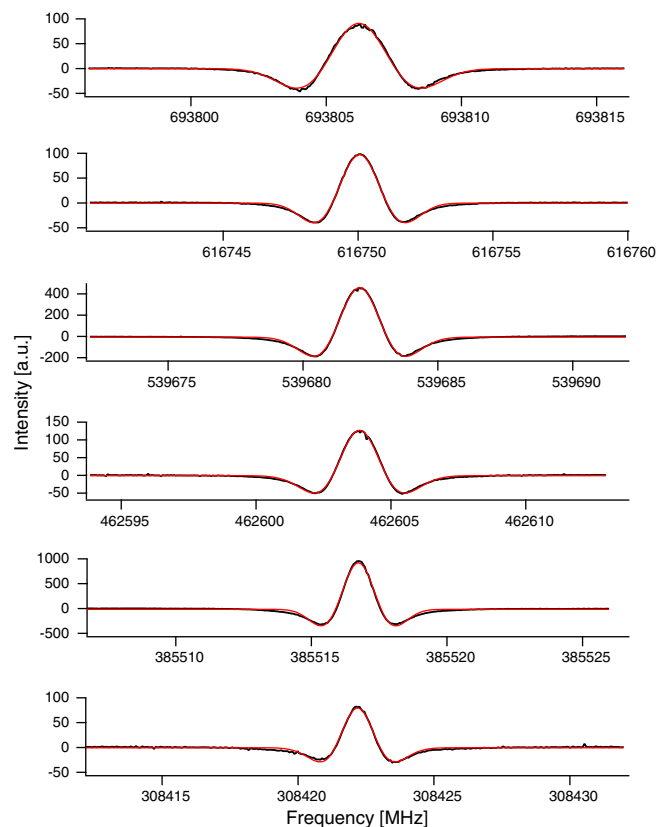


Fig. 3. Previously measured transitions of N_2D^+ . The experimental spectra are shown in black, and the best-fit second derivative Gaussian lineshapes used to determine the center frequency of each line are shown in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

Observed transitions of N_2H^+ compared to previous measurements. All uncertainties are reported as 1σ values.

$J'-J''$	Amano et al. [19] (MHz)	Cazzoli et al. [20] (MHz)	This work (MHz)
4–3	–	372670.5135 (0.0150)	–
4–3	372672.509 (0.050)	372672.4633 (0.0150)	372672.4715 (0.0031)
4–3	–	372674.8760 (0.0150)	–
5–4	465824.777 (0.030)	465824.7770 (0.0300)	465824.7868 (0.0030)
6–5	558966.503 (0.030)	558966.5030 (0.0300)	558966.5397 (0.0026)
7–6	652095.570 (0.030)	652095.5700 (0.0300)	652095.5914 (0.0030)
8–7	745209.868 (0.030)	745209.8680 (0.0300)	745209.9354 (0.0033)
9–8	838307.1 (1.0)	–	838307.3434 (0.0030)
10–9	931386.2 (1.0)	–	931385.7690 (0.0038)
11–10	1024443.2 (1.0)	1024443.0250 (0.0300)	1024443.0723 (0.0243)

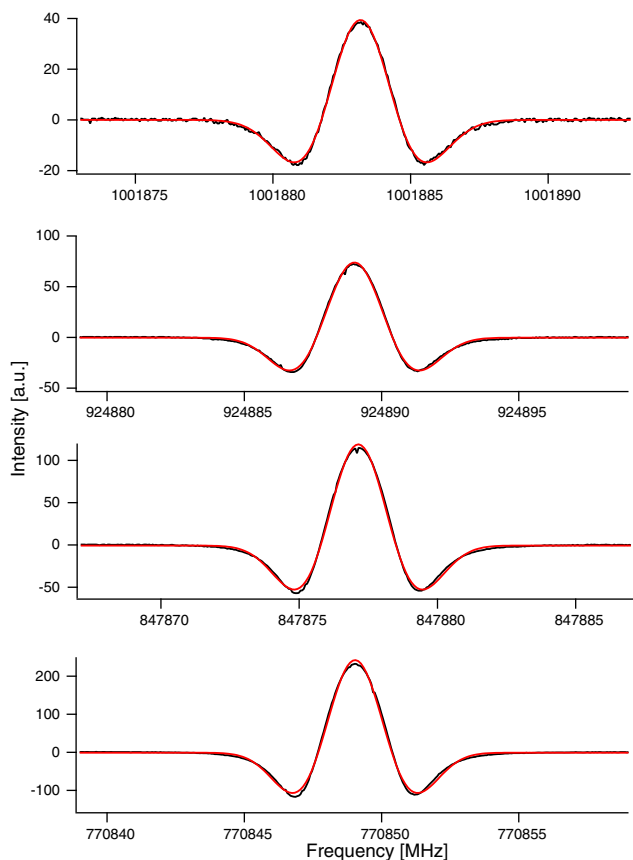


Fig. 4. Newly-observed transitions of N_2D^+ . The experimental spectra are shown in black, and the best-fit second derivative Gaussian lineshapes used to determine the center frequency of each line are shown in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

3.1. THz spectroscopy of N_2H^+

The measured spectra for N_2H^+ are shown in Fig. 2, along with the best-fit second derivative Gaussian lineshape for each line. These best-fit lines were used to determine the center frequencies of the observed lines. In Table 1 we give a summary of the observed transitions, including the quantum numbers for the transition ($J'-J''$) and a comparison between our measurements and the previously measured frequencies as given by Amano et al. [19] and Cazzoli et al. [20]. There is excellent agreement between our measurements and those previously reported.

3.2. THz spectroscopy of N_2D^+

We also searched for the known rotational transitions of N_2D^+ using the same initial settings as for N_2H^+ , and confirmed its formation within the hollow-cathode discharge. Figs. 3 and 4 show the known transitions for N_2D^+ and the newly measured lines, respectively. The best-fit second derivative Gaussian is also shown for each line in these figures; these best-fit lines were used to determine the center frequencies of the observed lines. In Table 2 we give a summary of the observed transitions, including the quantum numbers for the transition ($J'-J''$) and a comparison between our measurements and the previously measured frequencies as given by Dore et al. [18] and Amano et al. [19]. For the transitions that have not been previously observed, we also list the calculated transitions as given in the Cologne Database for Molecular Spectroscopy (CDMS) [24,25], and in the Jet Propulsion Laboratory Catalog for Molecular Spectroscopy (JPL catalog) [26]. There is excellent agreement between our measurements and those previously reported. However, for the newly-measured lines, there are discrepancies ranging from 0.2 to 4 MHz between the experimental values and the frequency predictions included in the CDMS and JPL catalogs. While it is not surprising for there to be discrepancies between catalog predictions and measured values, differences of this magnitude are significant when comparing to observational spectra, which often have spectral resolutions ≤ 1 MHz. Additionally, given that N_2H^+ and N_2D^+ are often used to trace the kinematics in dense interstellar clouds, these new measurements are crucial for guiding astronomical observations where even slight shifts in frequency can confuse spectral interpretation.

Using our experimental results, a new spectral analysis has been carried out for N_2D^+ using the CALPGM suite of programs [27]. A standard linear top Hamiltonian including the rotational constant (B) and the centrifugal distortion constant (D) was used. We include in this analysis all previously-measured lines for N_2D^+ as reported by Dore et al. [18] and Amano et al. [19], and all new lines measured in the current work. In cases where new measurements have been conducted for a previously-measured transition, we used the line frequencies determined in the current work. The refined parameters obtained from the current analysis of N_2D^+ are given in Table 3 and compared to the results given by Dore et al. [18] and Amano et al. [19].

We have not included the nuclear quadrupole coupling constants (eQq_1 and eQq_2) or the spin-rotation constants (C_1 and C_2) in the present analysis since the hyperfine splitting was not resolved in our measurements. Although these values are reported by Dore et al. [18], they were determined through a fit of the hyperfine components of the $J'-J'' = 1-0$ transition, while the B and D constants were determined in a separate analysis. Likewise, Amano et al. [19] only report the B and D parameters. We therefore limit our comparison to those parameters. The values for B and D

Table 2
Observed transitions of N_2D^+ compared to previous measurements and catalog predictions. All uncertainties from this work are reported as 1σ values.

Previously-Observed Lines $J'-J''$	Amano et al. [19] (MHz)	Dore et al. [18] (MHz)	This work (MHz)
4–3	–	308422.267 (0.020)	308422.1889 (0.0035)
5–4	–	385516.721 (0.020)	385516.7336 (0.0030)
6–5	–	462603.852 (0.020)	462603.8352 (0.0024)
7–6	539682.101 (0.030)	–	539682.0966 (0.0023)
8–7	616750.016 (0.030)	–	616750.0565 (0.0024)
9–8	693806.156 (0.030)	–	693806.2113 (0.0037)
Newly-Measured Lines $J'-J''$	CDMS [24,25] (MHz)	JPL [26] (MHz)	This work (MHz)
10–9	770849.0342 (0.0324)	770850.6058 (1.1884)	770849.0345 (0.0031)
11–10	847877.1579 (0.0447)	847879.3354 (0.1634)	847877.1391 (0.0028)
12–11	924889.0647 (0.0597)	924891.9705 (2.1736)	924889.0102 (0.0026)
13–12	1001883.2828 (0.0778)	1001887.0478 (2.8154)	1001883.1800 (0.0028)

Table 3Spectroscopic parameters of N₂D⁺ determined from this work using SPFIT in the CALPGM program suite [27] and compared to literature values [18,19].

Parameter (MHz)	Dore et al. [18] ^a (MHz)	Amano et al. [19] ^a (MHz)	This work ^b (MHz)
B	38554.7523(26)	38554.7571(12)	38554.7467(11)
D	0.061552(47)	0.061571(21)	0.0614743(44)
<i>e</i> Q <i>q</i> ₁	−5.6587(42)	–	–
<i>e</i> Q <i>q</i> ₂	−1.3713(73)	–	–
C ₁	4.80(84) × 10 ^{−3}	–	–
C ₂	7.6(11) × 10 ^{−3}	–	–
Microwave RMS	–	–	0.056

^a It is not clear whether the uncertainties reported for the previous studies have been processed using the PIFORM program [28] to obtain standard uncertainties. Therefore, the uncertainties listed here are taken directly from those reported in the literature.

^b Uncertainties reported for the current work are standard errors determined from the output of SPFIT and processed using the PIFORM program [28].

obtained here agree well with the studies of Dore et al. [18] and Amano et al. [19], though not within the reported uncertainties. It is not clear whether the uncertainties reported for the previous studies have been processed using the PIFORM program [28] to obtain standard uncertainties; the uncertainties listed in the tables are taken directly from those reported in the literature. Therefore, a direct comparison cannot easily be made. Nonetheless, reasonable agreement is obtained given the degree to which the work presented here extends the measurements. Most significantly, our work provides refinement on the centrifugal distortion constant, which is now determined to an order of magnitude greater precision. Given this improvement, a spectral prediction based on this refined fit is valuable to guide higher frequency observational studies that rely upon accurate line center information. The associated SPFIT fit file for the analysis presented here and the refined spectral prediction up to 2 THz have been included in the [Supplementary data](#).

4. Conclusions and relevance to astrophysics

Here we present a new DC-discharge hollow-cathode instrument combined with a THz spectrometer that is dedicated to spectral characterization of radicals and ions of astrophysical interest. We benchmarked the instrument by observing known transitions of N₂H⁺ and N₂D⁺, and measured four previously unobserved rotational transitions of N₂D⁺ at frequencies above 700 GHz. We present an updated analysis of the N₂D⁺ spectrum incorporating these new measurements, along with the associated molecular parameters and a refined spectral prediction.

Laboratory spectrometers with these demonstrated capabilities are needed to support the rapidly advancing field of far-infrared observational astronomy. Unstable molecules such as radicals and ions drive the chemistry of space. However, as is demonstrated by the work presented here, spectral information for even the simplest species is often not available at the higher frequencies accessed by new observatories such as Herschel, ALMA, and SOFIA. Given the new broadband and highly sensitive heterodyne receivers that have been implemented at these far-IR observatories, detection of molecular lines is now a routine part of almost all astronomical observations. Laboratory instruments such as the one presented here, that offer a combination of rapid spectral acquisition and high sensitivity coupled with formation mechanisms for unstable molecules, are the best path forward for supporting these observational studies.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jms.2014.09.012>.

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