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Dipole Moments of HCO^+ and NH^+ from Cyclotron Frequency Polarizability Shifts

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Using single ions in a precision cryogenic Penning trap and by measuring the small shifts to their cyclotron frequencies due to their electric polarizability, the ground state electric dipole moments of HCO^+ and NH^+ have been determined. The results are $\mu(\text{HCO}^+) = 1.543(12) ea_0$, and $\mu(\text{NH}^+) = 0.782(11) ea_0$, which agree with theoretical predictions.

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I. INTRODUCTION

As first demonstrated for the case of CO^+ by Thompson et al. [1], the electric polarizability, and hence electric dipole moment of a polar molecular ion can be determined by measuring the rotational-state-dependent shifts to its cyclotron frequency in a strong magnetic field. Subsequently, the same method was used in our laboratory to obtain the dipole moment of PH^+ [2]. Here we apply the method to the astrophysically important ion HCO^+ (the formyl cation) [3-5], and also to NH^+ , which we chose because it was predicted by Cheng et al. [6] to have a particularly large polarizability. To our knowledge NH^+ has not yet been observed space, but is believed to be important in the formation of ammonia in interstellar molecular clouds [7,8].

Electric dipole moments of molecular ions are necessary for evaluating rotational line strengths and decay rates and also have application to the theory of dissociative recombination [5]. For simple molecules, current molecular structure theory is assumed to provide reliable dipole moments, and, for neutrals, calculations have been verified by measurement of Stark energy shifts. However, for molecular *ions*, which are obviously accelerated by strong electric fields, besides the previous cyclotron frequency shift

measurements on CO^+ and PH^+ , other experimental checks of predicted dipole moments have been indirect and of limited accuracy, *e.g.* see [9-11].

II. METHOD

A. Polarizability Shifts to the Cyclotron Frequency

An ion undergoing cyclotron motion in a Penning trap with uniform magnetic field \underline{B} experiences a $\underline{v} \times \underline{B}$ motional electric field proportional to its cyclotron radius. By considering the additional radial force due to the gradient of the resulting Stark (or polarization) energy, it can be shown that the cyclotron frequency f_c of an ion of mass m in a magnetic field \underline{B} is shifted by a fraction [1,6]

$$\frac{\Delta f_c}{f_c} = -\frac{\alpha_{XX}(i)B^2}{m} \quad (1)$$

where

$$\alpha_{XX}(i) = 2 \sum_{j \neq i} \frac{|\langle j | \mu_X | i \rangle|^2}{E_j - E_i} \quad (2)$$

is the static dipole polarizability corresponding to an electric field perpendicular to the magnetic field (which we take to be along the Z-axis), and is given in terms of the electric dipole transition matrix elements $\langle j | \mu_X | i \rangle$ and unperturbed energies E_i . (We assume $f_c \ll |E_j - E_i|/h$, so the molecular ion responds adiabatically to the rotation of the motional electric field in its rest frame.)

For linear molecules in the Born-Oppenheimer approximation, the dipole matrix elements between adjacent rotational states in eqn. (2) can be related to the conventional body-frame static electric dipole moment μ . Hence, using an effective Hamiltonian with other parameters derived from spectroscopy, this ‘‘orientation’’ contribution to the polarizability can also be expressed in terms of μ [12]. For the lowest rotational levels of certain small polar molecules this contribution can be as large as 10^4 to 10^5 atomic units (1 a.u. of polarizability = $(4\pi\epsilon_0) a_0^3$, where a_0 is the Bohr radius), and dominates over

other contributions to the total polarizability by three orders of magnitude. Hence, assuming this is the case, from the measured polarizabilities we can determine an experimental value for μ .

B. Cyclotron Frequency Measurement

In this work the cyclotron frequencies of single ions were measured using an 8.53 tesla cryogenic Penning trap which has been developed for high precision measurement of atomic masses [13-16]. In this spectrometer the only motional mode of the ion directly detected is the axial motion at frequency f_z near 213 kHz. This is detected via image currents using a high- Q superconducting resonant inductor and a DC-SQUID. The modified-cyclotron and magnetron modes, with frequencies f_{ct} and f_m respectively, are addressed by coupling them to the axial mode, using tilted quadrupolar rf drives [17]. The modified cyclotron frequency f_{ct} is measured using the so-called Pulse-and-Phase (PNP) technique [13], which measures the cyclotron phase accumulated following pulsed excitation of the trap-cyclotron mode. The magnetron frequency f_m is calculated from f_{ct} , f_z and the “trap-tilt-angle” [15], which is obtained from less-frequent measurements of f_m by the avoided-crossing technique [17]. The “true” cyclotron frequency, $f_c = (1/2\pi)qB/m$, is then derived from f_z , f_{ct} and f_m using the Brown-Gabrielse invariance theorem [18].

Single ions were created directly inside the Penning trap by merging an electron beam from a field-emission point, with a current of a few nA and an energy of 900 eV, with a tenuous molecular beam. Both beams entered the trap axially through small holes in the end-cap electrodes. After each attempt at making the desired ion, all unwanted ions were removed from the trap by selectively exciting their axial motions. The molecular beams were produced by heating a few mg of appropriate material in an external oven consisting of a slotted, 1 mm diameter, stainless-steel tube. HCO^+ was made from formaldehyde vapor, produced by heating polyoxymethylene (DelrinTM). NH^+ was made from ammonia which we initially produced by heating a sample of lithium which had been exposed to moist air, and subsequently, by heating a sample of NH_4Cl .

To allow for the effect of variation of the magnetic field on the cyclotron frequency, we alternately measured the cyclotron frequency of the polarizable ion and of a reference ion of similar mass-to-charge ratio. Polarizability shifts to the cyclotron frequency of the polarizable ion were then expressed as changes to the ratio of its cyclotron frequency to that of the reference. For the HCO^+ measurements, the reference ion was $^{28}\text{SiH}^+$ (made from silane), and for $^{14}\text{NH}^+$, $^{15}\text{N}^+$ (made from >99% enriched $^{15}\text{N}_2$). The dipole moment and polarizability of SiH^+ are small and the corresponding shift was allowed for in the analysis, see below. To facilitate the interchange of the ion of interest and its reference, we trapped both ions simultaneously, and then alternated them between the center of the trap, where the cyclotron frequency was measured, and a relatively large radius cyclotron orbit which served to temporarily “park” the other ion [16,19,20]. The cyclotron frequencies of the polarizable ion and its reference were then alternately measured over runs lasting up to 14 hours, limited by the need to refill a liquid nitrogen dewar, or else the loss of either ion, due to charge exchange with background gas.

III. POLARIZABILITY SHIFT MEASUREMENTS ON HCO^+

A. Cyclotron Frequency Measurements

The HCO^+ data set consisted of 25 runs obtained over a two-week period and made use of only two HCO^+ ions. For the cyclotron frequency measurements the cyclotron radius was 120 μm while the parking radius was 1.0 mm. Each run consisted of several repetitions of a sequence consisting of four f_c measurements on HCO^+ , followed by two for the reference ion $^{28}\text{SiH}^+$, see Fig. 1. In the nominally 4.2 K environment of the Penning trap, the HCO^+ ion, in thermal equilibrium with the black-body radiation in the trap, is predominantly in one of the three lowest rotational levels, $J = 0, 1, 2$, of the lowest vibrational level of its $X^1\Sigma_0$ electronic ground state. This is linear with an experimentally determined rotational constant $B_0 = 44.594$ GHz [4]. As Fig. 1 shows, transitions between these rotational states occurred sufficiently frequently that we could sample the different polarizabilities by taking repeated cyclotron frequency measurements with the same ion pair.

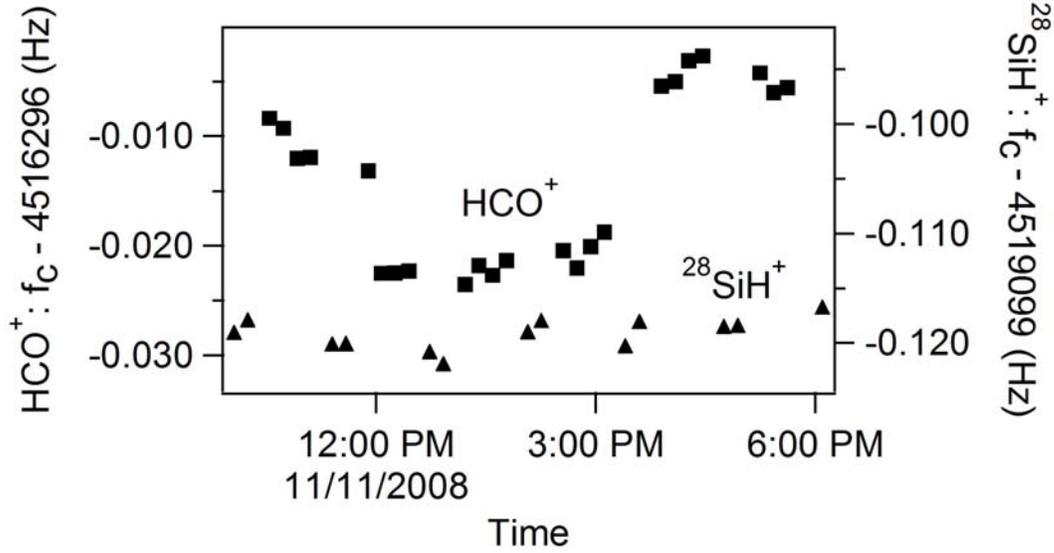


FIG. 1. Example of a run of cyclotron frequency (f_c) measurements on a HCO^+ ion using a $^{28}\text{SiH}^+$ ion as a reference. The larger changes in f_c of the HCO^+ ion occur due to transitions between rotational states with different polarizability.

Two methods for interpolating the SiH^+ f_c data were used for obtaining the ratio corresponding to the time of each measurement of f_c on the HCO^+ ion. The first fitted the $^{28}\text{SiH}^+$ data to a polynomial, and then used the equation for the polynomial to obtain an interpolated value. The second (piece-wise) method used the average of the two $^{28}\text{SiH}^+$ measurements before and after each HCO^+ measurement. The entire set of data was then converted to a series of ratios using these two procedures. This ratio data (using the polynomial interpolation) is shown in Fig. 2. Here we have subtracted the expected cyclotron frequency ratio without polarizability shifts, $R(\text{ref}) = 1.000\,620\,616\,529(23)$, which corresponds to the mass ratio of the ions determined from the value for the atomic mass of ^{28}Si from ref. [20], and of H and ^{16}O from [21], combined with molecular and ionic energies of formation from [22,23].

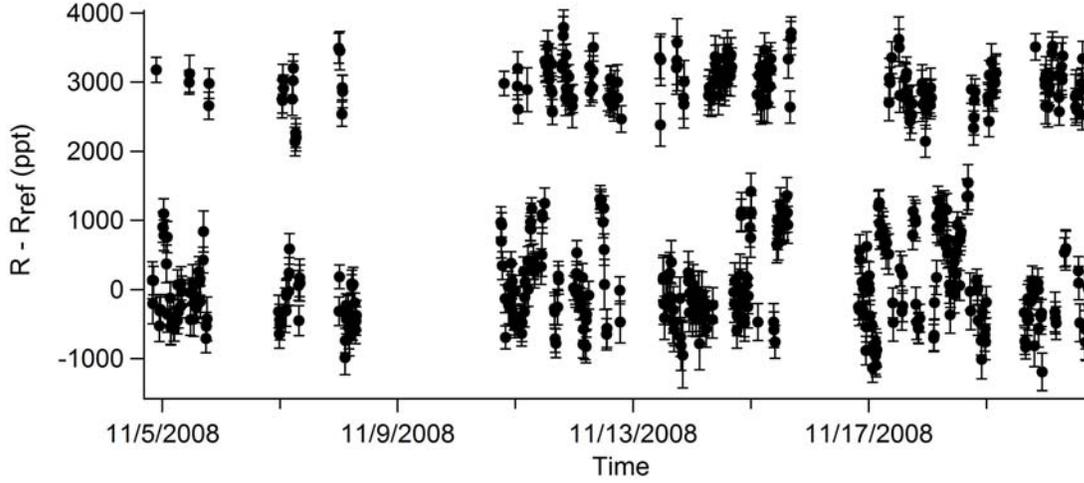


FIG. 2. All cyclotron frequency data for HCO^+ expressed as the ratio $R = f_c[\text{SiH}^+]/f_c[\text{HCO}^+]$. The vertical axis is proportional to the polarizability of the HCO^+ ion. (1 ppt = 10^{-12} .)

B. Extracting the Dipole Moment

To extract the HCO^+ dipole moment we first converted the ratio data to a histogram of number of measurements versus the ratio R , see Fig. 3.

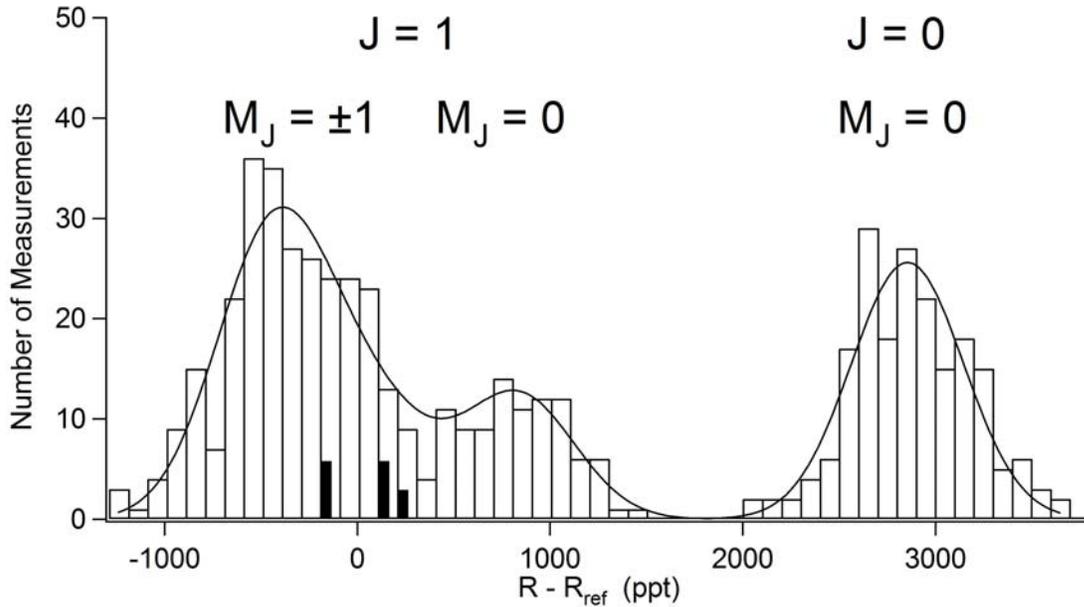


FIG. 3. Histogrammed cyclotron frequency shift data for the HCO^+ ion from Figure 2 indicating the various rotational states. The curve is a least-squares fit to the histogram (the reduced χ^2 for

this fit is 1.02). The solid bars indicate the position and amplitude of the contributions from the $J=2$ substates for the temperature returned from the fit. Contributions from higher J substates, which have smaller polarizability shifts and amplitudes, are negligible.

We fitted the histogram with sums of Gaussian line shapes,

$$n(R) = \sum_{J,M} \left\{ A_{J,M} \exp \left[-\frac{(R - b\Delta R_{J,M} - R_0)^2}{2\sigma^2} \right] \right\} \quad (3)$$

where $J, M = (0,0), (1,0), (1,\pm 1), (2,0), (2,\pm 1), (2, \pm 2)$. Here R_0 is the ratio that would be observed without the polarizability shift of HCO^+ , while the $\Delta R_{J,M}$ are the calculated shifts of the ratio corresponding to the states $(J, \pm M)$, assuming a dipole moment of $1 ea_0$. The parameter b , which the fit determines, is then equal to the observed dipole moment squared. The parameter σ corresponds to the scatter of our measurements of the cyclotron frequency. The $\Delta R_{J,M}$ were obtained using eqn. (1) and the rigid rotor approximation for the orientation polarizabilities [12],

$$\alpha_{xx}(J, M_J) = \begin{cases} \frac{\mu^2}{3B_0} & \text{for } J=0 \\ \left[\frac{J(J+1) - 3M_J^2}{2J(J+1)(2J-1)(2J+3)} \right] \frac{\mu^2}{B_0} & \text{for } J \neq 0 \end{cases} \quad (4)$$

To ensure convergence of the fit it was necessary to constrain the relative amplitudes of the component peaks. We did this by assuming a Boltzmann distribution between the different states. Hence, the relative amplitudes of the peaks are related to an effective rotational temperature, T_r , through $A_{J,M} = A \exp[-(hB_0J(J+1)/k_B T_r)]$, (where h is the Planck constant and k_B is the Boltzmann constant), reducing the number of parameters the fit has to determine. Using this procedure we obtain $|\mu| = 1.534(9) ea_0$, where the uncertainty is from the fitting routine. Varying the histogram bin size a factor of two, in either direction, changed this result by less than 0.1%, which is negligible.

As an alternative procedure for obtaining the dipole, that does not require detailed assumptions about the relative amplitudes of the peaks, we use the histogram to separate the raw data into a group corresponding to $J = 0$, which has the polarizability $\mu^2/3B_0$, and to a group for $J > 0$, for which the average polarizability is zero. Taking the difference in the centroids of these groups, and converting the ratio shift into a polarizability difference, gives $|\mu| = 1.545(10) ea_0$. For our final result we take the average of these two values for $|\mu|$, and include half their difference in quadrature. We also allow for the shift that results when we use the ratio data obtained from the piece-wise instead of the polynomial interpolation procedure. We do this by adding half this shift, that is $0.0075/2 ea_0$, and including this amount in the final error in quadrature as an additional uncertainty. Our final result for the dipole is hence $|\mu| = 1.543(12) ea_0$.

The effective rotational temperature obtained from the Gaussian fit was $T_R = 5.85(0.45)$ K, higher than the 4.2 K of the vacuum housing surrounding the Penning trap electrodes. As a possible explanation, we note that the average temperature of the Penning trap electrodes could be higher than 4.2 K due to heating by the rf-drives used in the cyclotron frequency measurements.

The value of R_0 returned by the fit corresponds to an observed $R = f_c[\text{SiH}^+]/f_c[\text{HCO}^+] = 1.000\ 620\ 616\ 530(25)$. The ground state of the SiH^+ ion has a $^1\Sigma_0$ electronic structure, and, because of its high rotational constant this ion is predominantly in its lowest rotational state. Using the dipole in ref. [6], the polarizability shift in our Penning trap is estimated to shift $f_c(\text{SiH}^+)$, and hence the observed R , down by 7.3(2) ppt [24]. The observed ratio is also shifted due to coulomb interaction between the inner ion and the parked ion [19]. While most of the ion-ion interaction effects should cancel, a dynamical shift due to coupling of the axial modes, which leads to a repulsion of their frequencies, should result in an increase of R of +26(+22/-11) ppt, where the error estimate allows for a 10% uncertainty in the actual parking radius of the outer ion. Allowing for both of these shifts we obtain a corrected $R = 1.000\ 620\ 616\ 511(33)$. This is in good agreement with $R(\text{ref}) = 1.000\ 620\ 616\ 529(23)$ as given above, corresponding to the mass ratio of the ions as determined from masses in the literature.

C. Thermal Radiation Induced Transition Rate

Although not used in obtaining the dipole moment, it is interesting to consider the transition rate between the rotational states. Assuming transitions from $J = 0$ to $J = 1$ are due to absorption of black-body radiation in the trap, the mean lifetime for an HCO^+ to remain in the $J = 0$ level is $1/\Gamma_{\text{abs}}$, where $\Gamma_{\text{abs}} = 3\langle n \rangle A_{10}$, where A_{10} , is the Einstein A -coefficient for spontaneous decay from $J = 1$ to 0, and $\langle n \rangle = 1/[\exp(2hB_0/k_B T) - 1]$, is the mean number of black-body photons per mode at the transition frequency, and the factor of 3 allows for the three M_J states of $J = 1$. Using the usual expression for the A -coefficients of electric-dipole transitions of a rigid rotor [12,25], and the above value for the dipole moment, the predicted mean lifetime is 3.9 hours at 4.2 K. By comparison, we observed 10 jumps from $J = 0$, for a total time observed in $J = 0$ of 2040 minutes, implying the mean lifetime in $J = 0$ was 3.4(1.1) hours. This agreement between the measured and predicted lifetimes is perhaps better than expected, since the copper electrodes of the trap effectively form a microwave cavity around the ion [18], which should modify the density of radiation modes at the transition frequency, and hence modify the effective A -values and transition rates.

IV. POLARIZABILITY SHIFT MEASUREMENTS ON NH^+

A. Cyclotron Frequency Measurements

The ground state of NH^+ corresponds approximately to Hund's case (a) and is designated $^2\Pi_{1/2}$ [26,27]. Because of the high rotational constant, $B_0 = 460$ GHz, the ion remains in the $J = 1/2$ rotational level. However, this level is split into two lambda-type doubling components of opposite parity, with a zero-field splitting of approximately 13.5 GHz [27]. This leads to very large polarizabilities for the two parity components, which are nearly equal in magnitude but opposite in sign [6]. Because of the smaller transition energy and dipole moment, transitions between the opposite parity components were too

infrequent to enable a polarizability shift spectrum to be built up by repeated measurements on the same NH^+ ion. The mean lifetime against spontaneous decay of the upper, negative parity component is estimated to be 285 days, while including transitions stimulated by black-body radiation, the mean lifetime is 42 days. Instead, a new $^{14}\text{NH}^+$ ion was made in the trap for each of 17 runs of cyclotron frequency measurements of $^{14}\text{NH}^+$ compared to $^{15}\text{N}^+$. After analysis of the run data, the $^{14}\text{NH}^+$ ion would be found to have been in the upper or lower parity state. However, in the 150 hours of data taking, one run did show a transition from the upper to the lower state, see Fig. 4.

Because the different runs involved remaking the NH^+ ion, more effort was made to reduce amplitude dependent systematic shifts to the cyclotron frequency. Consequently we chose the cyclotron radius for the measurements to be $60\ \mu\text{m}$ while the parking radius was approximately $1.67\ \text{mm}$. However, this small cyclotron radius and lower mass resulted in poorer detection signal-to-noise ratio and hence increased scatter in the ratio measurements compared to $\text{SiH}^+/\text{HCO}^+$. For these NH^+/N^+ measurements an additional difficulty was that the vacuum in the trap had degraded, which prematurely ended several runs after a few hours due to loss of one of the ions.

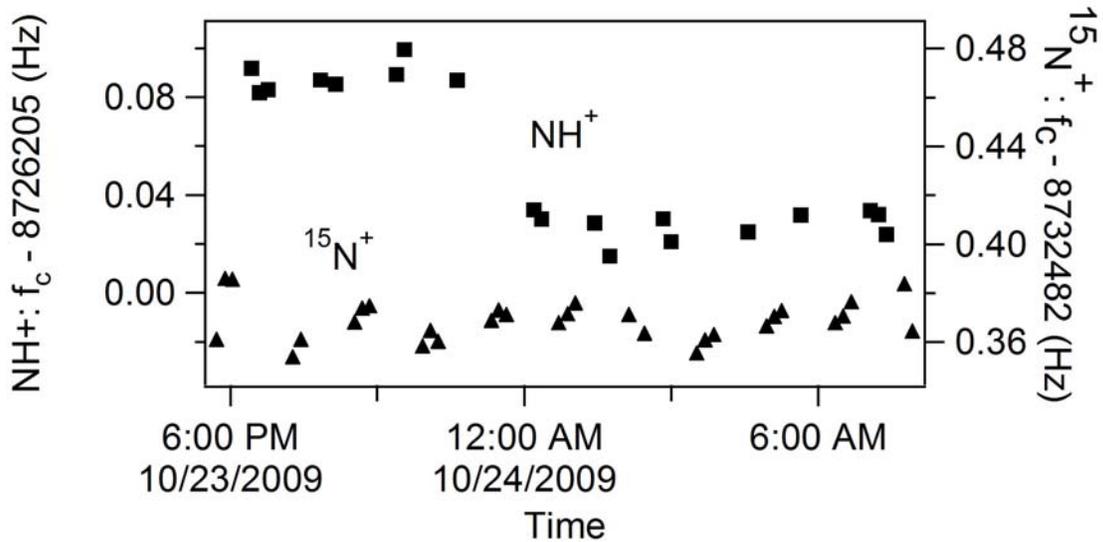


FIG. 4. Cyclotron frequency data for $^{14}\text{NH}^+$ compared to $^{15}\text{N}^+$. This is the only run of 17 showing a transition between the two lambda-type doubling parity states of the $\text{NH}^+ X^2\Pi_{1/2}, v=0, J=1/2$ rotational ground state. The transition is from the upper level, $J=1/2^-$ (which has negative polarizability and hence higher cyclotron frequency) to the lower level, $J=1/2^+$.

B. Extracting the Dipole Moment

Each of the 17 runs of alternate cyclotron frequency measurements for NH^+ versus $^{15}\text{N}^+$ was converted into a ratio by fitting a common polynomial as a function of time with an offset between the ions, as in our usual procedure for precision atomic mass measurements [15,16]. For the run that showed the “jump” in cyclotron frequency we fitted the sections before and after the jump separately. Hence we obtained 18 measurements of the ratio $f_c[\text{NH}^+]/f_c[^{15}\text{N}^+]$, of which 10 corresponded to the upper, negative parity (and also negative polarizability) component. These results are shown in Fig. 5.

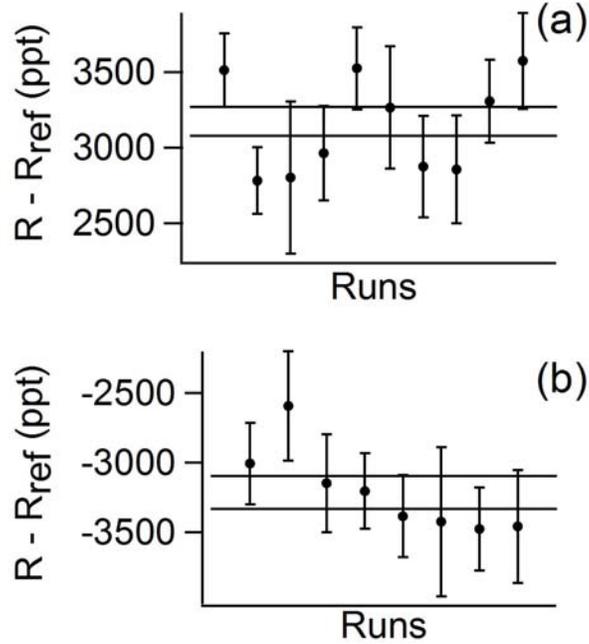


FIG. 5. Measurements of $R = f_c[^{14}\text{NH}^+]/f_c[^{15}\text{N}^+]$ divided into groups corresponding to (a), the upper (-ve polarizability), and (b) the lower, (+ve polarizability) lambda-type doubling component of $^{14}\text{NH}^+ X^2 \Pi_{1/2}, v=0, J=1/2$ ground state. The bands indicate the weighted averages with one standard deviation uncertainties.

For NH^+ , the polarizabilities of the lambda-doubling components of the groundstate cannot be related simply to the dipole moment; a further complication is that the Zeeman effect, although relatively small, leads to a significant dependence of the polarizabilities on magnetic field and M_J . Hence, we made use of the polarizability calculations of Cheng et al. [6], and compared the predicted shifts as given in Table I, which assume a theoretical dipole of $0.7897 ea_0$, with the measured shift obtained from the data in Fig. 5.

TABLE I. Polarizabilities α_{XX} and resultant cyclotron fractional frequency shifts, $\Delta f_c/f_c$, for a magnetic field of 8.53 tesla, of the $M_J = \pm 1/2$, positive and negative parity components of the NH^+ $X^2\Pi_{1/2}$, $v=0$, $J=1/2$ ground state, from the theoretical calculations of Cheng *et al.* [6].

J	M_J	α_{XX} (au)	$\Delta f_c/f_c$ (ppb)
$1/2^+$	$-1/2$	64300	-3.095
$1/2^+$	$+1/2$	74205	-3.571
$1/2^-$	$-1/2$	-71009	3.417
$1/2^-$	$+1/2$	-61105	2.941

The uncertainties in the ratio measurements in Fig. 5 are too large to be able to assign them unambiguously to different M_J states. Consequently, we averaged the data in the upper and lower parity states and obtained their difference, which gave $\Delta_{meas} = 6386(150)$ ppt. We then obtained our measured value for the dipole by simply scaling the theoretical dipole with $(\Delta_{meas}/\Delta_{calc})^{1/2}$, where $\Delta_{calc} = 6512$ ppt, is the average shift obtained from Table I. However, allowance for our lack of knowledge of the M_J state of each ion in Fig. 5 leads to an additional uncertainty. Assuming a multinomial distribution between the M_J states, this is estimated to be 114 ppt. Our measured dipole is hence $|\mu| = 0.782(11) ea_0$.

Taking the average of the measured cyclotron frequency ratios for the two parity states, we obtain an uncorrected average $f_c[\text{NH}^+]/f_c[^{15}\text{N}^+]$ ratio of 0.999 281 153 725(76), where the uncertainty is purely statistical. All systematic frequency shifts are estimated to

be below 10 ppt and so are negligible. Allowing for the average polarizability shift to the cyclotron frequency of NH^+ , as obtained from Table I, namely $-77(57)$ ppt, we obtain a measured mass ratio $M[^{15}\text{N}^+ / ^{14}\text{NH}^+] = 0.999\,281\,153\,802(95)$. Again, the uncertainty in the polarizability correction is due to our inability to resolve the different M_J states. This corrected ratio is in good agreement with the mass ratio $0.999\,281\,153\,755(65)$, which is obtained from the masses of ^1H , ^{14}N and ^{15}N in ref. [21] (and which was used as R_{ref} in Fig. 5); and also with $0.999\,281\,153\,779(51)$, obtained using the mass difference $M[^{14}\text{N}] - M[^{12}\text{C}^{16}\text{O}]$ measured in ref. [1], and the masses of ^1H , ^{16}O and ^{15}N from ref. [21].

V. CONCLUSION

In Tables II and III we compare our measured dipole moments of HCO^+ and NH^+ with some of the more recent theoretical values. (Because we measure the square of the dipole moment, our results provide no information on the sign. The theoretical values for the NH^+ dipoles are converted from debye using $1\,ea_0 = 2.541\,58$ debye). As can be seen, there is good agreement between theory and our experiment for these two ions, which have quite different electronic structure. Further, because of the paucity of other accurate experimental values, our measurements help validate the use of the same calculational procedures for the dipoles of other small molecular ions, which may have chemical and astrophysical importance.

TABLE II Comparison of theory and experiment for the dipole moment of HCO^+

Source	Method	μ (ea_0)
Yamaguchi et al. [28]	Theory	1.530(2)
Botschwina et al. [29]	Theory	1.534(4)
This work	Experiment	1.543(12)

TABLE III Comparison of theory and experiment for the dipole moment of NH^+

Source	Method	μ (ea_0)
Cheng et al. [6]	Theory	0.7897(80)
This work	Experiment	0.782(11)

We note that the experimental precision for measuring polarizability shifts and hence dipole moments can be improved. For instance, using the simultaneous cyclotron frequency measurement technique of ref. [1], an order of magnitude could be gained. Rapid switching between the states of different polarizability, for instance by inducing transitions with microwaves, would also enable higher precision. We also note that it would be interesting to extend these techniques to more complex ions where the calculations of the dipole moments are less accurate. Because of the quadratic dependence of the polarizability shift on magnetic field, and because the shifts are largest for the rotational ground state, this would be facilitated by the use of a Penning trap with a higher magnetic field, operated at a temperature below 4.2 K.

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