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THE FINE-STRUCTURE INTERVALS OF $^{14}N^+$ BY FAR-INFRARED LASER MAGNETIC RESONANCE[1,2]

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ABSTRACT

The far-infrared laser magnetic resonance spectra associated with both fine-structure transitions in $^{14}N^+$ in its ground ^3P state have been recorded. This is the first laboratory observation of the $J = 1 \leftarrow 0$ transition and its frequency has been determined two orders of magnitude more accurately than previously. The remeasurement of the $J = 2 \leftarrow 1$ spectrum revealed a small error in the previous laboratory measurements. The fine-structure splittings (free of hyperfine interactions) determined in this work are

$$\Delta E_{10} = 1461.13190\ (61)\ \text{GHz}$$

$$\Delta E_{21} = 2459.38006\ (37)\ \text{GHz}\ .$$

Zero-field transition frequencies which include the effects of hyperfine structure have also been calculated. Refined values for the hyperfine constants and the g_J factors have been obtained.

Subject headings: atomic data — ISM: atoms — line: identification — radio lines: ISM

1. INTRODUCTION

Although most of the far-infrared emission in our Galaxy is a continuous spectrum from interstellar dust heated by starlight, some sharp spectral lines from the gaseous component of the interstellar medium are superposed on it. The fine structure transitions in C^+ (^2P) at 158 μm and in N^+ (^3P) at 122 and 205 μm are prominent in this emission (Wright et al. 1991) and provide useful probes of the large-scale structure. Galactic extinction is insignificant at these wavelengths and the ionization potential of hydrogen (13.60 eV) lies between those of carbon (11.3 eV) and nitrogen (14.53 eV). Consequently, N^+ emission is associated only with the warm ionized interstellar gas.

Both fine-structure transitions within the ground state of N^+ have now been detected by observational astronomers. The 122 μm line was first observed by Rubin et al. (1989) in a bright southern H II region with a grating spectrometer mounted on the Kuiper airborne observatory (see also Erickson et al. 1991). Both transitions were later seen in the interstellar gas in the Milky Way by Wright et al. (1991) using a Michelson interferometer on-board the *Cosmic Background Explorer* (*COBE*). Extragalactic detection of the two transitions was reported shortly afterwards by Petuchowski et al. (1992) in a nearby galaxy M82, again from the Kuiper observatory. Although the frequency of the transition at 122 μm had been measured accurately in the laboratory before these observations (Cooksy, Hovde, & Saykally 1986), that for the 205 μm transition was only poorly known, the best available value being inferred from measurements in the vacuum ultraviolet (Eriksson 1983). Indeed, the astronomical observation by Wright et al. (1991) was the first direct measurement of this interval. These authors claimed a 1 σ accuracy of 270 MHz.

The developing use of heterodyne and Fabry-Perot receivers on airborne platforms to detect atomic and molecular lines in the far-infrared from astronomical sources highlights the need for much more accurate measurements of the important fine-structure intervals in atoms. The $^3P_1$–$^3P_0$ transition in N^+ (N II) is certainly one such interval. Accurate knowledge of the rest frequency is also required for relative velocity measurements of different components of the interstellar gas. For example, the determination of the rotation curve at the Galactic center by observation of the 158 μm line of C^+ provides evidence for a black hole (Lugten et al. 1986). The frequencies must be known to within a few megahertz to be useful for these purposes. Far-infrared laser magnetic resonance (LMR) has proved itself to be a powerful method for obtaining this information in the laboratory. A large number of atomic fine-structure intervals have now been measured by this technique; indeed the earlier laboratory measurement of the $J = 2 \leftarrow 1$ transition of N^+ at 122 μm was made in this way.

In this paper, we report the first laboratory detection of the $J = 1 \leftarrow 0$ transition in $^{14}N^+$ in its ground ^3P state by far infrared LMR. Not only has this enabled us to measure its frequency very accurately but it has also allowed us to correct the previously reported value for the frequency of the $J = 2 \leftarrow 1$ transition (Cooksy et al. 1986) which was 10 MHz in error. These observations have been made possible by the development of a new microwave discharge source for the production of reactive ions and molecules.

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2. EXPERIMENTAL DETAILS

The LMR apparatus used in this work has been described in some detail elsewhere (Sears et al. 1982). Briefly, it consists of a far-infrared gain cell pumped transversely by a grating-tuned CO_2 laser and separated from the intracavity sample region by a polypropylene beam splitter set at the Brewster angle. The sample region is situated between the 38 cm, ring-shimmed, cobalt-nickel pole caps of an electromagnet which produces a homogenous field region about 7.5 cm in diameter. The field is stabilized to the signal from a rotating coil magnetometer which is calibrated periodically against a proton NMR fluxmeter. We estimate the magnetic flux density (B_0) measurements to be accurate to 0.01 mT below 0.1 T and to $10^{-4}B_0$ above this flux density. When a transition in the atomic sample is tuned into resonance with the laser frequency, the total far-infrared power inside the laser cavity changes and is modulated at 40 kHz by a pair of Helmholtz coils. The laser output is detected with a liquid helium-cooled, photoconductive detector and the signal is processed by a lock-in amplifier.

The N^+ ions were generated in the sample volume with a new microwave discharge source which has been developed specifically for the production of ions and other transient species. The details of its construction have been given elsewhere (Varberg, Evenson, & Brown 1994). The source was designed to operate in high magnetic fields (indeed its performance is enhanced by the presence of a magnetic field) and to produce a plasma which extends out into the far-infrared radiation field. The discharge produces considerable noise on the far-infrared laser output and the microwave power was often reduced to improve the signal-to-noise ratio. The typical power fed to the microwave cavity was 30 W. The N^+ ions were formed by flowing ultra-high purity helium through the discharge with a very small amount of nitrogen added. Typical pressures employed were 0.67 Pa (5 mtorr) of N_2 and 130 to 200 Pa (1 to 1.5 torr) of He. Both these pressures were critical; in particular, the signals disappeared completely if the pressure was reduced below 130 Pa.

3. RESULTS AND ANALYSIS

In studying N^+, we first repeated the observation of the $J = 2 \leftarrow 1$ spectrum with the 122.5 μm line of CH_2F_2 recorded in the previous work by Cooksy et al. (1986). Once the signal had been optimized, we found that we were able to detect the spectrum with a much improved signal-to-noise ratio. Considerable signal averaging had been required in the earlier work whereas we were able to record the spectrum with good signal-to-noise ratio in a single scan with a 300 ms time constant. A typical spectrum, recorded in this case with the 121.2 μm line of $^{13}CH_3OH$, is shown in Figure 1. The ^{14}N hyperfine structure is very obvious.

The improved signal-to-noise ratio allowed us straight away to detect the LMR spectrum associated with the $J = 1 \leftarrow 0$ transition in $^{14}N^+$, using the 203.6 μm line of $^{13}CH_3OH$. It was this observation which had eluded previous workers. We discovered that the performance of the discharge was strongly field dependent (the glowing plasma became tightly pinched as the magnetic field increased) and that the N^+ concentration varied with magnetic field also. An example of a recording of the resonance for the $J = 1 \leftarrow 0$ transition is shown in Figure 2. For this transition, the ^{14}N hyperfine splitting is very small in both upper and lower states and is not resolved in our experiments.

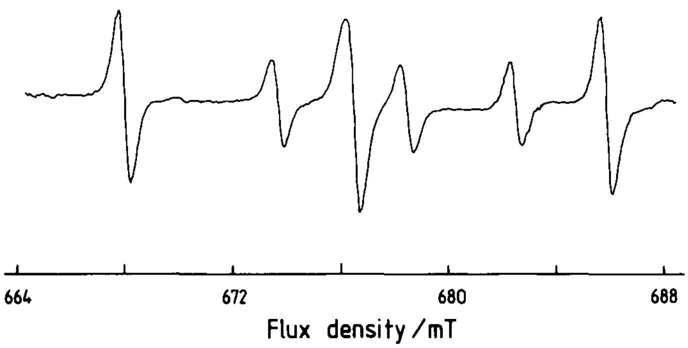

FIG. 1.—Far-infrared laser magnetic resonance spectrum associated with the $J = 2 \leftarrow 1$ transition of $^{14}N^+$ in its ground ^3P state, recorded with the 121.2 μm line of $^{13}CH_3OH$, pumped by the 10R(28) line of a CO_2 laser. The spectrum was recorded with the oscillating magnetic field perpendicular to the applied magnetic field ($\Delta M_J = \pm 1$). The output time constant of the lock-in amplifier was 0.3 s. The main triplet are the three hyperfine components of the $M_J = 2 \leftarrow 1$ transition and the three more closely spaced lines are the $M_J = 1 \leftarrow 0$ transition. Three, still weaker hyperfine components of the $M_J = 0 \leftarrow -1$ transition all lie unresolved under the main central line.

After these initial observations, we measured the LMR spectra for both fine structure transitions of N^+ with several laser lines; the details of the laser lines are given in Table 1. The need for these extended measurements was obvious in the case of the $J = 1$–0 transition because it had not been detected directly before. However, we discovered that a remeasurement was also required for the $J = 2$–1 spectrum. Not only did our improved signal-to-noise ratio result in more accurate measurements but also an incorrect value for one of the laser frequencies used in the earlier work produced a proportionate error in the fine-structure interval (the laser line in question was the 120.5 μm line of CD_2F_2, see Table II of the paper by Cooksy et al. 1986). Because of the importance of determining the zero-field frequencies as accurately as possible, we have also remeasured the frequencies of the four 122 μm laser lines used in this work by measuring the beat frequencies when mixed with a suitable, known pair of CO_2 laser frequencies in a metal-insulator-metal (MIM) diode. The frequencies obtained are given in Table 1. One of these values, that of the 212.2 μm line had not been measured before. The values for the other three all differ slightly from the previous values (Inguscio et al.

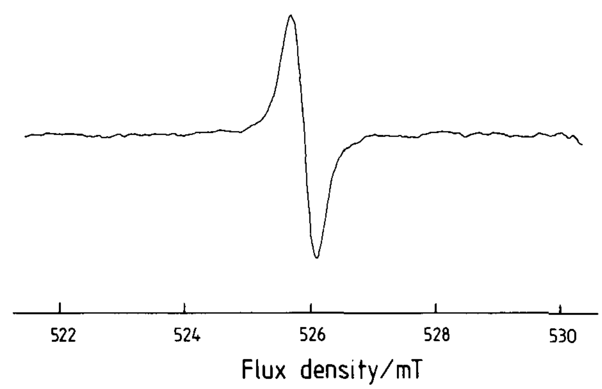

FIG. 2.—Far-infrared laser magnetic resonance spectrum associated with the $J = 1 \leftarrow 0$ transition of $^{14}N^+$ in its ground ^3P state, recorded with the 203.6 μm line of $^{13}CH_3OH$, pumped by the 10R(16) line of a CO_2 laser. The spectrum was recorded in perpendicular polarization with the 0.3 s output time constant. The three hyperfine components all lie within the single line width of the $M_J = 1 \leftarrow 0$ transition.

TABLE 1

SUMMARY OF OBSERVATIONS OF THE FINE-STRUCTURE TRANSITIONS IN N^+ BY FAR-INFRARED LASER MAGNETIC RESONANCE

	FAR-INFRARED LASER			
N^+ TRANSITION	Gas	Pump	$\lambda(\mu m)$	ν(MHz)
$J = 1 \leftarrow 0$......	CD_2F_2	10R(38)	207.8	1442454.3[a]
	$^{13}CH_3OH$	10R(16)	203.6	1472199.4[a]
$J = 2 \leftarrow 1$......	CH_2F_2	9R(22)	122.5	2447970.9[b]
	CD_3OD	10R(28)	122.3	2451203.9[b]
	CD_3OH	10R(38)	122.2	2454226.1[b]
	$^{13}CH_3OH$	10R(28)	121.2	2473604.7[b]

[a] Frequency taken from the review article by Inguscio et al. 1986.
[b] Frequency measured in this work.

1986) but must be considered to be more reliable because they were made with a transversely pumped far-infrared laser. The earlier measurements were made with a longitudinally pumped laser and were subject to small pulling effects from the CO_2 pump laser.

The detailed measurements of the various spectra recorded are given in Table 2. These measurements were used to determine the parameters of a Russell-Saunders effective Hamiltonian for a ^3P state as described, for example, by Cooksy et al. (1986). The values of the parameters obtained in a least-squares fit are given in Table 3 and the associated residuals are given for each data point in Table 2. Consistent with our stronger signals, the quality of fit of our data is better than that of the previous study. We have obtained a revised and much more reliable value for the $J = 2$-1 fine-structure interval, about 10 MHz higher than the earlier value (see Table 3). We have also made the first observation of the $J = 1 \leftarrow 0$ transition by LMR and determined its frequency with high accuracy. The values for the two g-factors differ quite significantly from the previous values because they depend directly on the laser frequencies, one of which was in error in the previous work. On the other hand, the ^{14}N hyperfine parameters are very similar to the values obtained earlier but are now more precisely determined.

With the corrected laser frequencies, the $^{15}N^+$ resonance fields reported previously (Cooksy et al. 1986) give a value for the $J = 2$-1 fine-structure interval for this isotope of 2459.3905(15) GHz. The fine-structure isotope shift $\Delta E_{21}(^{15}N^+)$-$\Delta E_{21}(^{14}N^+)$ of 10.4(15) MHz is therefore still in good agreement with the value of 10.1 MHz calculated by Veseth (1987).

TABLE 2

LASER MAGNETIC RESONANCE DATA FOR $^{14}N^+$ IN ITS GROUND ^3P STATE

J	M_J	M_I[a]	ν_L(GHz)	B_0(mtorr)	(Obs − Calc) (MHz)
$1 \leftarrow 0$.....	$-1 \leftarrow 0$	0	1442.4543	891.61	−0.4
	$1 \leftarrow 0$	0	1472.1994	525.99	0.1
$2 \leftarrow 1$.....	$-2 \leftarrow -1$	1	2447.9709	534.16	−1.3
	$-1 \leftarrow 0$	1		537.96	−1.2
	$-1 \leftarrow 0$	0		542.19	−0.6
	$-2 \leftarrow -1$	0		543.54	−1.4
	$-1 \leftarrow 0$	−1		547.19	−0.5
	$-2 \leftarrow -1$	−1		552.20	−1.5
	$-2 \leftarrow -1$	1	2451.2039	380.23	1.6
	$-1 \leftarrow 0$	1		384.44	1.6
	$-1 \leftarrow 0$	0		388.69	1.9
	$-2 \leftarrow -1$	0		389.61	1.5
	$-1 \leftarrow 0$	−1		393.62	−0.3
	$-2 \leftarrow -1$	−1		398.27	−1.1
	$-2 \leftarrow -1$	1	2454.2261	236.12	−0.4
	$-1 \leftarrow 1$			240.59	−0.1
	$-1 \leftarrow 0$	−1		250.08	1.6
	$-2 \leftarrow -1$	−1		254.27	0.3
	$2 \leftarrow 1$	1	2473.6047	668.00	−1.5
	$1 \leftarrow 0$	1		673.63	−2.5
	$2 \leftarrow 1$	0		676.45	−0.8
	$1 \leftarrow 0$	0		678.43	−2.3
	$1 \leftarrow 0$	−1		682.35	0.2
	$2 \leftarrow 1$	−1		685.84	−2.4
	$2 \leftarrow 1$	1	2488.5534	1377.91[b]	6.0
	$2 \leftarrow 1$	0		1386.71[b]	−0.5
	$2 \leftarrow -1$	−1		1396.16[b]	−4.1

[a] The transitions obey the selection rule $\Delta M_I = 0$.
[b] Measurement from the earlier work of Coosky et al. 1986. These three data were given zero weight in the least-squares fit.

TABLE 3

PARAMETERS DETERMINED FROM THE FAR-INFRARED LASER MAGNETIC SPECTRUM OF $^{14}N^+$

Parameter	This Work[a]	Previous Values
ΔE_{10} (GHz)....	1461.13190 (61)	1459.1,[b] 1460.56 (27)[c]
ΔE_{21} (GHz)....	2459.38006 (37)	2459.3703[d]
$g_{J=1}$	1.500976 (65)	1.50032[d]
$g_{J=2}$	1.500914 (46)	1.50033[d]
A_1 (MHz)	0.97 (97)	
A_2 (MHz)	94.59 (43)	95.5[d]
A_{10} (MHz)	−70.90[e]	
A_{21} (MHz)	−81.17[e]	
B (MHz)	−3.64 (28)	−3.6[d]

[a] The numbers in parentheses represent 1 σ uncertainty estimates, in units of the last quoted decimal place.
[b] Value determined from the ultraviolet spectrum of N^+ (Eriksson 1983).
[c] Value determined from direct astronomical observation by Wright et al. 1991.
[d] Value determined from the previous FIR LMR study (Cooksy et al. 1986).
[e] Parameter constrained to this value, taken from the theoretical calculation by Schaefer & Klemm 1970.

4. DISCUSSION

Both fine-structure intervals of $^{14}N^+$ in its ground state ^3P state have now been measured with a 1 σ accuracy of better than 1 MHz in a laboratory experiment. The improvement in our knowledge of the $J = 1$–0 interval is considerable; the previous values were determined by optical spectroscopy

TABLE 4

CALCULATED VALUES FOR THE ZERO-FIELD FREQUENCIES OF THE FINE STRUCTURE TRANSITIONS IN $^{14}N^+$

TRANSITION			
J	F	ν(GHz)	RELATIVE INTENSITY[a]
$1 \leftarrow 0$	$1 \leftarrow 1$	1461.1264 (12)[b]	2.009
	$2 \leftarrow 1$	1461.1338 (12)	3.349
	$0 \leftarrow 1$	1461.1390 (22)	0.198
$2 \leftarrow 1$	$1 \leftarrow 0$	2459.0828 (16)	0.837
	$1 \leftarrow 2$	2459.0880 (23)	0.042
	$1 \leftarrow 1$	2459.0954 (7)	0.628
	$2 \leftarrow 2$	2459.2899 (15)	0.628
	$2 \leftarrow 1$	2459.2974 (11)	1.884
	$3 \leftarrow 2$	2459.5655 (6)	3.516

[a] The relative intensity is given by the square of the magnetic dipole transition moment, $\langle LSJ'IF' \| (m/\mu_B) \| LSJIF \rangle^2$.
[b] Estimated uncertainty (1 σ).

(1450.1 GHz; Eriksson 1983) and from astrophysical observation [1460.56(27) GHz; Wright et al. 1991]. Our value is some 600 MHz larger and 500 times more accurate than the astronomically determined number. The value for the $J = 2$–1 interval has been corrected for an error in one of the laser frequencies used in the earlier measurement by Cooksy et al. (1986). If required, the frequencies could be measured even more accurately in a tunable far-infrared experiment, see for example Zink et al. (1991). The calculated zero-field frequencies for $^{14}N^+$ are given in Table 4. These values will help astrophysical searches for the transitions by heterodyne methods. The g-factors for N^+ in the $^3P_2$ and $^3P_1$ components are determined to be somewhat larger than the values obtained previously, when corrected for the error in the laser frequency. These values are now much closer to those for similar atoms like C and O. For C, the values for g_1 and g_2 are 1.501122 and 1.501109, respectively (Wolber et al. 1970) whereas for O, they are 1.500986 and 1.500921, respectively (Radford & Hughes 1959).

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REFERENCES

Cooksy, A. L., Hovde, D. C., & Saykally, R. J. 1986, J. Chem. Phys., 84, 6101
Erickson, E. F., Colgan, S. W. H., Simpson, J. P., Rubin, R. H., Morris, M., & Haas, M. R. 1991, ApJ, 370, L69
Eriksson, K. B. S. 1983, Phys. Scripta, 28, 593
Inguscio, M., Moruzzi, G., Evenson, K. M., & Jennings, D. A. 1986, J. Appl. Phys., 60, R161
Lugten, J. B., Genzel, R., Crawford, M. K., & Townes, C. H. 1986 ApJ, 306, 691
Petuchowski, S. J., Bennett. C. L., Haas, M. R., Erickson, E. F., Lord, S. D., Hollenbach, D. J., Rubin, R. H., & Colgan, S. W. J. 1992, BAAS, 24, 764
Radford, H. E., & Hughes, V. W. 1959, Phys. Rev., 114, 1274
Rubin, R. H., Haas, M. R., Erickson, E. F., Simpson, J. P., & Colgan, S. W. J. 1989, BAAS, 21, 1213
Schaefer, H. F., & Klemm, R. A. 1970, Phys. Rev., A1, 1063
Sears, T. J., Bunker, P. R., McKellar, A. R. W., Evenson, K. M., Jennings, D. A., & Brown, J. M. 1982, J. Chem. Phys., 77, 5348
Varberg, T. D., Evenson, K. M., & Brown, J. M. 1994, J. Chem. Phys, 105, 2437
Veseth, L. 1987, Phys. Rev. A35, 1931
Wolber, G., Figger, H., Haberstroh, R. A., & Pensilin, S. 1970, Z. Phys., 236, 337
Wright, E. L., et al. 1991, ApJ, 381, 200
Zink, L. R., Evenson, K. M., Matushima, F., Nelis, T., & Robinson, R. L. 1991, ApJ, 371, L85