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Laboratory rotational ground state transitions of NH_3D^+ and CF^+

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ABSTRACT

Aims. This paper reports accurate laboratory frequencies of the rotational ground state transitions of two astronomically relevant molecular ions, NH_3D^+ and CF^+ .

Methods. Spectra in the millimetre-wave band were recorded by the method of rotational state-selective attachment of He atoms to the molecular ions stored and cooled in a cryogenic ion trap held at 4 K. The lowest rotational transition in the *A* state (ortho state) of NH_3D^+ ($J_K = 1_0-0_0$), and the two hyperfine components of the ground state transition of CF^+ ($J = 1-0$) were measured with a relative precision better than 10^{-7} .

Results. For both target ions, the experimental transition frequencies agree with recent observations of the same lines in different astronomical environments. In the case of NH_3D^+ the high-accuracy laboratory measurements lend support to its tentative identification in the interstellar medium. For CF^+ the experimentally determined hyperfine splitting confirms previous quantum-chemical calculations and the intrinsic spectroscopic nature of a double-peaked line profile observed in the $J = 1-0$ transition towards the Horsehead photon-dominated region (PDR).

Key words. astrochemistry – ISM: molecules – methods: laboratory: molecular – line: identification – molecular data

1. Introduction

Molecular cations are important constituents of the interstellar medium (ISM). Exothermic and barrierless ion-molecule reactions are the key drivers of the chemistry in many interstellar environments, such as the diffuse medium, photon-dominated regions (PDRs), and dense, cold molecular clouds. In many cases molecular cations have also proven to be excellent probes of the physical conditions in a variety of astronomical sources. Recent examples are the detection of ArH^+ in the diffuse galactic and extragalactic interstellar medium as a tracer of almost purely atomic hydrogen gas (Barlow et al. 2013; Schilke et al. 2014; Müller et al. 2015), and the observation and use of the ortho/para-ratio of H_2D^+ as a chemical clock to determine the age of a molecular cloud (Brünken et al. 2014b). One essential prerequisite for the detection and use of new molecular probes is the knowledge of highly accurate ($\Delta\nu/\nu < 10^{-6}$) rotational transition frequencies from laboratory experiments. In the case of reactive molecular ions, standard absorption spectroscopy through electrical discharges is often hampered by production yields of the target ions that are too low and spectral contamination from a multitude of simultaneously generated molecular species. In particular rotational ground state transitions, often the most readily observed lines in the cold interstellar medium, are difficult to measure in the high excitation conditions of a laboratory plasma. These limitations can be overcome by employing sensitive action spectroscopic techniques on mass-selected ions in cryogenic ion traps. In our group we have in recent years developed several of these techniques based on laser induced reactions (LIR; Schlemmer et al. 1999, 2002) and demonstrated their potential to determine highly accurate rotational

transition frequencies (Asvany et al. 2008; Gärtner et al. 2010, 2013; Jusko et al. 2014).

Here we present high-resolution measurements of the rotational ground state transitions of NH_3D^+ and CF^+ , whose astrophysical importance and previous laboratory studies are summarized in the remainder of this section. In Sect. 2, we introduce the experimental setup and the method of rotational state-selective attachment of helium atoms to mass-selected ions stored in a cryogenic (4 K) 22-pole ion trap instrument (Asvany et al. 2014) that was previously applied in our group for rotational spectroscopy of C_3H^+ (Brünken et al. 2014a), and we present experimental results and spectroscopic analyses on both ions. In Sect. 3 we discuss our results in the context of recent astrophysical observations.

The ammonium ion, NH_4^+ , is related to nitrogen chemistry in the interstellar medium, which has obtained renewed interest in recent years owing to astronomical observations of light nitrogen hydrides (NH , NH_2 , NH_3) with *Herschel*/HIFI in cold protostellar (Hily-Blant et al. 2010; Bacmann et al. 2010) and diffuse gas (Persson et al. 2010, 2012). In the cold interstellar medium NH_4^+ , which is formed by subsequent hydrogenation reactions starting from N^+ with H_2 , is assumed to be the gas-phase precursor of the ubiquitous ammonia molecule, NH_3 , which is the dominant product of its dissociative recombination with electrons (e.g. Le Bourlot 1991; McElroy et al. 2013, and references therein). Ammonia, once formed either by the above gas-phase route or by sublimation from ices in warmer regions of the ISM, can be transformed back to NH_4^+ by exothermic proton transfer reactions, dominantly with H_3^+ , so that the chemistry of these species is closely linked. The high deuterium fractionation of ammonia seen in many dark clouds (Roueff et al. 2000; Saito et al. 2000; Lis et al. 2002, 2006; van der Tak et al. 2002) is caused

primarily by similar transfer reactions with deuterated forms of H_3^+ , producing deuterated variants of NH_4^+ , followed by dissociative recombination with electrons (Rodgers & Charnley 2001; Flower et al. 2006; Sipilä et al. 2015).

Whereas NH_4^+ , a spherical top molecule, is not observable by radio astronomy, its mono- (and doubly-) deuterated forms have comparatively large permanent electric dipole moments (0.26 D in the case of NH_3D^+ , Nakanaga & Amano 1986) and possess rotational transition lines in the mm- and sub-mm wavelength range. The monodeuterated variant NH_3D^+ was recently tentatively detected towards the massive star-forming region Orion-IRc2 and the cold prestellar core B1-bS (Cernicharo et al. 2013). In both sources a spectral feature at 262 816.7 MHz was observed and identified as the $J_K = 1_0-0_0$ rotational ground state transition of NH_3D^+ based on accompanying high-resolution infrared data of the ν_4 vibrational band (Doménech et al. 2013), which significantly reduced the uncertainty of the transition frequency prediction compared to an earlier study (Nakanaga & Amano 1986). Nevertheless, the reported frequency uncertainty of ± 6 MHz is comparable to the typical spacing between spectral features in a line-rich source like Orion, allowing for ambiguity in the line assignments. Here we present a direct laboratory measurement of the observed rotational transition, with two orders of magnitude higher accuracy, lending additional support to the identification of NH_3D^+ in space.

The fluoromethylidyne cation, CF^+ , has been detected in a variety of interstellar environments, namely in two PDRs (Neufeld et al. 2006; Guzmán et al. 2012a), in several diffuse and translucent galactic gas clouds (Liszt et al. 2014, 2015), in the envelope of a high-mass protostar (Fechtenbaum et al. 2015), and recently even in an extragalactic source (Muller et al. 2016). The main interest in CF^+ observations lies in its formation pathway: CF^+ is formed by an exchange of the fluorine atom of hydrogen fluoride (HF) in a bimolecular reaction with ionized atomic carbon (C^+), and thus can serve as a molecular tracer for HF and C^+ (Neufeld et al. 2005, 2006; Guzmán et al. 2012a; Liszt et al. 2015). Both of these species are keystones in astrochemistry, HF is the main reservoir of fluorine in the ISM and a useful probe of molecular H_2 column density, whereas C^+ is the main gas-phase reservoir of carbon in the diffuse ISM, providing the dominant cooling process via its $^2P_{3/2}-^2P_{1/2}$ fine structure transition at 158 μm (1.9 THz). Neither the C^+ fine structure line nor the rotational ground state line of HF (at around 1.2 THz) are observable from the ground, whereas CF^+ (with a rotational constant of around 51.3 GHz) has many accessible transitions at mm wavelengths. Its rotational spectrum is well studied up to 1.6 THz by absorption spectroscopy through magnetically enhanced negative glow discharges of CF_4 and H_2 (Plummer et al. 1986; Cazzoli et al. 2010, 2012). The CF^+ ground state transition, however, had not been observed in the laboratory plasma. In fact, the highest resolution measurement of this line so far comes from its astronomical observation in the Horsehead PDR (Guzmán et al. 2012a). Interestingly, the authors found a double-peaked feature at the expected CF^+ ($J = 1-0$) transition frequency in this narrow-line source, which they originally attributed to kinematic effects based on similarity to the observed C^+ line profile. Shortly thereafter, however, quantum chemical calculations revealed that the line profile can be explained spectroscopically by hyperfine splitting (hfs) caused by the non-zero nuclear spin ($I = 1/2$) of the fluorine nucleus (Guzmán et al. 2012b). The low temperatures achievable in our cryogenic ion trap experiments enabled us to resolve the hyperfine splitting of the CF^+ ground state transition experimentally for the first time

and to compare the derived fluorine spin rotation constant with the quantum chemical calculations.

2. Laboratory measurements and results

The ground state rotational transitions of NH_3D^+ and CF^+ were recorded in a cryogenic 22-pole ion trap instrument (FELion, almost identical to the one described in Asvany et al. 2014) with the method of rotational state-selective attachment of He atoms to the cold and mass-selected ions that was developed in our laboratory and recently applied to measure several rotational lines of linear C_3H^+ (Brünken et al. 2014a). In the following we provide a brief description of the general method, before giving specific details on the NH_3D^+ and CF^+ experiments and analysis.

Ions are produced in an ion storage source by electron impact ionization of suitable precursor gases. After selecting the target ions with a quadrupole mass-filter, they enter the 22-pole ion trap in a short (few 10 ms) pulse, where they are stored and efficiently cooled close to the ambient temperature (4 K) via collisions with helium gas, which is constantly admitted to the trap. Ternary collision processes of the stored ions with helium lead to the formation of weakly bound ion-He complexes, which in turn can dissociate again by binary collisions with the helium atoms (collision induced dissociation; CID). At the low temperature and high number density of He ($\sim 5 \times 10^{14} \text{ cm}^{-3}$) in the trap, up to 10% of the primary ions are converted to ion-He complexes at equilibrium, which is typically reached after several 100 ms storage time. Rotational spectra are recorded by irradiating the stored ions continuously with radiation from a narrow-bandwidth, mm-wave source, and counting the number of He-ion complexes formed after a fixed storage time as a function of excitation frequency. For this we make use of the fact that the helium attachment rate depends on the internal (rotational) excitation of the ion, as described in Brünken et al. (2014a). To account for long-term fluctuations in the ion signal, we perform alternating measurements at the set frequency and a fixed offset frequency and give the spectroscopic signal in relative units scaled to the ion-He counts recorded at the offset position (depletion signal $S = \frac{N_{\text{off}} - N_{\text{on}}}{N_{\text{off}}}$).

2.1. Rotational transitions of NH_3D^+

NH_3D^+ was produced in the ion storage source from a mixture of ammonia (NH_3) and D_2 at a ratio of 2:1 and pressure of $\sim 5 \times 10^{-6}$ mbar in combination with an electron impact ionization energy of 20 eV. For the measurements around 10 000 mass-selected NH_3D^+ ions ($m = 19$ u) were stored in the trap at 4 K in the presence of helium gas at number densities between $(4-7) \times 10^{14} \text{ cm}^{-3}$, resulting in 400–700 observed $\text{NH}_3\text{D}^+\bullet\text{He}$ complexes after a storage time of 600 ms. Ions were irradiated continuously with the output of a narrowband ($\Delta\nu \ll 1$ kHz) frequency multiplier chain (Virginia Diodes Inc. WR9.0M-AMC in combination with a WR2.8 \times 3 tripler, yielding a total frequency multiplication by 27) driven by a rubidium-clock referenced microwave synthesizer (Rohde und Schwarz SMF100A). For the spectrum shown in Fig. 1 the radiation was coupled to the trap via a conical horn antenna through a 0.8 mm thick CVD diamond window (diameter 18 mm) without additional focusing elements, resulting in $\sim 30 \mu\text{W}$ radiation power in the trap region.

The rotational $J_K = 1_0-0_0$ ground state transition of ortho- NH_3D^+ recorded in this way is shown in the upper panel of Fig. 1. We observe a peak depletion signal of $\sim 4\%$ in the number of $\text{NH}_3\text{D}^+\bullet\text{He}$ complexes at the transition

Table 1. Measured and predicted rotational transitions of NH_3D^+ (in the vibrational ground state).

J	K	J'	K'	Frequency [MHz]	o-c [kHz] ^(a)	Reference
1	0	0	0	262816.904(15)	0	exp. this work
2	1	1	1	525571.97(28)		pred. this work
2	0	1	0	525589.65(13)		pred. this work
3	1	2	1	788247.58(49)		pred. this work
3	0	2	0	788274.10(51)		pred. this work

Notes. Numbers in parentheses represent experimental or predicted 1σ uncertainties. Predictions up to $E_{\text{low}} = 30 \text{ cm}^{-1}$. ^(a) Observed-calculated (o-c) differences with respect to the spectroscopic parameters given in Table 2.

frequency of 262 816.904(15) MHz, with a linewidth (FWHM) of 213(13) kHz obtained by fitting a Gaussian line-shape function to the data. Assuming a purely Doppler broadened line this would correspond to a kinetic ion temperature of 24(3) K, considerably higher than the ambient trap temperature (4 K, corresponding to a linewidth of 86 kHz). The larger linewidth can partly be explained by unresolved underlying hyperfine structure (hfs) due to the nuclear quadrupole moments of the N and D nuclei in NH_3D^+ , with the main contribution from the D nuclei leading to a splitting of the $J_K = 1_0-0_0$ transition into three main components (with 1:5:3 intensity ratio) separated by ~ 100 kHz (C. Puzzarini, priv. comm.). We indeed observe the appearance of a low-frequency shoulder in the spectrum at the expected position of the weak $F = 1-0$ hyperfine component when increasing the radiation power by a factor of 7, i.e. to a level where the individual hfs components become saturated (see lower panel of Fig. 1). The higher excitation power was achieved by using an elliptical focusing mirror ($f = 43.7$ mm) in combination with a larger diameter (63 mm) z -cut Quartz window to couple the radiation into the trap region. We checked carefully for possible saturation-induced shifts in the derived transition frequency of the unresolved hfs-multiplett. At the lower power settings they are of the order of several kHz and are contained in the stated 15 kHz uncertainty of the fitted line measurement (Table 1).

The prolate symmetric rotor NH_3D^+ contains three identical hydrogen nuclei with spin $I_{\text{H}} = 1/2$ and consequently occurs as an ortho and a para spin isomer with $I_{\text{H},\text{total}} = 3/2$ and $1/2$, respectively. Rotational levels of A symmetry ($K = 0$ and $K = 3n$) belong to the ortho isomer, those of E symmetry ($K = 3n \pm 1$) to the para isomer. Since collisional or radiative transitions between the two spin isomers are highly forbidden, and spin-conversion reactions are likely hindered by substantial barriers and therefore do not proceed (Barlow & Dunn 1987), we expect that the cooled and stored NH_3D^+ ions retain their 1:1 formation ortho/para-ratio, i.e. that half of them belong to the para isomer. For the para $J_K = 2_1-1_1$ ground state transition, we expected a depletion signal similar to that of the observed ortho ground state line. However, integration down to an rms of 0.3% (using 15 kHz steps and a nominal trap temperature $T = 4$ K) in a 3 MHz scan around the predicted line position at 525 572.0(3) MHz resulted in only a tentative 2σ detection of a weak feature at 525 571.16(3) MHz, i.e. within 3σ of its predicted value. There are two possible reasons for the significantly lower depletion signal. First, the achievable radiation power at 525.6 GHz is about a factor 15 less than at 262.8 GHz, resulting in insufficient radiative pumping at the transition frequency. Second, the change in ternary rate coefficient is significantly lower between higher J (or K) levels. Similar arguments hold for the next higher ortho transition, $J_K = 2_0-1_0$, which was not detected after integrating down to an rms level of 0.9%

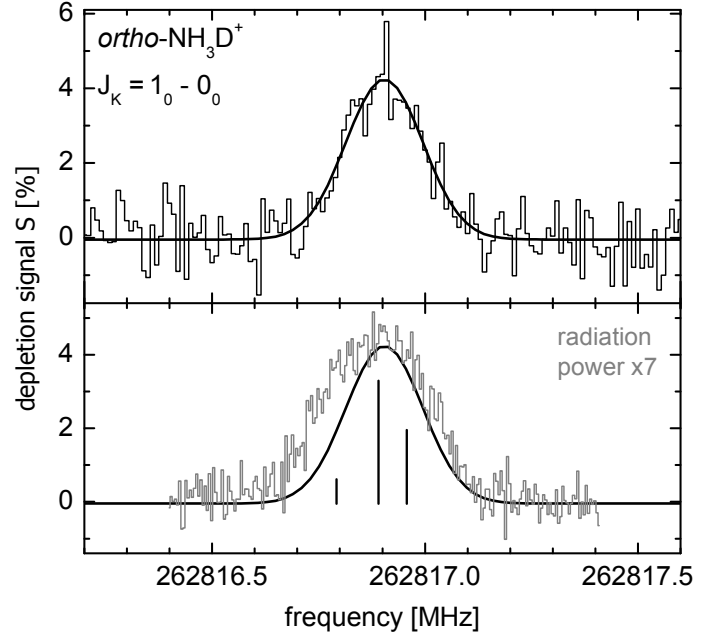


Fig. 1. *Top:* measured rotational ground state transition $J_K = 1_0-0_0$ of ortho- NH_3D^+ (black histogram). About 10 000 mass-selected NH_3D^+ ions were stored for 600 ms in the cryogenic ion trap (4 K) in the presence of a high number density of helium ($\sim 4-7 \times 10^{14} \text{ cm}^{-3}$) and continuous irradiation with tunable narrowband mm-wavelength radiation ($\sim 30 \mu\text{W}$ power in the trap region). The absolute number of helium complexes formed over the storage time was $\sim 400-700$. The spectrum is averaged over 100 iterations, and the line centre position was extracted from fitting a Gaussian line-shape function to the data (black line). *Bottom:* the same line recorded with seven times higher radiation power (grey histogram). The estimated hfs components due to the deuterium nuclear quadrupole moment and their relative intensities are shown as black bars (C. Puzzarini, priv. comm.). The Gaussian fit function of the unsaturated line is shown for comparison (black line).

(at 15 kHz scan step size) in a 2.5 MHz bandwidth centred on the predicted 525 589.65(13) MHz line position, even when increasing the nominal trap temperature to 9 K, i.e. increasing the thermal population of the initial 1_0 level to 20%.

The measured $J_K = 1_0-0_0$ transition frequency of NH_3D^+ (see Table 1) was analysed together with the previously reported IR ro-vibrational data from Doménech et al. (2013) with the *spcat/spfit* programme suite (Pickett 1991), employing a prolate symmetric rotor Hamiltonian and neglecting hyperfine terms. The derived spectroscopic parameters of the vibrational ground state are given in Table 2 together with those obtained from analysing the ro-vibrational data alone. As expected, inclusion of the one high-resolution rotational transition significantly

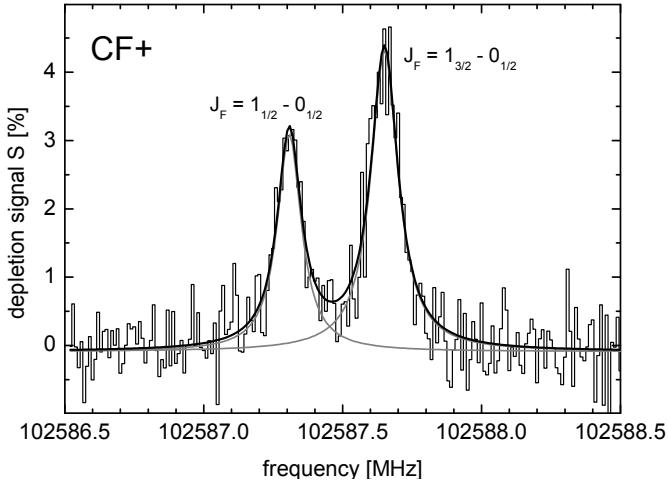


Fig. 2. Rotational ground state transition $J = 1-0$ of CF^+ with resolved hyperfine structure (black histogram) measured by storing about 8000 mass-selected CF^+ ions for 600 ms in a cryogenic 22-pole ion trap (4.2 K) in the presence of a high number density of helium ($\sim 4 \times 10^{14} \text{ cm}^{-3}$) and continuous irradiation with tunable narrowband mm-wavelength radiation ($\sim 10 \mu\text{W}$ power in the trap region). The relative depletion signal for both lines is of the order of a few percent, with an absolute number of around 400 helium complexes formed over the storage time. The spectrum is averaged over 320 iterations, and the line centre positions were extracted from fitting a Voigt line shape function to the data (grey curves).

improves the accuracy of the B_0 rotational constant, whereas all higher order terms retain their uncertainty and the purely K -dependent terms A_0 and D_K needed to be kept fixed in the analysis. Even though the inclusion of the tentatively detected para $J_K = 2_1-1_1$ ground state transition changes the spectroscopic parameters and predicted transition frequencies within less than three times their predicted 1σ uncertainty, we did not include this line in the analysis because of its very low signal-to-noise value. Predictions of astronomically relevant rotational transition frequencies with lower state energies up to 30 cm^{-1} are presented in Table 1.

2.2. The ground state rotational transition of CF^+

CF^+ is efficiently produced in the ion storage source from pure tetrafluoromethane (CF_4 synthetic grade, at a pressure of $\sim 2 \times 10^{-5}$ mbar) at an ionization energy of 40 eV. About 8000 mass-selected CF^+ ions ($m = 31 \text{ u}$) were stored in the 22-pole ion trap at a nominal temperature of 4.2 K in the presence of helium at a number density of $4 \times 10^{14} \text{ cm}^{-3}$. Under these conditions around 400 $\text{CF}^+\bullet\text{He}$ complexes are formed after 600 ms storage time. We used the output of a solid-state frequency tripler (Virginia Diodes Inc. AMC 375) pumped with an atomic-clock referenced synthesizer (Rohde und Schwarz SMF100A) to record the spectrum of the CF^+ $J = 1-0$ line in a 2 MHz window (scanned with 10 kHz steps) centred at 102 587.53 MHz, i.e. the line position predicted from the earlier mm-wave measurements of higher J transitions (Cazzoli et al. 2012).

The resulting spectrum of the CF^+ ground state transition is shown in Fig. 2. The two hyperfine components attributed to the $J_F = 1_{1/2} - 0_{1/2}$ and $J_F = 1_{3/2} - 0_{1/2}$ ($F = J + I$, with $I = 1/2$ the fluorine nuclear spin) are clearly resolved. The line centre frequencies of the two components given in Table 3 were obtained from fitting a double Voigt line shape function to the data. The

Voigt line shape is a consequence of combined line broadening due to the ions kinetic temperature, and due to power broadening, which is of the same order of magnitude ($\gamma = 38(10)$ kHz for the stronger hfs component) at the radiation power $P \sim 10 \mu\text{W}$ used to record the lines shown in Fig. 2. A Doppler temperature $T = 36(15)$ K can be derived from the Gaussian contribution to the linewidth, $\sigma = 34(8)$ kHz, but this value is likely overestimated because of incomplete deconvolution of the Gaussian and Lorentzian line parameters. In fact, when increasing the power P we observe the expected \sqrt{P} -dependent increase of the linewidths, where the Lorentz linewidth (HWHM) is given by $\gamma = \mu E / \hbar$, μ is the transition moment of the transition, and $E \propto \sqrt{P}$ is the electric field strength of the exciting radiation. Also, the linewidth of the $J_F = 1_{3/2} - 0_{1/2}$ line is twice as large as that of the $J_F = 1_{1/2} - 0_{1/2}$ component, as expected from the twice as large transition moment. This saturation effect can also explain why we do not observe the theoretically expected 1:2 intensity ratio for the two hfs components shown in Fig. 2. At $P > 250 \mu\text{W}$ the two hyperfine components can no longer be resolved.

We performed a least-squares fit of the experimental rotational transition frequencies of CF^+ from this work and all previous studies (compiled in Table 3) to a diatomic rotor Hamiltonian including the fluorine spin-rotation interaction constant C_I . Our best-fit rotational constant B_0 and centrifugal distortion constant D_0 (Table 4) agree within their 1σ uncertainties with those from Cazzoli et al. (2012) and, as in this study, the sextic centrifugal distortion constant H_0 was kept fixed to that of Gruebele et al. (1986) derived from ro-vibrational measurements. The spin-rotation constant C_I is experimentally determined to an accuracy of 3 kHz, reflecting the high accuracy of our experimental line positions, and is in perfect agreement with the quantum-chemically calculated value reported in Guzmán et al. (2012b), which is also given in Table 4. From the spectroscopic constants all experimental transition frequencies can be reproduced to within their experimental uncertainty (Table 3). The table also gives rest frequency predictions for additional rotational transitions of CF^+ up to 1.5 THz (not including hfs splitting).

3. Discussion and conclusions

In this work we present a highly accurate ($\Delta\nu/\nu = 6 \times 10^{-8}$) experimental frequency for the $J_K = 1_0-0_0$ rotational ground state transition of ortho- NH_3D^+ that can directly be compared to available astronomical observations. The narrow spectral emission feature at 262 816.73(10) MHz detected by Cernicharo et al. (2013) toward the cold prestellar core B1-bS agrees within twice its experimental uncertainty with our experimental value of 262 816.904(15) MHz. The small discrepancy might be attributed to uncertainty in the LSR velocity (v_{LSR}) of the source. Using the laboratory rest frequency we obtain a v_{LSR} of 6.7 km s^{-1} from the astronomical line. This value is well in the range of observed v_{LSR} in single dish observations of Barnard B1-b (e.g. Lis et al. 2006; Daniel et al. 2013; Cernicharo et al. 2014), but falls somewhat between the systemic velocities of 6.3 km s^{-1} and 7.2 km s^{-1} associated with the two embedded B1-bS and B1-bN cores derived from high-spatial resolution observations of, for example N_2H^+ , by Huang & Hirano (2013). Nevertheless, from a purely spectroscopic view our laboratory measurements support the assignment of the astronomical lines observed in B1-bS and Orion IRC2 to NH_3D^+ . Ancillary support

Table 2. ground state spectroscopic parameters of NH₃D⁺.

Parameter	This work	Doménech et al. (2013)
A_0 (MHz)	[175 438.5464] ^a	[175 438.5464] ^a
B_0 (MHz)	131 412.1315(130)	131 412.08(88)
D_J (MHz)	1.8397(53)	1.8396(112)
D_{JK} (MHz)	4.420(82)	4.404(88)
D_K (MHz)	[0.0] ^a	[0.0] ^a
wrms	0.94	

Notes. Numbers in parentheses represent 1σ uncertainties. The ground state lines from this work (Table 1) were fitted together with ro-vibrational data from Doménech et al. (2013). ^(a) Parameter was kept fixed in the fit to the value from Nakanaga & Amano (1986).

Table 3. Measured and predicted rotational transitions of CF⁺.

J	J'	F	F'	Frequency [MHz]	o-c [kHz] ^a	Reference
1	0	1/2	1/2	102 587.308(4)	0.6	exp. this work
1	0	3/2	1/2	102 587.649(3)	0.7	exp. this work
2	1			205 170.520(20)	9	Cazzoli et al. (2010)
3	2			307 744.351(20)	-20	Cazzoli et al. (2010)
4	3			410 304.565(20)	9	Cazzoli et al. (2010)
5	4			512 846.493(20)	-16	Cazzoli et al. (2012)
6	5			615 365.671(9)		pred. this work
7	6			717 857.486(9)		pred. this work
8	7			820 317.395(11)		pred. this work
9	8			922 740.843(13)		pred. this work
10	9			1 025 123.275(30)	1	Cazzoli et al. (2012)
11	10			1 127 460.137(30)	8	Cazzoli et al. (2012)
12	11			1 229 746.851(27)		pred. this work
13	12			1 331 978.890(35)		pred. this work
14	13			1 434 151.691(45)		pred. this work
15	14			1 536 260.652(100)	24	Cazzoli et al. (2012)

Notes. Numbers in parentheses represent experimental or predicted 1σ uncertainties. ^(a) observed-calculated (o-c) differences with respect to the spectroscopic parameters given in Table 4.

Table 4. Ground state spectroscopic parameters of CF⁺.

Parameter	This work	Cazzoli et al. (2012)	Guzmán et al. (2012b)
B_0 (MHz)	51 294.14713(93)	51 294.14672(98)	
D_0 (kHz)	189.9277(54)	189.9267(47)	
H_0 (Hz)	[0.07] ^a	[0.07] ^a	
C_I (kHz)	227.3(33)		229.2 ^b
wrms	0.50		

Notes. Numbers in parentheses represent 1σ uncertainties. The two hfs components from this work were fitted together with 7 rotational lines from Cazzoli et al. (2010) and Cazzoli et al. (2012) (see Table 3). ^(a) Fixed to the experimental value by Grubele et al. (1986). ^(b) Calculated value at the CCSD(T)/cc-pCV6Z level.

for this identification can be obtained by the observation of additional rotational transitions, for which accurate rest frequencies can now be predicted from our spectroscopic analysis (Tables 1 and 2). The para ground state transition is of particular interest, since it will give information on the ortho/para-ratio of NH₃D⁺, which is intimately linked to the spin state ratios of ammonia and H₃⁺ and their deuterated variants (Sipilä et al. 2015). Unfortunately, both the $J_K = 2_1-1_1$ para ground state line and the next higher ortho transition $J_K = 2_0-1_0$, both at around 525.6 GHz, are extremely difficult to observe from ground.

Both transitions were covered in the HEXOS (*Herschel*/HIFI Observations of ExtraOrdinary Sources) line survey towards Orion KL (Crockett et al. 2014, 2015) using the HIFI instrument

(de Graauw et al. 2010) on the *Herschel* Space Observatory (Pilbratt et al. 2010). Spectra extracted from the publicly available archival data show no spectral features with significant intensity above the rms value of $\sigma = 20$ mK (in T_A^* units) at the two predicted transition frequencies. This is in accordance with the expected estimated peak intensity of around 25 mK for this line based on the intensity of the $J_K = 1_0-0_0$ line (~ 200 mK) observed by Cernicharo et al. (2013) with the 30 m IRAM telescope towards the IRc2 position (only 3'' offset of the HEXOS survey pointing position). Our estimate assumes that NH₃D⁺ is present in the compact ridge region (with a source size of a few arcseconds), based on the observed $v_{LSR} = 9$ km s⁻¹ and narrow linewidth usually attributed to this component. In this case the

$J = 2-1$ emission lines seen with the 40'' *Herschel* beam are severely more diluted than the $J = 1-0$ line observed with the IRAM 30 m telescope (10'' beam). Furthermore, we assumed thermalization of the rotational levels with an excitation temperature of >80 K (except for the ortho:para ratio, which was set to 1) because of the rather small Einstein coefficients for spontaneous emission A_{ij} of the order $4 \times 10^{-5} \text{ s}^{-1}$ and an H_2 density of 10^6 cm^{-3} in the compact ridge (Crockett et al. 2014). The cold prestellar cloud B1-bS, exhibiting much fewer and narrower lines at sub-millimetre wavelengths than the complex Orion region, is likely a better target to search for confirming transitions of NH_3D^+ ; the two 525.6 GHz lines should be of similar intensity as the detected ortho ground state line, assuming a rotational excitation temperature of 12 K. Their detection, however, needs to wait for the next generation receivers on board the airborne SOFIA observatory. An alternative is to search for higher deuterated variants of the ammonium ion, i.e. NH_2D_2^+ and ND_3H^+ , as suggested by Cernicharo et al. (2013). The feasibility of spectroscopic studies on these species, the prerequisite for an astronomical search, is discussed below.

Owing to the low ion temperatures and thereby narrow Doppler widths achievable in our trap experiments, we were able to resolve the two hyperfine components of the CF^+ $J = 1-0$ rotational ground state transition and extract their transition frequencies to within 3–4 kHz, i.e. to a relative accuracy better than 10^{-7} . From this we accurately determined the spin-rotation interaction constant to $C_I = 227(3)$ kHz. This value is in excellent agreement with a high-level theoretical value of 229.2 kHz that was used by Guzmán et al. (2012b) to account for an observed double-peaked line structure in the CF^+ $J = 1-0$ transition towards the Horsehead PDR (Guzmán et al. 2012a). Thus our spectroscopic experiments confirm the intrinsic nature of the astronomically observed line structure, ruling out that it stems from kinematic effects.

State-selective attachment of He atoms to mass-selected, cold molecular ions, used in this work for the spectroscopy of NH_3D^+ and CF^+ , is a very powerful and general method for rotational spectroscopy. Owing to the low internal ion temperature, this method is particularly well suited to probe rotational ground state transitions, which are difficult to observe with standard absorption experiments through high-temperature plasmas. In contrast to the more established action spectroscopic method of laser induced reactions (LIR; Schlemmer et al. 2002), the method directly probes purely rotational transitions, which for LIR is only possible in specific cases (as for H_2D^+ , Asvany et al. 2008) or through IR-mm-wavelength double resonance techniques (Gärtner et al. 2013; Jusko et al. 2014). Moreover, a suitable endothermic reaction scheme is needed for LIR, whereas the attachment of He to the cold ions, and, even more importantly, a rotational state dependency of the attachment process needed for the spectroscopic scheme, has been observed in our laboratory for a considerable number of cations. These are, apart from NH_3D^+ and CF^+ presented here, C_3H^+ (Brünken et al. 2014a), CO^+ , HCO^+ , CD^+ (Kluge 2015), CH_2D^+ , and CD_2H^+ (discussed in forthcoming publications). The observable depletion signal for a given rotational transition depends on various experimental parameters and intrinsic properties of the studied molecular ion, as we have thoroughly investigated on known rotational transitions of CD^+ and HCO^+ (Kluge 2015). Under the premise that the participating rotational states exhibit a difference in the ternary attachment rate, the depletion signal will be stronger, the more the population ratio of the two levels changes, upon resonant excitation, from the initial thermal Boltzmann distribution (i.e. without radiative excitation). In the best case, when

radiative processes dominate over collisional processes, the population ratio of the two states reaches “radiative” equilibrium given by the ratio of their statistical weights. The method therefore profits from the low achievable ion temperature and is best suited for ground state transitions with large rotational energy spacing.

Although the presented method is very sensitive in the sense that only a few thousand mass-selected molecular ions are needed to record rotational spectra, searching for unknown transitions over ranges larger than a few 10 MHz is very time consuming owing to the long experimental cycle times (around 2 s per frequency point) and the multiple iterations needed to achieve a sufficient signal-to-noise ratio for detecting depletion signals of the order of typically only several percent. A very promising approach towards recording rotational transitions of new species, such as the higher deuterated variants of NH_3^+ , is to reduce significantly the experimental search range by obtaining accurate predictions for pure rotational transitions from preceding measurements of their ro-vibrational spectra with high accuracy via LIR (if applicable) or LIICG (Laser Induced Inhibition of Complex Growth, as described for ro-vibrational spectroscopy in Asvany et al. 2014, 2015; Jusko et al. 2016). That frequency accuracies below 1 MHz can be achieved in this way has been demonstrated in our group on the examples of CH_2D^+ (Gärtner et al. 2010, 2013), deuterated variants of H_3^+ (Jusko et al. 2016), and by determining the ground state combination differences of CH_5^+ (Asvany et al. 2015) by using a narrow-linewidth OPO as an infrared radiation source, in the latter two studies referenced to a frequency comb (Asvany et al. 2012), and taking advantage of the low ion temperatures in the trap instruments. Once accurate predictions of the rotational transitions are available, they can be recorded directly with the method of state-selective attachment of He atoms presented here, or by LIR IR-mm-wavelength double resonance methods, if applicable, thus providing highest accuracy and resolution needed for a comparison to radio-astronomical observations, as demonstrated here in the case of NH_3D^+ and CF^+ .

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