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Chih-Hsuan Chang, Preston G. Scrape, and David J. Nesbitt

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Sub-Doppler slit jet infrared spectroscopy of astrochemically relevant cations: The NH stretching mode in ND_3H^+

Chih-Hsuan Chang,[1] Preston G. Scrape,[2] and David J. Nesbitt[2,3,4]
[1] *Spectra Sensors, 4333 W. Sam Houston Pkwy N., Suite 100, Houston, Texas 77043, USA*
[2] *JILA, National Institute of Standards and Technology and University of Colorado, Boulder, Colorado 80309, USA*
[3] *Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309, USA*
[4] *Department of Physics, University of Colorado, Boulder, Colorado 80309, USA*

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High-resolution rotationally resolved spectra of the N–H stretch vibrational mode (ν_1) of jet-cooled ND_3H^+ ions are collected and analyzed in a sub-Doppler slit-jet infrared spectrometer. The isotopomeric ammonium ions are generated by proton transfer from $H_3{}^+$ to ND_3 in a discharge of an ND_3/H_2 gas mixture, whereby the slit jet expansion cools the nascent ND_3H^+ ions into lower rotational states. Rotational assignments are confirmed by four-line combination differences that agree to within the spectrometer precision (9 MHz). Based on precision two-line ground-state combination differences and a symmetric top Hamiltonian, the B, D_J, and D_{JK} rotational constants for the ground vibrational state of ND_3H^+ are determined with high precision for the first time. Approximate rotational constants for the ν_1 excited state are also determined, with a band origin at 3316.8425(19) cm^{-1} and in remarkable (~0.1 cm^{-1}) agreement with high level anharmonic theoretical predictions by Guo and co-workers [J. Phys. Chem. A, **120**, 2185 (2016)]. Our results allow us to predict several low-J pure rotational transitions of ND_3H^+, which we hope will support future studies of this important ion in laboratory and astronomical rotational spectroscopy. *Published by AIP Publishing.*
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I. INTRODUCTION

The ammonium ion, $NH_4{}^+$, is a crucial species in a broad range of applications including Brønsted acid-base chemistry,[1] biochemistry,[2,3] astrochemistry,[4] and atmospheric chemistry.[5] The key role of this ion has motivated experimental and theoretical studies of its structure and dynamics under a variety of conditions, for instance, while solvated with pure water[6,7] or with proteins,[8] while immobilized in crystals of inorganic ammonia derivatives,[9,10] or even in the form of a "metal" that could occur naturally in planetary cores.[11,12] In the gas phase, the rotationally resolved spectrum of $NH_4{}^+$ in its ν_3 antisymmetric stretch mode was reported independently by Crofton and Oka[13,14] and by Schäfer *et al.*[15,16] via the technique of velocity modulation laser absorption spectroscopy. Crofton and Oka[14] also assigned the spectrum of the ion's fully deuterated isotopologue $ND_4{}^+$ in the 4.0 μm region. Polak *et al.*[17] later reported rotational assignments of the deformation (ν_4) mode of $NH_4{}^+$, with the same vibrational mode later refined by Park *et al.*[18] to improve the spectroscopic constants.

There have been considerably fewer studies of *partially* deuterated ammonium ions. This lack of spectroscopic information has proven especially unfortunate in the context of astrochemical detection of ammonium. Specifically, $NH_4{}^+$ itself, a spherical top, has no dipole moment and is therefore invisible to rotational spectroscopic methods. By way of contrast, the partially deuterated isotopologues have permanent electric dipole moments[19] and thus can be detected by their pure rotational transitions. Indeed, Cernicharo *et al.* detected a spectral feature at 262 816.7 MHz in the direction of Orion and B1-bS that they tentatively assigned to the $J_K = 1_0$–0_0 transition of NH_3D^+.[20] This ion had previously been studied in the ν_4 antisymmetric stretch region by Nakanaga and Amano.[19] Following the work of Cernicharo *et al.* were reports by Doménech *et al.* that expanded and refined the previous measurements of the ν_4 band,[21] a forthcoming report by ourselves that observes the ν_1 symmetric stretch for the first time, and a report by Stoffels *et al.* of the first *laboratory* observation of the $J_K = 1_0$–0_0 transition of NH_3D^+.[22] This last work proved necessary to support the assignment of Cernicharo *et al.*, with all of the above studies agreeing with the initial assignment to NH_3D^+ in the interstellar medium.

There is currently no comparable body of work on the triply deuterated ion, ND_3H^+, without which a search for this species in the interstellar medium would be impossible. Detection of this ion is crucial not merely as an additional marker for $NH_4{}^+$, but moreover because the degree of deuterium fractionation in a system provides a valuable probe of its temperature, kinetics, and dynamics.[23,24] For instance, Rodgers and Charnley[25] proposed a gas-phase network to explain the unusual abundance of NH_2D and NHD_2 isotopologues of ammonia in the interiors of clouds such as L134N. The proposed model involves a series of chemical processes, including cosmic ionization, electron dissociation recombination, H_2 addition, and proton/deuteron transfer. Experimental support for this model will require simultaneous observation of several species, including each member of the series of $NH_xD_{4-x}{}^+$

ions, since the unusually high deuterium fractionation of ammonia in the interstellar medium strongly suggests that the deuterated ions are present there in abundance.[26–30] Indeed, deuterated ammonium ions are also the likely precursors of deuterated and partially deuterated ammonia molecules. The reason for this is that NH_3 is readily protonated by H_3^+, the deuterated variants of which (H_2D^+, HD_2^+, and D_3^+) are greatly enhanced in the interstellar medium due to differential zero-point energy effects.[25,31–33]

In this work, the high resolution, rotationally resolved infrared spectrum of ND_3H^+ in the NH stretching mode (ν_1) is studied using sub-Doppler spectroscopy in a slit-jet discharge configuration. Of primary interest, this approach allows us to study the rotational characteristics of the vibrational ground state with an eye toward astronomical applications while at the same time providing a first window into the rovibrational properties of the $v_1 = 1$ state as well as the fundamental chemistry, physics, and spectroscopy of this important ion. Previously, Jacox and Thompson studied the infrared spectrum of NH_4-d_n^+ trapped in a solid neon matrix and assigned fundamental frequencies of several vibrational modes.[34] On the theoretical side, Martin and Lee studied NH_4^+ and its deuterated variants with high level *ab initio* Coupled-Cluster Singles/Doubles and Perturbative Triples [CCSD(T)]/cc-pVTZ calculations, matching previous experimental measurements to within 10 cm^{-1}.[35] More recently, Guo and co-workers[36] have constructed a complete potential energy surface for NH_4^+ and, using a numerically exact kinetic energy operator, predicted anharmonically corrected vibrational band origins for each ammonium ion isotopologue up to several thousand wavenumbers of internal energy. Quite remarkably, their predictions have matched all experimental data so far to within 1 cm^{-1}.[36,37] The work reported herein on ND_3H^+ thus considerably expands the ongoing saga of NH_4^+ and its H/D isotopologues as well as provides fundamental benchmark tests of theoretical spectroscopy from a first principles quantum chemistry perspective.

II. EXPERIMENTAL SECTION

The sub-Doppler slit jet spectrometer used in this experiment, and its application to the study of many other radicals and molecular ions, has been described in detail elsewhere.[38–40] In particular, the same instrument was used by our group to study the ν_1 and ν_6 modes of $NH_2D_2^+$,[37] and aside from the choice of the ion precursor, this study is quite similar to that one. Only a brief description of key aspects of the experiment need be given here.

High resolution (∼1 MHz bandwidth) infrared radiation is generated by nonlinear difference frequency generation (DFG) within a Periodically Poled Lithium Niobate (PPLN) crystal (50 mm × 10 mm, Photonic) that is housed within a temperature-controlled holder. Laser light for the DFG is provided by a ring dye laser (<2 MHz linewidth, Spectra-Physics 380A with R6G dye) and an Ar^+ laser (Spectra-Physics Series 2000), with an accessible infrared range of approximately 2500–4500 cm^{-1}. IR power is measured by two liquid nitrogen-cooled InSb detectors, the "reference" and "signal" detectors. Half of the IR radiation is diverted directly to the "reference" detector through a beamsplitter, which allows us to electronically subtract common mode laser amplitude noise.[41] The remaining probe beam light (∼7 μW power) is directed through a supersonic expansion of ND_3H^+ ions, with the radiation multipassed in a 16-pass Herriot cell located 5 mm downstream from the throat (4 cm length × 300 μm width) of the slit-jet discharge jaw. The total absorption path length is thus 16×4 cm = 64 cm, after which the radiation is directed onto the "signal" detector. Technical laser amplitude noise which is common to both the signal and reference detectors is balanced and subtracted by home-built servo-loop-controlled differential amplifiers with a 1 MHz bandwidth.

Ions are created in the slit jet discharge from a flowing mixture of 5% ND_3 in H_2. At a discharge potential of 650 V, electron bombardment of H_2 produces H_2^+ ions, after which H_3^+ is generated via the fast Langevin process $H_2^+ + H_2 \rightarrow H + H_3^+$. Subsequent proton transfer from stable H_3^+ to the ND_3 then results in the exothermic formation of the target ND_3H^+ ion, which is then cooled by collisions in the supersonic expansion that relax the rovibrational population into lower-energy states. The 650 V discharge is modulated at 50 kHz, for which the modulated absorption profile is recovered via lock-in detection with a 10 kHz low pass filter.

The overall absorption noise level is estimated to be 1.1×10^{-5} rms in 10 KHz detection bandwidth. The detection sensitivity is thus within a factor of two of the shot noise limit, $1.3 \times 10^{-7}/\sqrt{\text{Hz}}$, which in turn yields a signal to noise ratio of S/N ∼ 50 for the strongest ND_3H^+ transitions observed. To estimate the ion density in the supersonic expansion, we use the Gaussian software[42] at the B3LYP/6-311++g(3df,3pd) level of theory to predict that the ν_1 mode reported herein has an integrated IR intensity of $\sigma_0 \approx 141.5$ km/mol. This value together with our absorption intensities allows us to estimate a number density of about 1.6×10^{10} ions/cm^3 of ND_3H^+ at the probe region.

Absolute frequency measurements are calibrated with respect to the $R(3)$ line in the asymmetric C–H stretching (ν_3) mode of C_2H_2 at 3304.166 74 cm^{-1}.[43] Relative frequencies are obtained by interpolating fringes from an ultra-stable optical transfer marker cavity with a 250 MHz free spectral range (FSR) and a frequency reproducibility for a typical line of ∼9 MHz. The sub-Doppler linewidths are approximately 110 MHz, with most of the broadening induced by the high H_2 content in the discharge expansion.

III. RESULTS AND DISCUSSION

A. Rotational analysis

Figure 1 shows a cartoon of the ND_3H^+ ion with its c principal axis of inertia, which by symmetry must align with the molecule's symmetry axis. Excitation of the N–H stretch mode (ν_1) is an $A_1 \leftarrow A_1$ parallel transition, which means its rotational structure follows the selection rule $\Delta K = 0$, where K is the quantized projection ($\mathbf{J}_c$) of total angular momentum ($\mathbf{J}$) along the molecule's symmetry axis (c). Our initial search for this band was guided by two predictions of its band origin. First, Martin and Lee in their high-level CCSD(T) calculations suggested a band origin of 3311.4 cm^{-1}.[35] Second, our own Gaussian frequency calculation at the

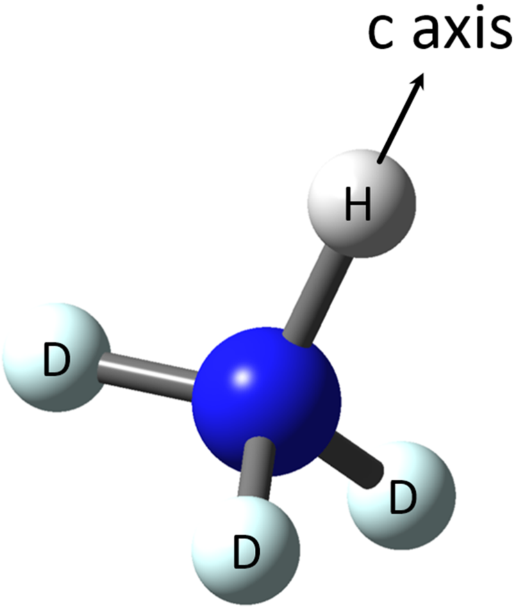

FIG. 1. Geometry of the triply deuterated ammonium ion isotopomer, ND_3H^+. Since this ion is an oblate symmetric top, the c-axis must be identical to the symmetry axis (along the N–H bond).

B3LYP/6-311++g(3df,3pd) level of theory with an empirical anharmonic correction factor of 0.9637 placed the band origin at 3321.7 cm^{-1}. Interestingly, after the present data were collected, the Guo group (Yu *et al.*) predicted a band origin of 3316.90 cm^{-1} based on a complete *ab initio* potential energy surface for $NH_4{}^+$;[36] which, as we explain below, matches the experimental result to within 0.1 cm^{-1}. The first identification of some spectral lines as arising from ν_1 was based on the appearance of a prominent (J′, K′) ← (J″, K″) *Q*-branch near 3317 cm^{-1} (see Fig. 2). A further spectroscopic clue comes from the nuclear spin weighting which is manifested at different *K* manifolds. Next, groups of *P* and *R* progressions (separated by ~2 *B* = 7.4 cm^{-1}) were also observed; these transition lines are shown in Figs. 3 and 4.

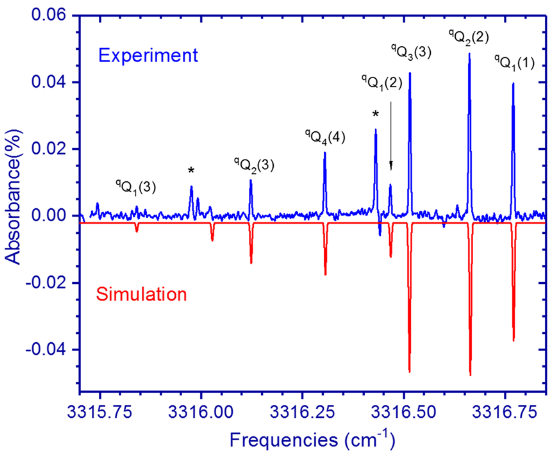

FIG. 2. Rotationally resolved spectrum near 3316 cm^{-1}, showing the *Q*-branch of the N–H stretch of ND_3H^+, with transitions labeled as $^qQ_K(J)$. The bottom trace is a simulated spectrum from PGOPHER, which agrees with the data quite well. Lines marked with (*) are not attributable to ND_3H^+.

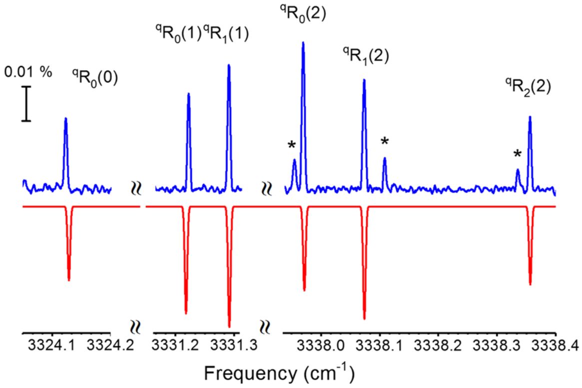

FIG. 3. Rovibrational transitions of the *R* branch progression. Lines marked with (*) are rovibrational transitions of $NH_2D_2{}^+$, which is formed in small concentrations in the discharge, likely due to ND_2H isotopomer contamination in the ND_3 gas sample.

The rovibrational transition energies and ground state combination differences have been fitted to the usual oblate symmetric top Hamiltonian for a non-degenerate (A_1) vibrational state including up to quartic centrifugal distortion terms,

$$E(J,K) = \nu_0 + BJ(J+1) + (C-B)K^2 - D_J J^2(J+1)^2 - D_{JK}J(J+1)K^2 - D_K K^4,$$

where the term ν_0 is of course identically 0 for the ground vibrational state. Spectral fits are performed using the least-squares fitting routines implemented in PGOPHER.[44] As an aside, it is worth noting that symmetric top rovibrational selection rules for transitions in an $A_1 \leftarrow A_1$ band prevent direct determination of the constants *C* and D_K. Therefore, analogous to the approach followed in studies of NH_3D^+,[19,21] we fix the ground-state D_K to 0 and the ground-state *C* to the experimentally determined B value in $ND_4{}^+$,[45] namely, 2.9855 cm^{-1}. To obtain maximally accurate spectroscopic constants for the lower vibrational level, we fit the v = 0 rotational constants separately using ground state combination differences. The excited-state constants are then fitted on their own, holding the ground-state constants fixed. The fitting results for *B*, D_J, and D_{JK} constants are summarized in Table II. As expected, the *C* constant of the $v_1 = 1$ state is quite close to that of the ground state, with a fractional difference of only

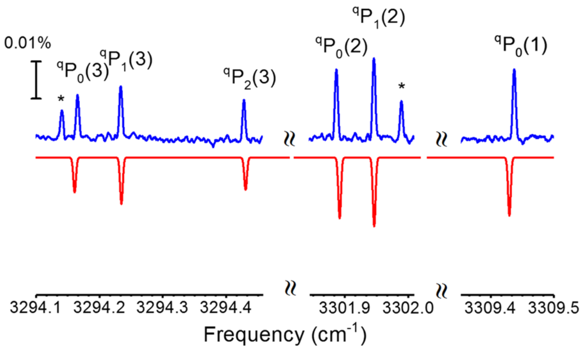

FIG. 4. Sample rovibrational transitions in the *P* branch progression of the NH stretch (v_1) vibrational band in ND_3H^+. Lines marked with (*) are not assigned but do not arise from ND_3H^+.

$\Delta C/C \approx -0.5\%$. Conversely, the B constants exhibit a 5-fold greater difference, $\Delta B/B \approx -2.5\%$. This distinction indicates that, as one might reasonably expect, the N–H stretching motion and the concomitant (very small) N–D motions induce much larger anharmonic changes to the vibrationally averaged bond length and moment of inertia mass projections *along* the c axis rather than perpendicular to it.

Error bars for the spectroscopic constants in the ground vibrational state are less than 1 MHz, which allows us to place tight estimates on pure rotational transitions of this ion. The error bars on the v = 1 spectroscopic constants, however, are appreciably larger. From the data in Table I (and to sharp eyes in Figs. 2 and 3), it is clear that these larger error bars arise because many of the predicted line positions do not precisely match their experimentally determined positions, especially in the $K = 0 \leftarrow 0$ manifold. Please see Fig. 5 for a plot of systematic residuals for transitions out of the different K states. Notably, the *assignments* of these weakly perturbed lines are completely unambiguous, thanks to internally consistent combination differences, internally consistent transition intensity ratios, and a lack of spectral congestion that might otherwise lead to an outright spectral misassignment. As a result, rather than an incorrect assignment, the poorer upper state fit quality points to very weak shifts (~0.01 cm^{-1}) in some of the upper state energy levels due to intramolecular vibrational coupling on a rotational state specific basis with the modest density of "dark" vibrational overtone and combination band states in the 3316 cm^{-1} region. It is not yet clear what the perturbation mechanism might be or which overtone/combination band states are responsible. However, a promising result can be found in the theoretical work of Guo and co-workers, which predicts two vibrational states with band origins within ~50 cm^{-1} of the N–H stretch ν_1.[36] One is an overtone of the ND_3 umbrella mode, $3\nu_3$, near 3263.02 cm^{-1}; the other is a combination of that umbrella mode with the N–D bend, $2\nu_3 + \nu_6$, at 3325.85 cm^{-1}. For now, we speculate that select rotational levels of these excited (but spectrally "dark") vibrational states may be sufficiently close to isolated rovibrational levels of ν_1 to cause weak shifts (perturbations) in the observed transitions. We hope to explore this direction further with a detailed deperturbation analysis, which, in principle, will provide first glimpses into near resonant combination band/overtone vibrational structures and thus additional tests on the accuracy of the *ab initio* anharmonic calculations of Guo and co-workers.[36]

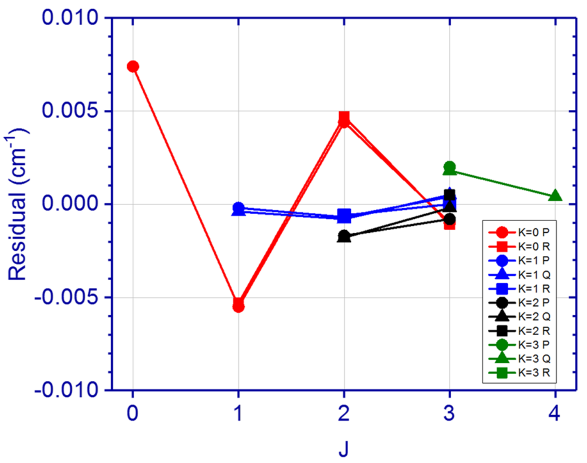

FIG. 5. Plot of the residuals in Table I, i.e., the difference between the predicted and experimental line positions. The red lines reflect transitions in the $K = 0 \leftarrow 0$ manifold, with similar patterns for the blue lines ($K = 1 \leftarrow 1$), black lines ($K = 2 \leftarrow 2$), and green lines ($K = 3 \leftarrow 3$). The plot highlights graphically the significantly larger residuals in the $K = 0 \leftarrow 0$ transitions, which are the source of the error bars for the v = 1 rotational constants in Table II.

TABLE I. Observed frequencies of transitions in the N–H stretch mode of ND_3H^+.

	$J'_{K'}$–$J''_{K''}$	ν_{obs}	
$R_2(2)$	3_2–2_2	3338.3564	0[a]
$R_1(2)$	3_1–2_1	3338.0736	−3
$R_0(2)$	3_0–2_0	3337.9700	10
$R_1(1)$	2_1–1_1	3331.2912	7
$R_0(1)$	2_0–1_0	3331.2229	−46
$R_0(0)$	1_0–0_0	3324.1234	52
$Q_1(1)$	1_1–1_1	3316.7699	4
$Q_2(2)$	2_2–2_2	3316.6619	23
$Q_3(3)$	3_3–3_3	3316.5148	−10
$Q_1(2)$	2_1–2_1	3316.4664	12
$Q_4(4)$	4_4–4_4	3316.3050	10
$Q_2(3)$	3_2–3_2	3316.1227	−1
$P_0(1)$	0_0–1_0	3309.4368	−75
$P_1(2)$	1_1–2_1	3301.9462	−2
$P_0(2)$	1_0–2_0	3301.8866	51
$P_2(3)$	2_2–3_2	3294.4282	23
$P_1(3)$	2_1–3_1	3294.2338	8
$P_0(3)$	2_0–3_0	3294.1656	−42
$P_3(4)$	3_3–4_3	3286.8744	−10
$P_2(4)$	3_2–4_2	3286.4841	0
$P_1(4)$	3_1–4_1	3286.2030	−1
$P_0(4)$	3_0–4_0	3286.1004	8

[a] Residual ≡ (observed − prediction) × 10^4.

From the above spectral fits, the NH stretch mode band origin (ν_1) is found at 3316.8425(19) cm^{-1}, which is quite close to (only 5 cm^{-1} higher than) Martin and Lee's prediction of 3311.4 cm^{-1} based on high level CCSD(T)/cc-pVTZ calculations.[35] Our own Gaussian calculations based on B3LYP/6-311++g(3df,3pd) with the usual anharmonic scaling factor (0.9637) place this band origin at 3321.7 cm^{-1}. Interestingly, both of these approaches seem to have worked quite well, matching the experimental band origin to within a very respectable 5–10 cm^{-1}. A much closer estimate was obtained by Yu *et al.*, who predicted a band origin of 3316.90 cm^{-1}, differing from the experimental value by less than 0.1 cm^{-1}. The quality of this agreement speaks to the remarkably successful interaction between first principles theoretical and experimental spectroscopy.

B. Boltzmann analysis and entangled spin states

The three equivalent D atoms in ND_3H^+ have non-zero nuclear spin ($\mathbf{I_D} = 1$), so the nuclear spin statistics are an important factor in the statistical weights of the ion rotational states. By a molecular symmetry argument,[46] if all nuclear spin configurations are equally probable, the possible permutations of the three identical D bosons result in a nuclear spin wavefunction of symmetry species $\Gamma_{ns} = 10A_1 \oplus A_2 \oplus 8E$. Provided we can completely neglect collisional relaxation and cooling of nuclear spin projections along the discharge expansion (i.e., assuming nuclear spin "adiabaticity"), the statistical weights would therefore be predicted to be $g_{\rm ns} = 22{:}11{:}16$ for rotational levels with $K = 0$, $K = 3n$ ($\neq 0$), and $K = 3n \pm 1$, respectively, where n is an integer. In other words, at high enough temperatures and on long enough time scales to achieve equilibrium, the ratio of $K = 0$, $K = 3n$, and $K = 3n \pm 1$ state populations relaxes to 22:11:16. However, it is not obvious whether this high-temperature, long-time final state will be realized under the conditions of a slit jet discharge. By way of testing this assumption of nuclear spin adiabaticity, the measured transition intensities allow us to independently probe the relative number densities in each rotational state. These densities, in turn, can inform on whether the rotational states remain populated with the expected "adiabatic" nuclear-statistical weights.

The integrated absorption intensity for a given transition $\nu_{J'K' \leftarrow J''K''}$ in thermal equilibrium can be written as

$$S_{J'K' \leftarrow J''K''} \propto g_{\rm ns} \cdot (2J''+1) \cdot \mathrm{HL}(J'',K'') \cdot \exp(-E_{rot}/\mathrm{k}_B \cdot \mathrm{T}_{rot}),$$

where $\mathrm{HL}(J'',K'')$ is the Hönl-London factor, $g_{\rm ns}$ is the nuclear spin weight for different K manifolds, T_{rot} is the rotational temperature in the slit-jet configuration, and k_B is the Boltzmann constant. Figure 6 shows our Boltzmann analysis for ND_3H^+ in the different $K = 0$, 1, and 2 states. First of all, the linear Boltzmann fits to the three K manifolds reveal a common rotational temperature of $\mathrm{T}_{rot} = 33(1)$ K, which is quite typical for slit jet discharges of ions.[37,47,48] The intercepts on the y-axis, after substituting the known values of the other parameters, determine the *relative* $g_{\rm ns}$ value for each K manifold. The experimental values of $g_{\rm ns}$ are found to be in the ratio of 21.5(8):11.0(9):14.9(8) for $K = 0$, $K = 3n$ ($\neq 0$), and $K = 3n \pm 1$, in rather remarkable quantitative agreement with the "adiabatic" nuclear spin molecular symmetry predictions of 22:11:16. Simply stated, the analysis in Fig. 6 demonstrates that the slit jet expansion (~10 μs) occurs on too rapid a time scale to permit cooling/collisional equilibrium between the D atom nuclear spin states. Alternatively summarized, the superposition of nuclear spin states in the different nuclear spin configurations of ND_3H^+ has been experimentally verified to remain "entangled" for at least 10 μs and very likely much longer.

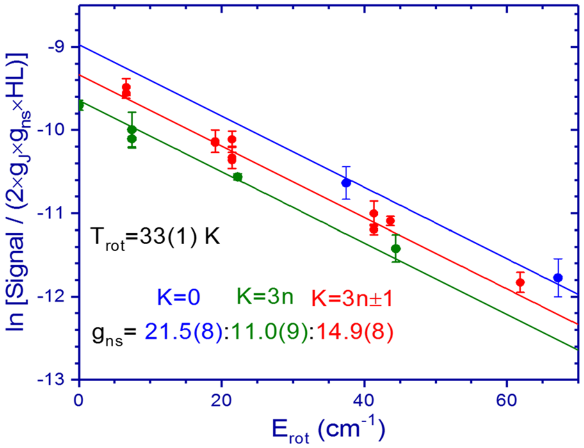

FIG. 6. Boltzmann plot of the rovibrational transition intensities. The slope is determined from the combined least-squared fit to three different nuclear spin manifolds and reveals a consistent rotational temperature of 33(1) K. The intercepts along the y-axis are used to determine $g_{\rm ns}$, the nuclear spin statistical weighting of the different K manifolds. The observed weighting agrees well with a prediction of 22:11:16 based on equal populations of each nuclear spin configuration in the high temperature limit.

TABLE II. Fitted spectroscopic constants (cm^{-1}) of ND_3H^+. Numbers in parentheses represent ±1σ error bars in the last significant digit.

	Ground	NH stretch (ν_1)
B	3.706 502(37)	3.649 17(82)
C	2.985 5[a]	2.975 08(59)
$D_J \times 10^{-4}$	0.582(17)	29.46(61)
$D_{JK} \times 10^{-4}$	−0.457(41)	−48.1(13)
$D_K \times 10^{-4}$	0[a]	19.9(11)
ν_0		3 316.842 1(20)
σ[b]	0.000 23	0.003 1

[a] Constrained.

[b] Residual standard deviation of the fit.

C. Astronomical application

As noted above, the crucial role of NH_4^+ and its isotopologues in the interstellar medium demonstrates the importance of astronomical detection of these species.[25–30] The isotopologues are especially interesting because the degree of deuterium fractionation in an astrochemical system provides a valuable probe of its temperature, kinetics, and dynamics.[23,24] Indeed, these motivations have already led to a number of high-resolution laboratory studies into the spectroscopy of NH_3D^+,[19,21,22] culminating in the astronomical detection of that ion by Cernicharo *et al.*[20] This "success story" of the detection of a key astrochemical ion speaks to the strong synergistic value of interplay between laboratory spectroscopy and astronomical observation. However, up to now there have been no comparable high-resolution spectroscopic data on the triply deuterated ion ND_3H^+.

To facilitate a search for ND_3H^+, we can use the rotational constants from infrared spectroscopy to predict microwave (rotational) transitions of the ion from the low-J rotational states populated in the interstellar medium. These predictions can be made with relatively high precision based on high-accuracy rotational constants for ND_3H^+ in the ground vibrational state, as reported in Table II. The most prominent pure rotational transition is likely to be the 1_0–0_0, which we predict to be at 222 229.3(20) MHz, where the uncertainty represents ±σ error bars. Based on the temperature and dynamics of the system, other feasible transitions might be the 2_0–1_0 at 444 416.7(29) MHz and the 3_0–2_0 at 666 520.3(24) MHz. These high-resolution predictions should greatly reduce the spectral search problems for microwave detection of ND_3H^+ in both terrestrial and interstellar contexts.

IV. SUMMARY

In this work, sub-Doppler (110 MHz) high-resolution rotationally resolved infrared spectra of the ND_3H^+ ion are observed and analyzed for the first time in the N–H stretch (ν_1) vibrational mode. The ND_3H^+ ion is generated by proton transfer from $H_3{}^+$ to ND_3 in a slit jet discharge, with a total of 24 transitions assigned. Based on these assignments, rotational constants for the lower and upper states are determined by linear least-squares fitting to a symmetric top Hamiltonian. The lower state is fitted by combination differences separately from the upper state, which permits isolation of the lower state fits from weak but ubiquitous perturbations in the upper state rovibrational energy levels. The band origin of the N–H stretching mode is determined to be 3316.8425(19) cm^{-1}, which is in remarkably close agreement with predictions from the *ab initio* anharmonic studies of Guo and co-workers.[36] The precise rotational constants determined for the ground vibrational state allow us to predict low-*J* rotational transitions of the ion with high precision. It is our hope that these predictions will prove to be useful in future microwave astronomical searches for this important ion in the interstellar medium.

ACKNOWLEDGMENTS

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