PHYSICAL REVIEW A VOLUME 16, NUMBER 2 AUGUST 1977

Precision measurement of the hyperfine structure and g_J factor of atomic nitrogen 14[*]

J. M. Hirsch,[†] G. H. Zimmerman, III, D. J. Larson, and N. F. Ramsey
Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts 02138

(Received 5 April 1977)

The dipolar and quadrupolar hyperfine coupling constants, A and B, respectively, and the atomic g_J factor have been measured for the ${}^4S_{3/2}$ ground state of atomic nitrogen 14. An atomic hydrogen maser oscillating at the $\Delta M_F = -1$ transition in a magnetic field ranging from 0.008 to 8 G was used as a detector of transitions in both hydrogen and nitrogen. The magnetic field was calibrated by the hydrogen Zeeman transition frequency. Values of the constants were found to be $A = 10\,450\,929.12(10)$ Hz, $B = 1.27(10)$ Hz, and $g_J = 2.002\,134\,652(64)$. These results are compared to current theoretical results and other experimental measurements.

I. INTRODUCTION

This paper reports the results of a precision study of the hyperfine structure of the ground state of atomic nitrogen 14. This study was undertaken to apply techniques developed in a study of hydrogenic g_J factors[1] to obtain a more precise result for atomic nitrogen. In addition, such a study could reveal possible experimental causes of the large discrepancy between the theoretical[2] and experimental[3] values for the quadrupole hyperfine coupling constant in nitrogen 14.

The experimental design is based on the use of a hydrogen maser oscillating on the $(F=1, M_F=1)$ to $(F=0, M_F=0)$ or π transition as a spin exchange spectrometer. Nitrogen atoms are introduced into the maser and population differences are created and transitions are detected through the mechanism of spin exchange.

II. ATOMIC NITROGEN

The ground-state electronic configuration for atomic nitrogen is $(1s^2 2s^2 2p^3)\,{}^4S_{3/2}$. Nitrogen 14 has a nuclear spin $I=1$. Thus both dipole and quadrupole hyperfine coupling are potentially present and the appropriate Hamiltonian is

$$H = A\vec{I}\cdot\vec{J} + B\,\frac{3(\vec{I}\cdot\vec{J})^2 + \frac{3}{2}(\vec{I}\cdot\vec{J}) - I^2J^2}{2I(2I-1)J(2J-1)} + g_J\mu_0\vec{J}\cdot\vec{H}_0 + g_I\mu_0\vec{I}\cdot\vec{H}_0,$$

where A and B are the dipole and quadrupole coupling constants and g_J and g_I are the electronic and nuclear g factors, respectively.

If the ground-state configuration were pure, both the dipole hyperfine constant, A, and the quadrupole constant, B, would be zero. There is no contact interaction in the unpaired p orbitals and the spin-dipole interaction averages to zero with the overall spherical symmetry. The spherical symmetry also implies zero quadrupole coupling. In reality, A is approximately 10 MHz and B is on the order of 1 Hz. B is the smallest internal atomic interaction ever measured. Its small size is most dramatically illustrated by comparison to the 10-MHz size that would be expected for electrons in the $2p$ shell in the absence of the spherical symmetry.

A calculation by Dutta *et al.*[4] has shown that the nonzero value for A results from the unsymmetric interaction between the three valence electrons with the spin-up and spin-down core S electrons. They obtain a value for A of 10.49(15) MHz, in agreement with the experimental value. The S-state mixing, however, preserves the spherical symmetry and still results in a zero value for B. Sandars[2] has shown that a nonzero value for B can be due to effects such as the breakdown of $\vec{L}\cdot\vec{S}$ coupling in the $2p$ state. Using relativistic Hartree-Foch wave functions, he obtains a value for B of -21 Hz which is in sharp disagreement with the experimental value.

Figure 1 shows the energy levels of atomic nitrogen as a function of applied magnetic field in the range appropriate to the present measurements. The hyperfine constants, A and B, were obtained largely from measured transition frequencies at low field (0.008 and 0.38 G) while the g factors were obtained from the frequencies of transitions at the highest available magnetic field (8 G).

III. EXPERIMENTAL METHOD

In this experiment the use of the hydrogen maser is twofold. First, it provides a high homogeneity, long-lived environment for the atomic nitrogen, and second, it is an instrument which can be made sensitive to transitions occurring within the nitrogen atoms. The two species of atoms are coupled through the mechanism of spin exchange. Inducing a transition in the hyperfine spectrum of atomic nitrogen which reduces the electron spin polarization also reduces the polarization of the hydrogen atoms and results in a decrease in maser output

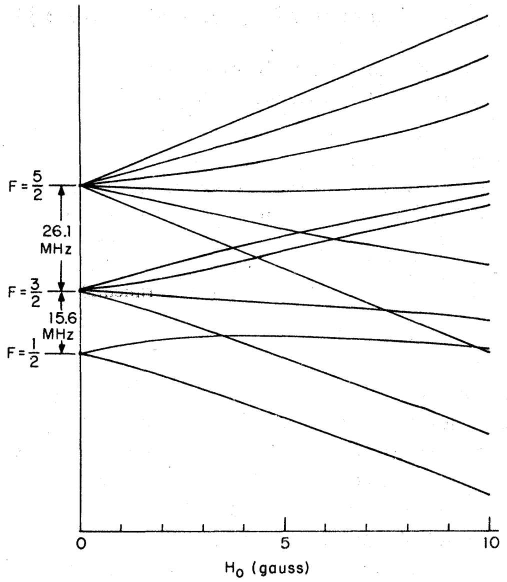

FIG. 1. Energy levels of atomic nitrogen in a magnetic field.

amplitude. This method of detection requires that the maser be oscillating on the π and not on the σ transition since the population difference and the spin exchange relaxation of the σ transition are not first-order dependent on the spin state of the colliding atoms.

A schematic diagram of the hydrogen maser used in these measurements is shown in Fig. 2. This maser is equipped with a solenoid and correction coils which provide a highly homogeneous magnetic field in the region of the storage bulb. The maser cavity is nearly spherical in shape and operates on the TE_{011} mode. A feedback circuit was used to multiply the Q of the cavity to a value of approximately 10^5.

The Teflon-coated quartz bulb contains both hydrogen and nitrogen atoms. The hydrogen atoms enter through a capillary array near the bottom of the bulb. This array serves to provide a geometrical storage time without the use of large stem region which can lead to magnetic field averaging problems. The nitrogen atoms enter the bulb through an approximately 4-mil hole in a 20-mil-thick Teflon disc at the top of the bulb. The disc provides the separation between the low pressure (10^{-7} Torr) bulb region and the higher pressure (10^{-2} Torr) stem region where the nitrogen atoms are produced. The nitrogen atoms are produced by dissociation of nitrogen molecules in a microwave discharge. The discharge was driven by a Raytheon Model CMD-5 diathermy unit which produces 100 W at 2450 MHz. The microwave discharge was contained in a tuned quarter-wave coaxial cavity.

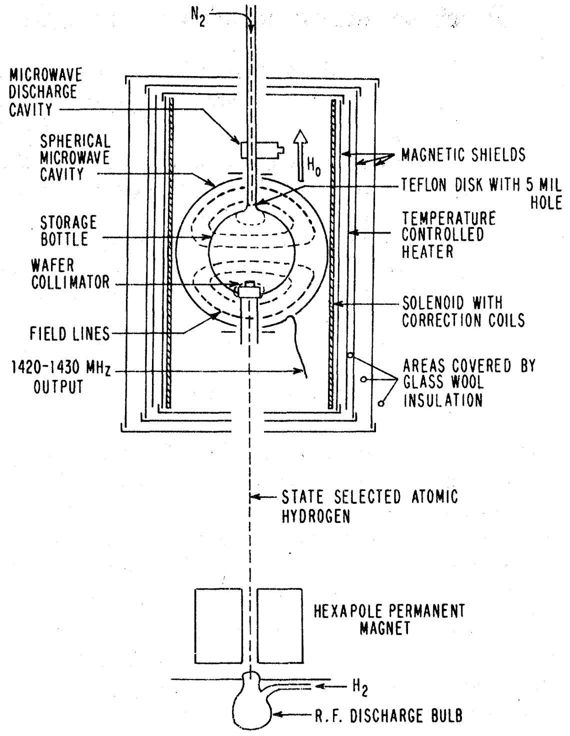

FIG. 2. Schematic diagram of the π maser.

The discharge in the upper bulb stem proved to be a simple and effective way of introducing nitrogen atoms into the maser. The only significant disadvantage of this arrangement was a substantial amount of heating of the maser cavity. An associated frequency drift occurred unless care was taken to isolate the cavity thermally as well as possible and to allow the system to come to thermal equilibrium before attempting to take any significant data.

Cavity mistuning shifts the frequency of the maser oscillation. Rather than use the field dependent $(F=1, M_F=1)$ to $(F=0, M_F=0)$ π maser frequency as a measure of the magnetic field, it was used to stabilize the field by phase locking it to a reference frequency with feedback provided by a correction solenoid. The hydrogen $(F=1,\ M_F=0)$ to $(F=1,\ M_F=-1)$ Zeeman transition frequency, which is not affected by cavity tuning, was then used as a measure of the magnetic field. With this scheme magnetic field stabilization is greatly simplified but drifts in maser-cavity frequency are converted into drifts in the magnetic field and thus had to be minimized to obtain accurate results.

One technique which helped reduce the effects of magnetic field drift was the taking of data on a nitrogen line and the hydrogen Zeeman line virtually simultaneously. Data were taken with the aid of a PDP-8 computer which controlled a frequency synthesizer supplying rf power to a coil of wire around the storage bulb inside the maser cavity. The synthesizer was stepped through the hydrogen Zeeman line and a nitrogen line in an alternating progression $\nu_{H1}, \nu_{N1}, \nu_{H2}, \nu_{N2}, \ldots$, until both lines were swept. Because of the alternation, no more than a few seconds difference in the average time of the sweeps could occur. The consistency of the data was enhanced by the application of this technique.

IV. RESULTS

Three series of measurements of nitrogen transition frequencies were made to determine the nitrogen hyperfine parameters. The first series was made at a magnetic field of 0.008 G and consisted of several determinations of the two hyperfine transitions and a single Zeeman transition. The second series, made at a field of 0.38 G, consisted of all nine Zeeman transitions and twelve hyperfine transitions. The final series at a magnetic field of 8 G consisted of the nine Zeeman transitions only.

Each time a nitrogen transition was swept, the hydrogen Zeeman transition was swept as a calibration of the magnetic field. Each line was fitted to a four-parameter Lorentzian line shape. Over 200 separate determinations of nitrogen lines were made. The resulting line centers were fitted at the lowest field to a three-parameter Hamiltonian $[A, B, g_J(N)/g_J(H)]$ while the centers at the two higher fields were fitted with a fourth parameter, $g_I(N)/g_J(N)$, as well.

Several tests were done to verify the consistency and reproducibility of the data in addition to explicit consideration of possible shifts described below. All of the lines were fitted to a five-parameter Lorentzian with an asymmetry parameter as the fifth parameter. These line centers were used to find values for the hyperfine constants and these were found to be in agreement with the values from the four-parameter line centers used in the final results. In addition, the variation in each of the parameters from run-to-run and from field-to-field was examined and found to be consistent with statistical fluctuations.

Another important test of the data was the value obtained for g_I/g_J in the nitrogen atoms. Combined with the value for g_J this resulted in a measured value of $g_I(\mathrm{N}) = 0.000\,219\,742\ (44)$. This is in agreement with the more accurate value obtained by a nuclear magnetic resonance measurement in ammonia,[5] $g_I(\mathrm{N}) = 0.000\,219\,745\,52\ (24)$. Since the frequency resolution necessary for the nuclear g-factor result is the same as that for the g_J measurements, the agreement is an indication that no large systematic errors are present in the data.

Three possible systematic effects are worthy of mention because of their appearance in similar high-precision measurements. Frequency shifts due to imperfect averaging of the magnetic field inhomogeneities were presumed to be present in a previous measurement of the nitrogen hyperfine structure.[3] These shifts are assumed to be due to the presence of a stem region in the storage bulb which has rather poor communication with the larger volume. In the present measurement the stem region was essentially eliminated by the use of the capillary array in the stem. Also a comparison with previous measurements of hydrogenic g_J factors on the same apparatus suggests that the field inhomogeneities are not a significant problem.

The use of the storage bulb to contain radiating atoms is accompanied by a surface-induced frequency shift, called the wall shift. The interaction with the wall is dominantly electrostatic and should be more significant for the hyperfine transitions than for the Zeeman transitions. The wall shift in the dipole hyperfine interaction can be estimated from the physically similar pressure shifts in buffer-gas storage cells. For example, the shift due to helium buffer gas measured for the nitrogen A coefficient is approximately $\frac{1}{30}$ of the shift for hydrogen atoms in helium.[6] Since the hydrogen wall shift in a 15-cm bulb is typically 20 mHz, the effect on the nitrogen A coefficient at the present level of precision should be negligible. Also, since the buffer-gas pressure shift measurements showed no shift in B at a level of 1% of the shift in A, we assume that there is no significant wall shift contribution to B. Since the theoretical prediction differs markedly from the experimental measurement of B, this assumption, however, reasonable, is presently being further investigated by experiments with different sized storage vessels.

Spin exchange collisions are known to result in frequency shifts which are a substantial fraction of the linewidth contributed by the collisions.[7,8] In the present experiment the size of spin exchange shifts was estimated by two methods. The first method used was to assume that the shift is proportional to the amount of change in electron spin polarization in a given transition. An additional parameter was then added to the fit to the Hamiltonian to allow for spin exchange shifts. This resulted in an estimate of 92 ± 85-mHz spin-exchange shift in A and B. This result is consistent with

TABLE I. Experimental and theoretical results for the hyperfine parameters in atomic nitrogen.

Technique	A (MHz)	B (Hz)	g_J	Ref.
H maser	10.45092906(19)	+1.32(20)		a
Optical pumping	10.4509294(18)	+1.3(5)		b
Atomic beam			2.002134(5)	c
Optical pumping			2.00213425(40)	d
This work	10.45092912(10)	+1.27(10)	2.002134652(64)	
Theory	10.49(15)			e
Theory		−21		f
Theory			2.002142	g

[a] S. B. Crampton, H. C. Berg, H. G. Robinson, and N. F. Ramsey, Ref. 3.
[b] R. E. Weiss, R. H. Lambert, and L. C. Balling, Ref. 6.
[c] B. D. Zak and H. A. Shugart, Ref. 10.
[d] P. Cheney and H. G. Robinson, Ref. 9.
[e] N. C. Dutta, E. Matsubara, R. T. Pu, and T. P. Das, Ref. 4.
[f] P. G. H. Sandars, Ref. 2.
[g] V. Beltran-Lopez and T. Gonzalez E., Ref. 11.

an independent estimate of spin-exchange shifts obtained by extrapolation of the g_J-factor results as suggested by Larson.[1] Since both techniques used to estimate the shifts are approximate in the present application, the shifts are used as an estimate of error and are not applied as corrections to the data.

The final results for A, B, and g_J are shown in Table I along with the results of other measurements and calculations. The errors in A and B are due largely to the estimate of spin exchange shifts (the statistical errors are three times smaller) while the error in g_J is statistical. No correction, other than a trivial time-based correction, was applied to the raw data to obtain these values. A is in good agreement with previous measurements[3,6] and is accounted for with good success by the theoretical calculation.[4] B and g_J agree with the previously most precise values[3,9,10] but differ significantly with the calculations.[2,11] The most startling disagreement is between the theoretical and experimental values for B.

---

*Work supported by the Office of Naval Research and the National Science Foundation.

†Present address: Shell Development Company, Bellaire Research Center, Houston, Tex. 77001.

[1] D. J. Larson and N. F. Ramsey, Phys. Rev. A 9, 1543 (1974).

[2] P. G. H. Sandars, J. Phys. (Paris) 31, C4-225 (1970).

[3] S. B. Crampton, H. C. Berg, H. G. Robinson, and N. F. Ramsey, Phys. Rev. Lett. 24, 195 (1970).

[4] N. C. Dutta, C. Matsubara, R. T. Pu, and T. P. Das, Phys. Rev. 177, 33 (1969).

[5] L. W. Anderson and F. M. Pipkin, Phys. Rev. 116, 87 (1959).

[6] R. E. Weiss, R. H. Lambert, and L. C. Balling, Phys. Rev. A 2, 1745 (1970).

[7] L. C. Balling, R. J. Hanson, and F. M. Pipkin, Phys. Rev. 133, A607 (1964).

[8] S. B. Crampton, H. G. Robinson, D. Kleppner, and N. F. Ramsey, Phys. Rev. 141, 55 (1966).

[9] P. Cheney and H. G. Robinson, Bull. Am. Phys. Soc. 18, 727 (1973).

[10] B. D. Zak and H. A. Shugart, Phys. Rev. A 6, 1715 (1972).

[11] V. Beltran-Lopez and T. Gonzalez E., Phys. Rev. A 2, 1651 (1970).