of the argon atoms with methane molecules would be approximately 10^8 per second per excited argon atom. The assumption that the cross section measured by Biondi for the destruction of metastable helium by argon applies to the argon-methane reaction leads to approximately 5×10^6 destructions (hence ionizations) per second per excited argon. Therefore an excited state lifetime of only a few microseconds would be long enough to explain the observed increases in ionization. The generally larger increases in ionization in impurities whose ionization potential is less than the 11.5-volt metastable state can be attributed to the utilization of the energy in the metastable state as well as that of the excited state in producing ionization.

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Hyperfine Structure of Nitrogen*

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The magnetic resonance spectrum of the ^4S ground state of atomic nitrogen-14 has been observed using the microwave absorption method. The magnetic-dipole hyperfine interaction constant is

$$A=10.45\pm0.02 \text{ Mc/sec.}$$

No evidence was obtained for electric quadrupole interaction.

INTRODUCTION

THE observation of magnetic resonance transitions between hyperfine sublevels in atoms is useful for measuring hyperfine interaction energies and, in many cases, for obtaining the nuclear moments as such. This is an important technique for evaluating nuclear quadrupole moments. The interaction of nuclear moments with a single valence electron outside closed shells can be calculated quite reliably.[1] A generally successful procedure for obtaining nuclear moments from a knowledge of the hfs interaction constants has been developed for this case and can be immediately extended to the case of a closed shell less one electron.[2] The situation with several valence electrons is considerably more complicated.[3] Goudsmit has evaluated theoretically the magnetic interaction for special configurations on LS coupling[4]; Breit and Wills have treated intermediate coupling.[5] Trees has developed generalized formulas, in terms of Racah's tensor algebra for complex spectra, for both the magnetic-dipole and electric-quadrupole interactions on LS coupling.[6]

In the present investigation the magnetic resonance technique has been applied to atomic nitrogen. It was initially hoped that fine-structure and hyperfine-structure interaction constants could be measured for both the ground and metastable states of the nitrogen atom, and that perhaps some estimate of the quadrupole moment of N^{14} could be obtained. However, useful analysis of observed spectra is severely limited by the presence of considerable configuration interaction in nitrogen. Experimental difficulties have prevented observation of magnetic resonance spectra from the metastable states. Observations in connection with the atomic-nitrogen source are, however, of some interest in the long-standing problem of "active" nitrogen.

The ground electronic configuration of the nitrogen atom is $2p^3$, which forms the Russell-Saunders terms ^4S, ^2D, and ^2P. The $^4S_{\frac{3}{2}}$ state is the normal ground state; the doublet states are metastable. It is well-known that the N^{14} nucleus possesses both magnetic-dipole and electric-quadrupole moments. According to the nonrelativistic LS coupling formulas of Goudsmit and Trees, the magnetic hfs interaction constant for the ground state vanishes; the constants for the metastable states are in the region of 100 Mc/sec. The quadrupole interaction vanishes for all states.

Since nitrogen is a light atom, deviations from LS coupling should be very small.[7] However, it is well-known that the observed electrostatic splittings of the ground-configuration terms depart significantly from those of LS theory, presumably because of configuration interaction with $2p^23p$ states.[8] Although the fine-structure intervals of the metastable doublet states would vanish according to LS coupling theory, small

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[1] H. B. G. Casimir, *Interaction Between Atomic Nuclei and Electrons* (Teyler's Tweede Genootschap, Haarlem, 1936).
[2] Davis, Feld, Zabel, and Zacharias, Phys. Rev. **76**, 1076 (1949).
[3] H. Lew, Phys. Rev. **91**, 619 (1953).
[4] S. Goudsmit, Phys. Rev. **37**, 663 (1931).
[5] G. Breit and L. A. Wills, Phys. Rev. **44**, 470 (1933).
[6] R. E. Trees, Phys. Rev. **92**, 308 (1953).
[7] D. R. Inglis, Phys. Rev. **38**, 862 (1931).
[8] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, London, 1935), p. 198.

negative splittings are observed in optical spectra which indicate the effects of spin-other-orbit and configuration interactions.[9]

Some years ago Jackson and Broadway performed a Stern-Gerlach experiment in an attempt to measure the magnetic moment of the product of a nitrogen discharge.[10] The trace on their chemical target indicated the presence of a component with $M_J g_J = \pm\frac{1}{3}$, which corresponds to the $^2P_{\frac{1}{2}}$ metastable state. However, they were unable to account satisfactorily for the absence of any indication of other states, all of which have larger Mg values (e.g., $^2P_{\frac{3}{2}}: Mg = \pm\frac{2}{3}, \pm 2$; $^4S_{\frac{3}{2}}: Mg = \pm 1, \pm 3$). It would also seem that, for any magnetic field reasonable in a Stern-Gerlach type of experiment, a virtually complete Paschen-Back effect would occur for the nearly-degenerate $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$ states (whereupon $Mg = 0, \pm 1, \pm 2$) which would invalidate the evidence for the presence of the $^2P_{\frac{1}{2}}$ state. In view of these inconsistencies, it appears that little confidence can be placed in their conclusions.

With the exception of the atomic nitrogen source, the experimental technique used in the present investigation was identical to that used in our precision measurement of the electron g factor in atomic hydrogen.[11] Atomic nitrogen vapor was pumped in a fused-silica tube through a 9185-Mc/sec resonant cavity located in a modulated, proton-controlled magnetic field. Absorption of microwave energy by the atomic vapor was detected when the magnetic field was adjusted such that a magnetic resonance transition coincided with the cavity frequency.

ATOMIC NITROGEN SOURCE

The production of atomic nitrogen is intimately connected with the phenomenon of "active nitrogen." Nitrogen excited in discharge tubes of certain types manifests greatly enhanced chemical activity and a yellow glow which persists after the excitation is removed, under some conditions remaining visible for an hour or more. The afterglow consists of certain well-known band systems of the neutral nitrogen molecule. The mechanism of this afterglow has been the subject of extensive investigation for many years. It is well established that the essential component of active nitrogen is atomic nitrogen, and that the necessity of three-body collisions (or chemical reactions) to bring about recombination of the atoms is responsible for the main features of long life and high energy content.

In order to explain the selective enhancement of the particular band systems present in the afterglow, it is necessary to assume that the metastable ^2D and ^2P atomic states as well as the metastable $A^3\Sigma_u^+$ molecular state are essential to the process. The theory of Cario and Kaplan[12] therefore postulated that a considerable fraction of the atoms in active nitrogen are in the metastable states. An extensive series of experiments by Okubo and Hamada, however, indicated that the actual concentration of metastable components is very small.[13] Cario was able to preserve the energetic function of the metastable atoms by assuming them to be short-lived intermediate products in a chain of interactions producing the afterglow.[14] Frost and Oldenberg searched unsuccessfully for infrared absorption bands due to the metastable molecular state and concluded that the metastable components, both molecules and atoms, have lifetimes of only a millisecond or less.[15] There are nonradiative processes of atomic recombination in addition to the process producing the visible afterglow.[16] Indeed, Rayleigh has estimated that only about 0.1 percent of the atoms and molecules present contribute to the afterglow under the brightest conditions.[17] Oldenberg has recently discussed some aspects of the active nitrogen problem.[18]

Active, or atomic, nitrogen is not formed in a high-voltage dc discharge of the type which is so successful for hydrogen.[11,19] A pulsed rf (electrodeless) discharge[20] or a condensed discharge[21] is required. The latter is a relaxation-oscillator arrangement in which the discharge tube, sometimes with a series air spark-gap, forms the intermittent element. In either type the dynamic nature of the process allows high fields to exist throughout the discharge tube rather than to be concentrated in the small region of the cathode fall of a dc glow discharge.

In the present investigation a condensed discharge was used to obtain nitrogen atoms in the ground ^4S state. A high-voltage power supply charged a 5-μf capacitor through a 20 000-ohm resistor. A long U-shaped tube with aluminum electrodes (identical to that used in our atomic hydrogen work)[11] was connected in parallel with the capacitor; discharge occurred about eight times per second. The 5-kv unloaded output of the power supply was reduced to a time-average of about 3.2 kv at 100 ma with relaxation-oscillator load. The walls of the discharge-tube exit tubulation were coated with metaphosphoric acid. Rayleigh observed that this treatment significantly prolonged the life of the afterglow.[20]

Tank nitrogen was introduced into the discharge tube near the electrodes by means of a reducing valve

[9] Aller, Ufford, and Van Vleck, Astrophys. J. **109**, 42 (1949).
[10] L. C. Jackson and L. F. Broadway, Proc. Roy. Soc. (London) **A127**, 678 (1930).
[11] R. Beringer and M. A. Heald, Phys. Rev. **95**, 1474 (1954).
[12] G. Cario and J. Kaplan, Z. Physik **58**, 769 (1929).
[13] J. Okubo and H. Hamada, Phys. Rev. **42**, 795 (1932).
[14] G. Cario, Z. Physik **89**, 523 (1934).
[15] A. A. Frost and O. Oldenberg, Phys. Rev. **48**, 66 (1935).
[16] D. E. Debeau, Phys. Rev. **61**, 668 (1942).
[17] Lord Rayleigh, Proc. Roy. Soc. (London) **A176**, 1 (1940).
[18] O. Oldenberg, Phys. Rev. **90**, 727 (1953).
[19] R. W. Wood, Phil. Mag. **44**, 538 (1922).
[20] Lord Rayleigh, Proc. Roy. Soc. (London) **A151**, 567 (1935).
[21] J. H. Greenblatt and C. A. Winkler, Can. J. Research **B27**, 721 (1949).

and capillaries. The pressure of the vapor in the microwave cacity was of the order of 0.1 mm; the discharge-tube pressure was somewhat higher.

With the arrangement just described, it was found that the condensed discharge, after running a few minutes, would cease operating unless water vapor was introduced by bubbling the input nitrogen through a water bottle. Apparently the peak fields available were insufficient to initiate discharge in dry nitrogen. Subsequently the discharge tube was shortened from 1.4 m to 0.9 m total length to increase the peak field. The condensed discharge then operated dependably with dry nitrogen, although the intensities of the visible afterglow and the magnetic resonance spectrum from the ^4S state were greatly diminished. The original intensities were immediately restored and sustained upon introduction of water vapor. There is considerable evidence that impurities do have an important effect on the characteristics of active nitrogen.[22] The present observation that afterglow and ground-state-atom concentration are dependent on the presence of a significant amount of water does not, however, seem to follow from previous results.[20] The Wood's-tube condensed discharge, with water vapor present, proved to be a dependable and copious source of ground-state nitrogen atoms. The afterglow was easily visible in the pumping line as far as the diffusion pump, about six feet from the discharge tube.

An extensive search was made for magnetic resonance spectra from the metastable ^2D and ^2P states, using a number of different types of discharge. No trace of these spectra was found. It was felt that the most promising source used in this search consisted of the production of active (i.e., ground-state-atomic) nitrogen with the condensed discharge and then subjecting the vapor stream to a weak electrodeless discharge of some sort immediately preceding the microwave cavity. The usefulness of a second discharge was suggested by the experiments of Bay and Steiner, who obtained the optical spectrum of atomic nitrogen from a second discharge tube in this manner; the intensity of the atomic lines correlated with that of the afterglow in the vapor stream emerging from their first discharge tube.[23] The proximity of the second discharge to the cavity was an effort to utilize short-lived (millisecond) metastable discharge products, such as the doublet states. It would appear that the input nitrogen should be free from impurities, including water vapor, to prolong the metastable lifetime.[15,22] However, its necessity in producing afterglow left unclear the desirability of either presence or absence of the water vapor. The greatly reduced ground-state spectrum from the "dry" condensed discharge could be interpreted as indicating that most of the atoms were in the metastable states. If so, assuming a total atomic concentration comparable to that from the "wet" discharge, then the metastable spectra should have been easily observable. It seems more reasonable that the dry discharge did not produce atoms of any sort so effectively.

The second discharge was a high-voltage ac transformer with interrupted primary.[22] The cavity entrance sleeve and a turn of heavy wire served as the external electrodes. A standard induction coil and a constant amplitude (CW) rf oscillator were also tried.

No attempt has been made to employ a carrier gas, such as helium.[24] The possibility of using a Philips-type discharge tube located in the magnetic field and immediately preceding the microwave cavity has been considered as a method of reducing to a minimum the transit time between discharge region and cavity. While this proposal has not been tried experimentally, it seems doubtful that it would prove to be a satisfactory source of metastable nitrogen atoms. For our present spectrometer we estimate very roughly that a concentration of the order of a percent is necessary in a given state.

GROUND-STATE SPECTRUM

A three-line spectrum arising from the $^4S_{\frac{3}{2}}$ ground state of the N^{14} atom was observed. The lines were of equal intensity and width and were equally spaced. This spectrum, corresponding to the strong-field (Back-Goudsmit) case, indicates a small magnetic hyperfine interaction but gives no evidence for electric quadrupole interaction.

For an atom with $J=\frac{3}{2}$ and $I=1$ there are twelve magnetic sublevels. The first-order strong-field energies are given by[2,3]

$$W(M_IM_J)=AM_IM_J+M_Jg_J\mu_0H+M_Ig_I\mu_0H.$$

The observed magnetic resonance spectrum consisted of the nine transitions of the type $\Delta M_J=\pm 1$, $\Delta M_I=0$. In the pure strong-field case these occur as three triply-degenerate lines, the separation of which is a measure of the magnetic hfs interaction constant A. At somewhat lower fields the off-diagonal hyperfine interactions must be included and these degeneracies would be removed. Quadrupole hfs would also remove the degeneracies. The sign of A cannot be obtained from the magnetic resonance spectrum.

Two major precision runs were made which agreed to 1.2 ppm. A constant microwave transition frequency $\nu\sim 9185$ Mc/sec was maintained throughout a run. The magnetic field at which the central line occurred was measured as a proton resonance frequency $\nu_p\sim$

[22] J. Kaplan, Phys. Rev. **54**, 176 (1938).
[23] Z. Bay and W. Steiner, Z. physik. Chem. **B3**, 149 (1929).
[24] T. R. Merton and J. G. Pilley, Proc. Roy. Soc. (London) **A107**, 411 (1925); O. S. Duffendack and R. A. Wolfe, Phys. Rev. **34**, 409 (1929).

13.96 Mc/sec. Each of the side lines was separated from the central line by a proton frequency $\delta\nu_p \sim 16$ kc/sec. The "peak-to-peak" line width[25] of each line was about 0.09 gauss (equivalent to 250 kc/sec in transition frequency at constant field). The 30-cycle/sec field-modulation peak-to-peak amplitude was also 0.09 gauss. The calculated asymmetry of the side lines about the central line due to off-diagonal hfs contributions is 20 cps in proton frequency, which was not quite observable. The calculated splitting of the three nearly degenerate components of each of the side lines due to this same effect is 40 cps, or ten percent of the observed line width.

We obtained the following results:

$$\frac{g_J}{g_p}=\frac{\nu}{\nu_p}\left[1-\left(\frac{\delta\nu_p}{\nu_p}\right)^2+\cdots\right]=658.1631\pm0.0010,$$

$$|A|=\delta\nu_p(\nu/\nu_p)=10.45\pm0.02 \text{ Mc/sec},$$

$$|B|<0.03 \text{ Mc/sec}.$$

[25] The spectrometer detector displays essentially the derivative of the absorption line-shape; see Fig. 6 of reference 11.

A small correction term arising from the off-diagonal hfs interaction has been included in evaluating the g-factor ratio. For LS coupling neglecting relativistic effects, $g_J(^4S_{\frac{3}{2}}\mathrm{N})$ is identical with the electron spin g factor. We have not evaluated relativistic corrections. Since no evidence for quadrupole hfs was detected, an upper limit for the quadrupole interaction constant $B(=eQq)$ has been estimated on the basis of line width.

DISCUSSION

The formulas of Trees for nonrelativistic LS coupling indicate that both the magnetic and quadrupole hfs interactions vanish in the ^4S state. The observed small but nonvanishing magnetic interaction is probably due to configuration interaction with $2p^23p$ or possibly $2s2p^33s$. The estimated interaction due to slight breakdown of LS coupling would contribute only a small portion of the observed splitting. Configuration interaction problems of this type have been considered by Koster and by Sachs.[26]

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[26] G. F. Koster, Phys. Rev. 86, 148 (1952); M. Sachs, Phys. Rev. 90, 1058 (1953).