Determination of the electric dipole moment of HN$_2^+$

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The electric dipole moment of the linear molecular ion HN$_2^+$ was determined by measuring the isotope shifts of the rotational g factors of different isotopic species. We studied the Zeeman effect of the $R(6)$ rotational transition at 650 GHz. In a magnetic field of 5.4 T the rotational transition split into two components, separated by 2.2–2.5 MHz. The g_R factors were determined for H^{14}N^{14}N$^+$, H^{14}N^{15}N$^+$, and H^{15}N^{14}N$^+$. The dipole moment for H^{14}N^{14}N$^+$ was determined as (3.4 ± 0.2) D, which is in excellent agreement with the theoretical value. The transitions were observed by direct absorption spectroscopy with a tunable FIR sideband spectrometer. The ions were generated in a modified anomalous discharge placed in a superconducting magnet.

INTRODUCTION

The permanent electric dipole moment of a molecule is a fundamental quantity reflecting its electronic structure. Knowledge of the electric dipole moment is essential for the calculation of rotational absorption intensities and radiative lifetimes. For neutral molecules Stark spectroscopy allows the determination of the electric dipole moment. Such measurements cannot be made for ions, because the electric field accelerates the ions towards the wall of the discharge tube. The lack of experimental data is in contrast to a large number of theoretical data obtained by *ab initio* calculations.

The first direct measurement of an electric dipole moment for an ion was carried out by Laughlin *et al.* for ArH$^+$. The dipole moment was determined from the measurement of the rotational Zeeman effect by far-IR laser spectroscopy. In subsequent measurements[1–3] the dipole moment of ArH$^+$ was determined as (1.4 ± 0.4), (1.6 ± 0.4), and (3.0 ± 0.6) D, whereas a theoretical value of 2.2 D was obtained by Rosmus.[4] Their experiments were based on theoretical considerations by Townes *et al.*,[5] who showed that the knowledge of the experimentally determinable rotational magnetic g_R factor for two different isotopic species allows the calculation of the electric dipole moment. The dipole moment was calculated using the following expression:

$$\mu = -eh/(16\pi^2 M_p \Delta z)(g_R'/B' - g_R/B) + 1/2(Qe\Delta z),$$
(1)

where μ, g_R, B, Δz are the electric dipole moment, the rotational g factor, the rotational constant of the isotopic species (a), and the shift in the center of mass upon isotopic substitution, respectively. The primed quantities are the corresponding quantities of the isotopically substituted species (b). Q is the net charge of the molecule. This expression was first applied to determine the sign of the electric dipole moment of CO,[6] which cannot be obtained by Stark spectroscopy. Because the electric dipole moment is proportional to the difference between two nearly equal quantities g_R'/B' and g_R/B, it is necessary to measure these ratios with a very high

precision in order to obtain an acceptable error for μ. The result is quite sensitive even to small systematic errors. This was discussed in the third measurement by Laughlin *et al.*,[3] where "systematic errors present in the previous data have been discovered and eliminated."

The application of Eq. (1) is based on the following assumptions:

(i) The structure of the molecule remains constant upon isotopic substitution. (ii) The validity of first order perturbation theory.

The first assumption implies that only the distance between the center of mass and each atom is changed, while the distance *between* the atoms is kept constant. This is not true in general, mainly due to the effects of the zero point vibrations, which are different for distinct isotopic species. It is possible to correct for this by extrapolating all measured rotational factors $g_R(r')$ to a common equilibrium value $g_R(r_e)$ for all isotopic species (r': value of r for $v = 0$). This was discussed in detail in Ref. 3, where various methods for an extrapolation of $g_R(r)$ have been proposed. For comparison the dipole moment was calculated from:

(1) ground state g factors without any extrapolation, yielding 2.85 D;

(2) extrapolated equilibrium g factors based on the analogy with HF using a Dunham expansion, which resulted in a dipole moment of 3.35 D;

(3) extrapolation using a vibrationally corrected g_R factor, calculated by a method developed by Gruebele *et al.*,[7] where the vibrational correction is determined from a fit of high resolution experimental data to a potential surface, yielding a dipole moment of 2.95 D.

Another *ab initio* study of Geertsen and Scuseria[8] presented more theoretical evidence supporting a dipole moment of 2.1 D. They pointed out that the use of a Dunham expression leads in general to unsatisfactorily large errors. They believe, that using a Dunham expansion can be the source of discrepancy between theoretical and experimental dipole moments. The lack of experimental vibrational corrections to the g factors was also considered by Laughlin *et al.* as an uncertainty in their data.

Our experimental setup is based on a FIR laser sideband spectrometer equipped for Zeeman measurements. The main features of the instrument and analysis are the following:

(1) The incorporation of a superconducting magnet, which allowed the measurements in high magnetic fields. For this purpose a modified discharge cell suitable for measurements in magnetic fields of 5 T was developed.

(2) The measurements were carried out at a fixed magnetic field. The consequences are discussed in the experimental section.

(3) The lines were fitted to a Voigt instead of a Lorentzian line profile. It will be shown that this is essential in the analysis of the present data.

As long as only g_R factors for $v = 0$ can be determined, it is important to restrict the isotopic substitution to the heavy nucleus. Since in the present work only the N atoms were substituted, the change in the reduced mass and hence the change of the zero point vibration is negligible. Therefore there is no need to extrapolate the rotational g factors for HN_2^+.

In this work the first determination of the dipole moment of the astrophysically important ion HN_2^+ is reported. The ion was first observed in interstellar space[9] and later in the laboratory, in the microwave,[10] infrared,[11] and in the FIR[12] region. HN_2^+ was found to occur in a large number of interstellar sources, where the wide distribution of HN_2^+ supported the ion–molecule theory of interstellar chemistry. Molecular abundances in radioastronomy are determined from rotational emission intensities. Therefore an experimental determination of the electric dipole moment with high accuracy would allow a test of the high precision *ab initio* result obtained by Botschwina[13] as well as furthering the knowledge of interstellar cloud chemistry.

EXPERIMENTAL

Because the electric dipole moment μ is proportional to the difference between two nearly equal quantities g_R'/B' and g_R/B, an error of $\sim 1\%$ in g_R will result in an error of 10% in μ for HN_2^+. Whereas the rotational constants B and B' are normally well known from microwave measurements,

g_R and g_R' have to be measured. In order to determine g_R the Zeeman splittings of pure rotational transitions in high magnetic fields were measured. According to the expression: $E = g_R \beta_I M_J H$ (H: magnetic field, β_I: nuclear magneton), which describes the Zeeman energy for a linear $^1\Sigma$ molecule, pure rotational transitions split in a magnetic field, perpendicular to the polarization of the laser, as $v = v_0 \pm \beta_I g_R H$, where v_0 is the transition frequency for zero magnetic field and the $+$ or $-$ signs correspond to allowed $\Delta M = \pm 1$ transitions, respectively. This means that two separate transitions can be observed, split by $\Delta v = 2g_R \beta_I H$. The accuracies of the frequency and the magnetic field both contribute in an equal manner to the final uncertainty of g_R. If measurements for the two isotopically substituted species are made in the same magnetic field, Eq. (1) can be modified to

$$\mu = -eh/(16\pi^2 M_p \Delta z 2\beta_I H)(\Delta v'/B' - \Delta v/B) + 1/2(Qe\Delta z), \qquad (2)$$

with Δv and $\Delta v'$ being the Zeeman splittings for the two species.

The accuracy of the magnetic field measurement in our experiment was limited to 0.1% by the homogeneity of the magnetic field. The contribution of this error to the determination of μ was negligible compared with other errors. A superconducting magnet which allowed separate measurements at a constant magnetic field was chosen to avoid measurements at different magnetic fields, which would require very precise absolute magnetic field measurements for each magnetic field. The superconducting magnet had the advantage of providing a large magnetic field combined with a high field stability (fluctuating less than 0.05%). The uncertainty in the frequency determination completely dominated the error in μ.

The lines were recorded in the far infrared (FIR), where the linewidth, determined by Doppler and pressure broadening, was sufficiently small. A low pressure (less than 100 mT) in the ion generating gas discharge was chosen in order to suppress additional pressure broadening. The resulting linewidth was 2.6 MHz (FWHM). The spectra were taken with the tunable far infrared spectrometer in Nijmegen, which will be described in detail elsewhere.[14] The overall setup is displayed in Fig. 1. The tunable FIR radiation
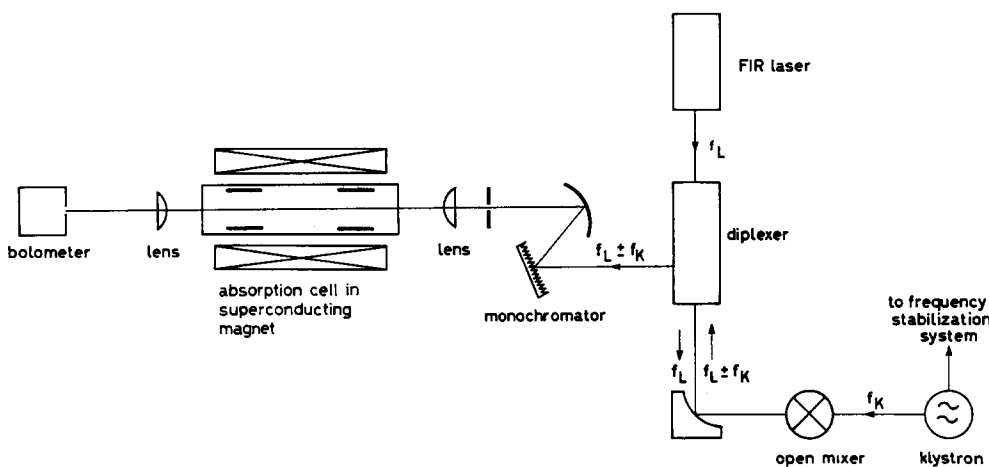

FIG. 1. Experimental setup.

was generated by mixing tunable microwaves with a CO_2 pumped FIR laser on a Schottky diode. The laser line used in the course of the experiment was the 716.1568 GHz line of formic acid (HCOOH). The spectra were recorded using frequency modulation of the microwave source (klystrons) and lock-in detection at $2f$ with a 1.5 K Si bolometer.

The ions were observed in a liquid nitrogen cooled discharge cell using a mixture of H_2 and N_2. The diameter of the discharge cell was 2.6 cm, adapted to the diameter of the magnet. In order to achieve a high accuracy in the frequency measurement, a production method with a high signal to noise ratio at low pressures was required. This could be accomplished by using an anomalous discharge. We used a setup similar to the one described by de Lucia *et al.*,[15] except that ours was modified for operation in high magnetic fields. De Lucia *et al.* applied a magnetic field of 300–400 G to extend the negative glow over the entire length of the discharge tube, thus increasing the ion density by two orders of magnitude. However, they found that the signal strength decreased after an optimum magnetic field of 300–400 G towards higher magnetic fields. This observation was reproduced in the present experiment. Furthermore, it was found that the decrease of the signal was accompanied by a decrease in the discharge voltage. For sufficiently high magnetic fields the discharge voltage became too low to further maintain a negative glow. Since for an anomalous discharge the current is proportional to the voltage, the maximum current for which an anomalous discharge could be observed, decreased with increasing magnetic field. In order to allow measurements at high magnetic fields (5.5 T)—the superconducting magnet provided the field for the negative glow extension as well as for the Zeeman spectroscopy—we used a modified cathode design, shown in Fig. 2. The adjustable cathode surface allowed the discharge voltage to be controlled and hence kept large enough at higher magnetic fields. This technique was first applied by Bohle *et al.*[16] at higher pressures (~ 2 Torr) where a special cathode design was essential. In the present work, the cathode surface was altered by sliding a glass tube inside the cathode, as can be seen in Fig. 2. Maximum signal to noise ratios were achieved with an uncovered cathode length of about 3 cm, which yielded a discharge current of 4 mA at a voltage of 1.2 kV.

Signals of the isotopic species $H^{14}N^{15}N^+$ and

TABLE I. Zero field transition frequencies for the $R(6)$ transition of HN_2^+ and Zeeman splittings at 5.444 T of the different isotopic species.

	Zero field frequency	Zeeman splitting
$H^{14}N^{15}N^+$	631.735 GHz	2562(10) kHz
$H^{15}N^{14}N^+$	638.327 GHz	2203(10) kHz
$H^{14}N^{14}N^+$	652.095 GHz	2434(20) kHz

$H^{15}N^{14}N^+$ were generated with a mixture of equal amounts of $^{14}N^{14}N$ and $^{15}N^{15}N$. With this mixture, all four species: $H^{14}N^{15}N^+$, $H^{15}N^{14}N^+$, $H^{14}N^{14}N^+$ and $H^{15}N^{15}N^+$ were produced in equal amounts. This indicates that N_2 is completely dissociated in an anomalous discharge before recombination occurs. For the production of $H^{14}N^{14}N^+$ a mixture of H_2 and $^{14}N^{14}N$ was used.

RESULTS

The Zeeman splittings of the $R(6)$ transitions of the three isotopic species: $H^{14}N^{15}N^+$, $H^{15}N^{14}N^+$, and $H^{14}N^{14}N^+$ were recorded in a magnetic field of $B = 5.444$ T. The zero field transitions were found within 20 MHz of the frequencies predicted by the constants obtained by previous measurements from Szanto *et al.*[17] and Sastry *et al.*[18] The zero field transition frequencies are given in Table I. The measured rotational transitions split by the Zeeman effect are shown in Figs. 3–5. The spectra were digitized and a curve fitting with approximately 170 points per spectrum was carried out. Each Zeeman component was fitted with a Voigt profile determined by four parameters: the height, the transition frequency, and the two widths of the Lorentzian and the Gaussian part, respectively. The linewidth was assumed to be the same for both Zeeman components of the same isotopic species, whereas the height and the transition frequencies of the two components were fitted independently. The intensity ratio of the two components is determined by the ratio of the right to left handed circularly polarized component of the incident radiation. This ratio can differ from 1, due to the various optical components in the spectrometer. The base line was fitted to a first degree poly-
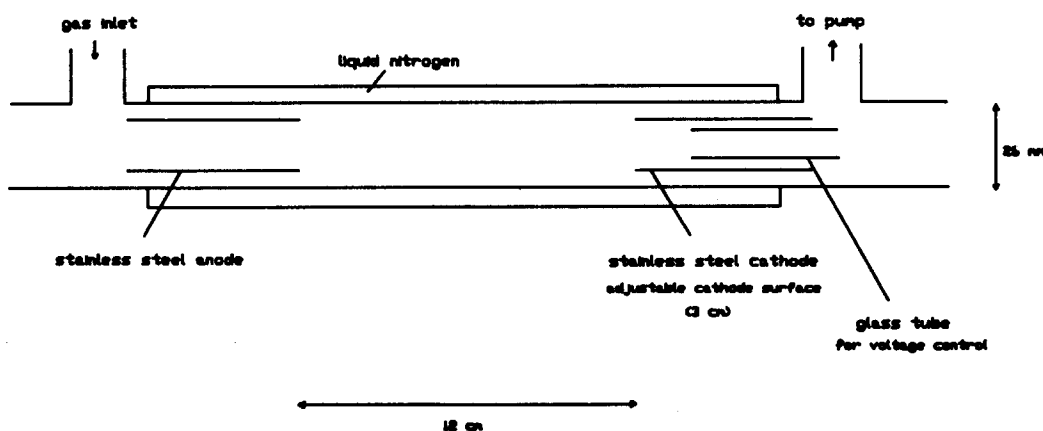

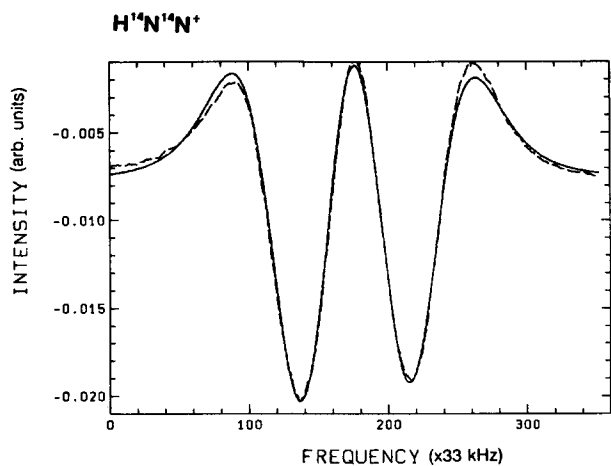FIG. 2. Modified discharge for measurements in high magnetic fields.

$H^{14}N^{14}N^+$

FIG. 3. Experimental (dotted) and fitted (solid) line profile for $H^{14}N^{14}N^+$, showing the Zeeman splitting at 5.444 T.
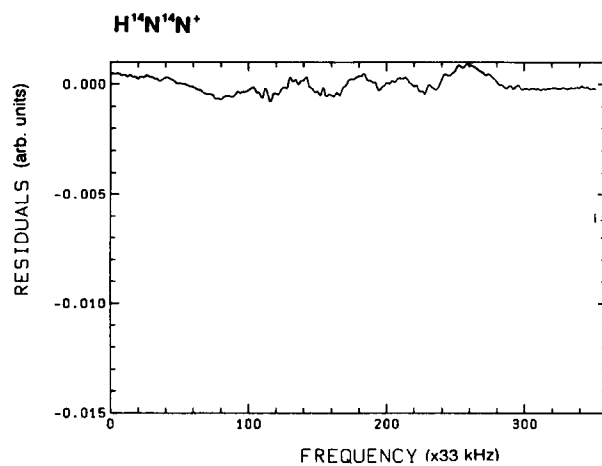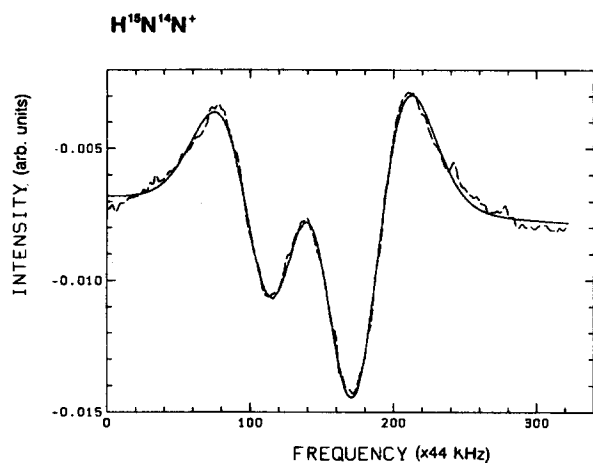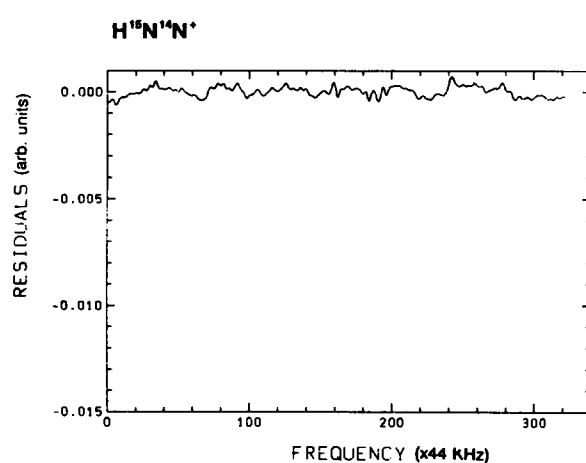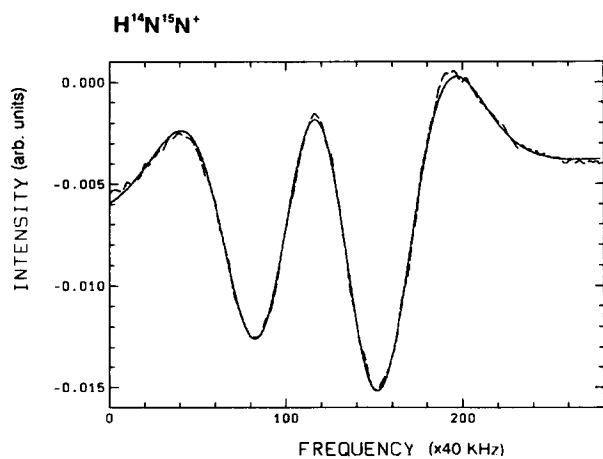
$H^{14}N^{14}N^+$

FIG. 6. Residual (experimental minus fitted line profile) for $H^{14}N^{14}N^+$ corresponding to Fig. 3.

$H^{15}N^{14}N^+$

FIG. 4. Experimental (dotted) and fitted (solid) line profile for $H^{15}N^{14}N^+$, showing the Zeeman splitting at 5.444 T.
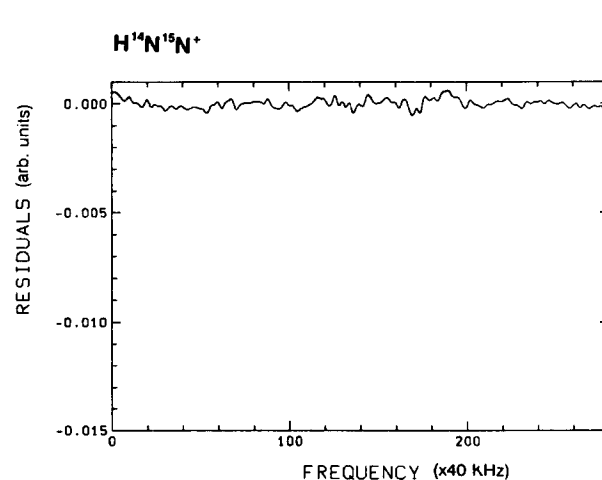
$H^{15}N^{14}N^+$

FIG. 7. Residual for $H^{15}N^{14}N^+$ corresponding to Fig. 4.

$H^{14}N^{15}N^+$

FIG. 5. Experimental (dotted) and fitted (solid) line profile for $H^{14}N^{15}N^+$, showing the Zeeman splitting at 5.444 T.
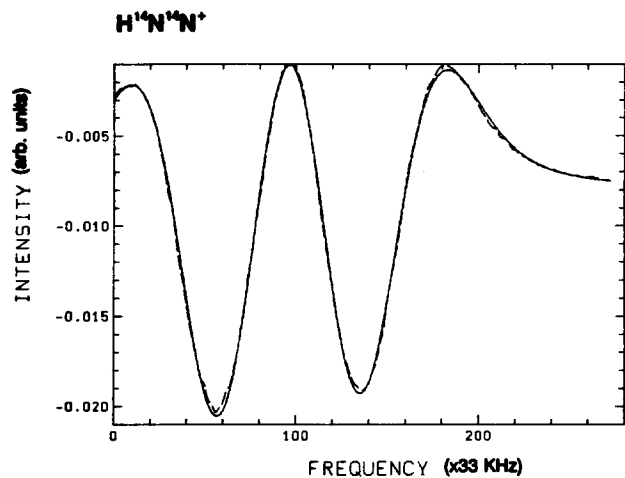
$H^{14}N^{15}N^+$

FIG. 8. Residual for $H^{14}N^{15}N^+$ corresponding to Fig. 5.

FIG. 9. Experimental and fitted line for $H^{14}N^{14}N^+$, leaving out the parts affected by a base line shift.

TABLE II. Dipole moments (in Debye units) derived from Zeeman splittings for different pairs of isotopic species.

	$H^{14}N^{15}N^+$	$H^{15}N^{14}N^+$	$H^{14}N^{14}N^+$
$H^{15}N^{14}N^+$ and $H^{14}N^{15}N^+$	3.46(15)	3.29(15)	3.37(15)
$H^{14}N^{14}N^+$ and $H^{14}N^{15}N^+$	3.3(6)	3.2(6)	3.2(6)
$H^{14}N^{14}N^+$ and $H^{15}N^{14}N^+$	3.6(4)	3.5(4)	3.5(4)

nomial. In total we fitted eight parameters. The result of the curve fits is shown in Figs. 3–5. If 80 instead of 170 data points were used the resulting Zeeman splitting changed by less than 5 kHz. The results from two successive scans of the same isotopic species deviated by less than 5 kHz. Based on these considerations we estimate that the frequency precisions in the splittings of $H^{14}N^{15}N^+$ and $H^{15}N^{14}N^+$ were 10 kHz. The residuals (observed minus calculated line profiles) for all three isotopic species are given in Figs. 6–8.

The scan of the $H^{14}N^{14}N^+$ spectrum showed a considerable, but reproducible, baseline offset (see Fig. 6), which resulted in a least-square deviation four times larger than that of the other two isotopic species. This base line offset is limited to a small part of the scan and is probably caused by fluctuations of the microwave power. A second fit, where this part of the scan was neglected, was performed (see Figs. 9 and 10). The Zeeman splittings obtained for the different fits changed by up to 20 kHz. Hence the overall error in $\Delta\nu$ for 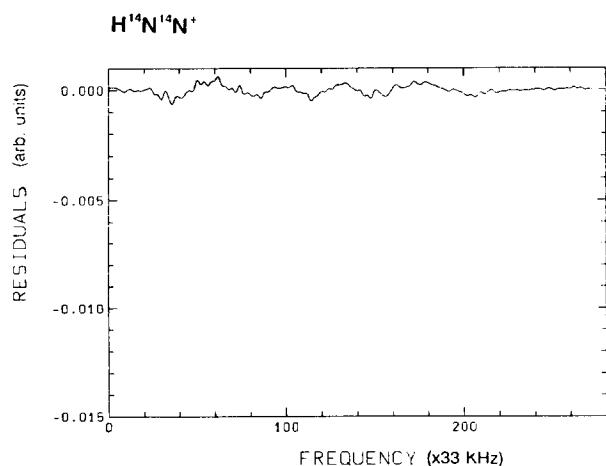$H^{14}N^{14}N^+$ was assumed to be 20 kHz. For the determination of the electric dipole moment, the Zeeman splitting was used as obtained from the second fit (Fig. 9).

The final Zeeman splittings for all isotopomers are listed in Table I. Using Eq. (2) the dipole moments of the different isotopic species for all data sets were calculated. The rotational constant B as well as the equilibrium geometry were taken from Ref. 17. The uncertainties in these numbers can be neglected compared with the estimated frequency errors. The results are given in Table II. The resulting dipole moment changed by 0.4 D if a curve fitting with a Gaussian profile instead of a Voigt profile was performed (with a Lorentzian profile by up to 1.0 D). Because the pressure broadening contributed 1/3 of the overall linewidth, the application of the Gaussian profile resulted in a least-square deviation, which was twice that obtained with a Voigt profile. This showed, that the use of a Voigt profile is essential at the level of accuracy required in our work.

Combining the rotational g_R factors of two isotopic species the dipole moment of both isotopic species in the center of mass can be found. The difference between the dipole moments of the isotopomers is given by the shift in the center of mass multiplied by the net charge of the ion, which gives the dipole moment for all isotopic species:

$$\mu - \mu' = eQ\Delta z,$$

where Q is the net charge and Δz the shift of the center of mass. Hence three different values for each isotopic species can be derived.

If we compare the dipole moments given in Table II, it can be seen that they agree very well within their estimated uncertainties. The weighted mean value for the electric dipole moment of $H^{14}N^{14}N^+$ (3.4 $\pm$ 0.2) D is in excellent agreement with the theoretical value obtained by Botschwina et al. (3.37 D).[13] The reliability of our data is supported by the fact that dipole moments determined in independent measurements agree with each other. This confirms the validity of Eq. (2) for the determination of the electric dipole moment in case of a restricted isotopic substitution (only the N atoms were substituted). In this context it would be interesting to compare these results with ab initio calculations of the functions $g_R(r)$, which are not yet available.

FIG. 10. Residual for $H^{14}N^{14}N^+$ corresponding to Fig. 9.

ACKNOWLEDGMENTS

[1] K. B. Laughlin, G. A. Blake, R. C. Cohen, D. C. Hovde, and R. J. Saykally, Phys. Rev. Lett. **58**, 996 (1987).
[2] K. B. Laughlin, G. A. Blake, R. C. Cohen, D. C. Hovde, and R. J. Saykally, Philos. Trans. R. Soc. London Sect. A **324**, 109 (1988).
[3] K. B. Laughlin, G. A. Blake, R. C. Cohen, and R. J. Saykally, J. Chem. Phys. **90**, 1358 (1989).
[4] P. Rosmus, Theor. Chim. Acta **51**, 359 (1979).
[5] C. H. Townes, G. C. Dousmanis, R. L. White, and R. F. Schwarz, Discuss. Faraday Soc. **19**, 56 (1955).
[6] B. Rosenblum, A. H. Nethercot Jr., and C. H. Townes, Phys. Rev. **109**, 400 (1958).
[7] M. Gruebele, E. Keim, A. Stein, and R. J. Saykally, J. Mol. Spectrosc. **131**, 343 (1988).
[8] J. Geertsen, and G. E. Scuseria, J. Chem. Phys. **90**, 6486 (1989).
[9] B. E. Turner, Astrophys. J. **193**, L83 (1974).
[10] R. J. Saykally, T. A. Dixon, T. G. Anderson, P. G. Szanto, and R. C. Woods, Astrophys. J. **205**, L101 (1976).
[11] C. S. Gudemann, M. H. Begemann, J. Pfaff, and R. J. Saykally, J. Chem. Phys. **78**, 5837 (1983).
[12] F. C. van den Heuvel and A. Dymanus, Chem. Phys. Lett. **92**, 219 (1982).
[13] P. Botschwina, Chem. Phys. Lett. **107**, 535 (1984).
[14] P. Verhoeve, E. Zwart, M. Versluis, M. Drabbels, J. J. ter Meulen, W. L. Meerts, A. Dymanus, and D. B. McLay, Rev. Sci. Instrum. **61**, 1612 (1990).
[15] F. C. De Lucia, E. Herbst, G. Plummer, and G. Blake, J. Chem. Phys. **78**, 2312 (1983).
[16] W. Bohle, J. Werner, D. Zeitz, A. Hinz, and W. Urban, Mol. Phys. **58**, 85 (1986).
[17] P. G. Szanto, T. G. Anderson, R. J. Saykally, N. D. Piltch, T. A. Dixon, and R. C. Woods, J. Chem. Phys. **75**, 4261 (1981).
[18] K. V. L. N. Sastry, P. Helminger, E. Herbst, and F. C. De Lucia, Chem. Phys. Lett. **84**, 286 (1981).