EFFECTS OF SPIN RELAXATION ON THE
EPR SPECTRUM OF GASEOUS N ATOMS

by

Robert L. Brown

Technical Report
to
Office of Naval Research
Washington, D. C.
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NOTE

The experimental work described here was conducted jointly by the author and by Dr. William R. Brennen of the Physical Chemistry Division. The spin relaxation problem arose during the course of an investigation proposed by Dr. Brennen on some properties of the Lewis-Rayleigh afterglow.

A manuscript based on this report will be submitted for publication in the Journal of Chemical Physics, under the joint authorship of R. L. Brown and W. R. Brennen.
ABSTRACT

Experimental evidence is presented which indicates that N atoms produced in a flow system by a microwave discharge through purified N₂ have a "spin-lattice" relaxation time T₁ of the order of 25 msec. In a fast flow system, the residence time of the atoms in the EPR magnet can easily be shorter than this. As a result, atoms which are generated outside of the magnet may arrive at the microwave cavity before they have had time to reach their equilibrium magnetization. Addition to the discharged gas of as little as 10 p.p.m. O₂ (which did not affect the N atom concentration) decreased the spin relaxation time, and led to increases as great as 7-fold in the N atom EPR signal. Because of the long relaxation time it was necessary to work at the low microwave power level of 0.006 μW to avoid saturation effects. Power saturation was governed primarily by the rate at which unsaturated atoms entered the cavity and not by collision relaxation processes. Interpretation of the effects of O₂ addition in terms of a two level spin model allowed us to estimate a value of ~1.5 x 10⁻¹⁶ cm² for the spin exchange cross section for N-O₂ collisions. Several qualitative observations regarding the nitrogen pink afterglow, electron production, and the effects of NO addition are also reported.
INTRODUCTION

Optical pumping experiments have shown that spin-disorientation cross sections are very small for $^2S$ alkali metal atoms in nonpolar, nonparamagnetic, buffer gases. Under conditions in which the disorienting effect of wall collisions is not too important (high buffer gas pressure, special wall coatings), these atoms can have "spin-lattice" relaxation times $T_1$ as long as several tenths of a second. The fact that N($^4S$) atoms have been oriented by optical pumping techniques via spin exchange collisions indicates that in a similar situation they also can have a long spin relaxation time. The very narrow, pressure independent, easily power saturated EPR absorption lines normally observed for N atoms are consistent with this possibility.

When using EPR as a N atom detector, one usually makes atoms by dissociating $N_2$ with a microwave discharge in a flow system. If the discharge is located outside the high field of the EPR magnet, the atoms will be generated in an unmagnetized condition. As they enter the high field region and flow toward the microwave cavity, magnetization will occur in a time characterized by the relaxation time $T_1$. In a fast flow system the residence time of the atoms in the magnet can easily be as short as several milliseconds. If this residence time were comparable to, or shorter than $T_1$, the atoms would arrive at the cavity before having reached their equilibrium magnetization (characterized by the field strength and the ambient temperature). This is the same as saying that, at the cavity, the population differences between the atom's Zeeman levels would be smaller than at equilibrium. The EPR absorption intensity would then be abnormally small. In such a situation,
any change in the flow velocity of the gas, or in $T_1$ (perhaps produced by adding a relaxing species like $O_2$) could change the absorption intensity even though the $N$ atom concentration $[N]$ at the cavity remained constant. Large errors could result if one tried to use EPR as a quantitative $N$ atom detector under these conditions.

During a study of the Lewis-Rayleigh afterglow, we obtained results which we believe can be explained by the mechanism just described. The principal observation was an enhancement of unsaturated $N$ atom EPR line intensities by $O_2$ added downstream from the discharge. Addition of only 10 p.p.m. $O_2$ gave increases as great as 7-fold. This, and much larger amounts, produced no change in the afterglow intensity. This is consistent with previous observations that i), small amounts of $O_2$ added to active nitrogen at room temperature do not change $[N]$ during msec time intervals, and ii), that the afterglow intensity is proportional to $[N]^2$. Further evidence that the signal increase did not arise from an increase in $[N]$ was the failure to observe an increase in the $N$ atom line width. When the afterflow intensity was increased, thereby implying an increase in $[N]$, a line width increase was observed. This would be consistent with a line width arising from $N-N$ spin exchange collisions. Below microwave power levels of about 0.05 $\mu$W, the degree of enhancement was independent of power. Although the enhancement was not noticeably dependent on the total pressure, it decreased slightly with increasing $[N]$. It also decreased with decreasing $N_2$ flow rate.
We have performed a number of experiments based on a model consisting of a two level spin system in a flow tube reactor to test this hypothesis of insufficient spin relaxation. The variation of the EPR signal with N₂ flow, pressure, N atom concentration, and O₂ concentration was measured at a low power level (0.006 μW, no noticeable power saturation). The relative N atom concentration was monitored by means of the afterglow intensity. Some of the measurements were repeated on systems containing He or Ar as a buffer gas instead of N₂. Also measured were the effects of power saturation under a variety of experimental conditions.

All of these experiments gave quantitative support to the model. The analysis indicated that N atoms in our system had values of T₁ of the order 25 msec in the absence of added O₂. If one assumes that disorienting collisions for O₂ with heat bath molecules have gas kinetic cross sections, then the data can be analyzed according to this model to give a value for the cross section for spin exchange between N and O₂.

APPARATUS

The spectrometer was of the superheterodyne type. It is similar to the S band instrument described elsewhere. Power saturation studies were carried out in the manner discussed by Goldsborough and Mandel. For this work, two precision rotating vane attenuators were used, one before the cavity and one before the detector. The second attenuator was used to keep the microwave power reaching the detector constant while the first was used
to increase power to the cavity. The power was measured with a calibrated bolometer detector. Because the work required very low power levels, it was not possible to lock the master oscillator to the cavity resonance. Instead it was locked to a microwave signal derived from a stable 5 MHz oscillator via a microwave harmonic generator. No evidence was found for any cavity detuning at resonance arising from the fixed frequency operation. A silver-plated cylindrical brass cavity (4.2 cm diameter, 2.9 cm length) was operated in the TE_{011} mode at 9206 MHz. With a quartz reaction tube inserted along its axis, the loaded Q was 6000. Low amplitude field modulation was at 1000 Hz. A trace of one of the N atom lines is given in Fig. 1 to show the line shape encountered in this work. The slight asymmetry of the line was believed to be caused by field inhomogenieties. Integrated line intensities were obtained by measuring the first moments. Absolute N atom concentrations were determined through titration with nitric oxide\textsuperscript{10} rather than by the O\textsubscript{2} calibration procedure described by Westenberg and deHaas\textsuperscript{11} With the spectrometer set to measure the narrow, easily power broadened N atom lines, it was inconvenient to increase the power and field modulation amplitude enough to obtain measurable O\textsubscript{2} signals.

A diagram of the reaction tube (10mm i.d.) and optical system is shown in Fig. 2. The afterglow was observed through a 1/8 inch hole drilled through the wall of the cavity. The photomultiplier was located sufficiently far from the EPR magnet so that its sensitivity was not affected by the field. All of the light path as well as the reaction tube up to the discharge was enclosed by an aluminum box to exclude extraneous light. Details of the light detection system and interference filter combination used to
isolate the afterglow bands of interest are described in Ref. 4. The photocurrent signal-to-noise ratio at the higher [N] was such that changes of 0.5% could be detected. Except for a glass light trap, all of the reaction tube was made of quartz. Before use, it was washed with dilute HF and distilled water. The pressure in the cavity was determined from the Poiseuille equation which was tested by measuring pressure at several points upstream from the cavity. It was routinely measured with a calibrated capacitance type differential manometer, checked occasionally against a McLeod gauge. Liquid nitrogen traps were located before the discharge and after the cavity. All glass systems were used to transfer N₂, He, and Ar from the gas storage cylinders, through pressure regulators containing metal diaphragms. Their flows were measured with calibrated ball-type flowmeters. The flows of added gases were measured by timing the pressure drop in a known volume; oil manometers were used here. To obtain measurable flows when small amounts of O₂ were to be added, mixtures of O₂ in N₂ as dilute as 1 part in 10³ were used. The O₂ was normally added at a point 27 cm upstream from the cavity center. After shutting off the O₂ flow at the needle valve labeled N in Fig. 2, the enhancement of the N atom signal decreased slowly because of the time required for O₂ to diffuse out of the rather long (~50 cm) section of tubing between N and the reaction tube. By opening the stopcock S₂ slightly, the stagnant O₂ containing gas in this inlet line could be flushed out. When this was done, the N atom signal decayed immediately to the value existing before the O₂ addition.
The main pump was of the Roots blower type. By means of an oil diffusion pump, the whole system was evacuated to a pressure of less than $0.5 \times 10^{-6}$ torr before use. All the gases used except $N_2$ were Matheson Ultra High Purity grade. The $N_2$ was Matheson "prepurified"; it was further treated by passage over a 1:1 titanium-zirconium alloy heated to 800° C. Effects of adding 0.1 p.p.m. O$_2$ to this purified $N_2$ (before the discharge) were observed. The discharge was powered by a 60 W, 2450 MHz medical diathermy unit.

**DESCRIPTION OF SPIN SYSTEM**

**Low Power Conditions**

We shall describe the behavior of the $N$ atom system in terms of a two level spin system, hoping that it will be a reasonably good approximation to the more complex system which actually exists. The treatment to be followed is similar to that given by Carrington. We let $[N^+]$ denote the number of atoms per cm$^3$ in the upper Zeeman level and $[N^-]$ the number in the lower. The intensity of an EPR absorption corresponding to a transition between two such levels will be proportional to the population difference $[N^-] - [N^+] = \Delta N$. We want to find out how $\Delta N$ changes with time from some initial specified value.

In the region from the start of the high field zone to the cavity, the rate of change of $N^+$ will be given by

$$\frac{d[N^-]}{dt} = W[N^+] - W \exp(-h\nu/kT) [N^-] \text{ in cm}^{-3} \text{ sec}^{-1}, \quad (1)$$
where $\hbar \nu$ is the energy separation of the Zeeman levels in the field, and $W$ is a rate coefficient for relaxation (sec$^{-1}$); it may depend on pressure, wall conditions, ambient temperature, the concentration of paramagnetic impurities, the N atom concentration, and the concentration of added $O_2$. In this two level approximation, $W$ is equivalent to $1/2T_1$, where $T_1$ is the "spin-lattice" relaxation time. Time, $t$, in this equation is to be determined from the relation $t = A \ell / f$, where $A$ is the cross sectional area of the flow tube, $\ell$ is the distance along the tube from the beginning of the high field region; $f$ is the volume flow rate of the gas (cm$^3$ sec$^{-1}$). Using the relationship $[N^+] = [N] - [N^-]$, where $[N]$ is the total N atom concentration, we can integrate (1). Solving for $\Delta N$ at the cavity we get,

$$\Delta N = 0.5 [N] [\theta + (\theta_0 - \theta) \exp(-2Wt_m)]$$  \hspace{1cm} (2)

where, $\theta = \hbar \nu/kT$, $\theta_0 = \hbar \nu/kT_0$, with $T_0$ the "spin temperature" at the beginning of the high field zone (at $t = 0$), $\exp(-\theta) \approx 1 - \theta$, and $t_m$ is the average time required for a sample of gas to flow from the beginning of the high field zone to the cavity. The length of this zone was estimated to be 15 cm; this value was used throughout the analysis. $[N]$ was assumed to remain constant. Visual examination of the afterglow intensity along the tube indicated that there was no significant change in $[N]$ in this section. Since we suppose that the Zeeman levels are equally populated as the atoms enter the high field region, we must have $T_0 = \infty$ at $t = 0$. This makes $\theta_0 = 0$ and (2) becomes,

$$\Delta N = 0.5 [N] \theta [1 - \exp(-2Wt_m)]$$ \hspace{1cm} (3)

At low microwave power levels (i.e. no saturation) the intensity of the EPR
signal should be proportional to $\Delta N$ as given by (3), since the change in $\Delta N$ in the short cavity section would be much smaller on a relative basis than the change in the longer section preceding the cavity.

### Saturation Effects

When saturation studies are made by means of the double attenuator technique, it can be shown that the signal is proportional to $\chi''$, the imaginary part of the magnetic susceptibility. This, in turn, will be proportional to the population difference $\Delta N$.

To analyze the effects of power saturation on the EPR signal, one could treat the section of reaction tube in the cavity in a fashion analogous to the derivation of (3), where now there would be additional terms representing transitions between $N^+$ and $N^-$ caused by microwave absorption and induced emission. Instead, we shall use a simpler approach which is satisfactory for our purposes. The standard expression for the effect of power saturation in a static two level system is (see Ref. 13 p. 38)

$$\Delta N = 0.5 \left[ N \right] \theta (W + p)^{-1} W,$$

where $p$ is a parameter which is proportional to the Einstein B coefficient and to the power incident on the cavity. In a flow system, unsaturated atoms are continuously entering the cavity, producing in effect, another source of relaxation in addition to $W$ of the order $1/t_c$ where $t_c = \Delta \ell_c / f$; $\ell_c$ is the effective length of the cavity for microwave transitions (about 1.5 cm in our apparatus). We shall simply add $1/t_c$ to $W$ in (4). Taking the reciprocal, we get,
\[(\Delta N)^{-1} = 2([N]_0)^{-1} \left[1 + (W + 1/t_c)^{-1} P\right]. \quad (5)\]

We shall further assume that the integrated line intensity is proportional to \(\Delta N\) as given by (5). This should be a fair approximation since the lines were partially broadened by magnetic field inhomogeneities so that their shape did not change markedly on saturation. If the reciprocal of the line intensity is plotted against the power incident on the cavity, one should get a straight line whose intercept to slope ratio will be a quantity proportional to \((W + 1/t_c)\). The more detailed treatment leads to a fairly complex expression for \(\Delta N\) which is difficult to apply to the analysis of the saturation data. It shows, however, that (5) is an approximate relationship between \(\Delta N\) and the parameters \(W\), \(t_c\), and \(P\), which should represent our data reasonably well. Therefore, the intercept to slope ratio defined above will be taken as a measure of the effective relaxation rate. The detailed treatment also shows that variations depicted by (3) in the spin temperature of the atoms reaching the cavity do not enter into the intercept to slope ratio.

Without the addition of \(O_2\) to the system, values of \(W\) of the order of 20 sec\(^{-1}\) were obtained. Since \(1/t_c\) was of the order of 1000 sec\(^{-1}\) for medium \(N_2\) flow rates, this flow relaxation effect would outweigh \(W\) unless very slow gas flows were used. Power saturation effects should therefore be expected to depend on the flow rate of the gas.
EXPERIMENTS AND RESULTS

In most of the work reported here, the intensity of the low field N atom EPR line was used as a measure of the population differences between the magnetic sublevels. No difference was ever detected between its intensity and those of the two higher field lines.

Experiments at Low Power Levels

As discussed earlier, the EPR intensity at low power levels, should be proportional to \( \Delta N \) as given by (3). We shall assume that the dependence of \( W \) on \( O_2 \) concentration is linear and write for \( W \),

\[
W = W_0 + Q[O_2], \quad (6)
\]

where \( W_0 \) and \( Q \) may depend on such things as pressure, wall conditions, temperature, impurity concentrations, or \([N]; [O_2]\) is the \( O_2 \) concentration. By adding \( O_2 \) to the system one can test the linearity of (6).

Determination of \( W_0 \) by measuring signal intensity as a function of \( N_2 \) flow. Consider the system without added \( O_2 \). We can solve (3) for \( \Delta W \) to get,

\[
\Delta W = \Delta W_0 = \log_e \left( 1 - \frac{\Delta N}{0.5[N]} \right) \quad (7)
\]

A plot of the experimentally observed quantity on the right hand side of (7) against \( t_m \), determined from the flow rate and the length of reaction tube in the field region, should be a straight line with an intercept whose value is zero, and a slope whose value is \( 2W_0 \). The quantity \( \Delta N/0.5[N] \) is the ratio of the observed signal to the equilibrium value. The equilibrium value
was determined either by extrapolating the observed $\Delta N$ to zero flow (at constant $[N]$ as monitored by afterglow) or by adding excess $^{14}O_2$ to relax the spin system. Both these methods were found to give the same results for $0.5[N]$.5.

Plots of (7) for data taken at two different pressures (2.1 and 6.5 torr) are shown in Fig. 3 along with details of the experimental conditions. As the $N_2$ flow was varied, the afterglow intensity was kept constant either by changing the power to the discharge or by shunting a portion of the $N_2$ around the discharge. Thus the runs were taken at constant $[N]$. The linearity and zero intercept of this plot shows that the observed dependence of signal intensity on flow at constant pressure and $[N]$ is well represented by (3). From the slope of the line, one gets a value of 19.6 sec$^{-1}$ for $W_0$. Within the experimental uncertainty $W_0$ was found to be the same at both pressures.

The 2.1 torr data are shown again in Fig. 4 where the points are the observed values of $\Delta N/0.5[N]$6 and the curve was calculated from (3) using $W_0 = 19.6$ sec$^{-1}$.

Dependence of $W_0$ on $[N]$ from signal versus flow data. Plots of data according to (7) at 2.1 torr and two different $N$ atom concentrations are shown in Fig. 5. The different values of the slopes show that $W_0$ increases somewhat with increasing $[N]$.

Variation of $W_0$ with $[N]$ from signal versus $[N]$ data at constant flow. For this experiment $[N]$ was monitored by means of the afterglow intensity. The equilibrium values of $\Delta N$ were obtained by adding excess $O_2$ to relax the system. A plot of $W_0$, determined through use of (7), as a function of $[N]$.
is shown in Fig. 6. The straight line drawn through these points shows that within experimental error the observed variation of \( W_0 \) with \([N]\) is linear in this range.

It must be pointed out that this variation with \([N]\) may be only apparent. To increase or decrease \([N]\), one must change the discharge power, or shunt some of the \(N_2\) around the discharge. Such changes could also modify in a complex way the concentration of discharge produced paramagnetic species which could relax the \(N\) atoms. Evidence for the presence of such species was found by comparing the EPR signal at high and low discharge power. At high power, the afterglow intensity was kept the same as under the low power condition, by shunting some of the \(N_2\) around the discharge. \([N]\) was therefore the same in both cases. The signal was found to be about 15% higher under the high power condition, indicating more relaxation.

**Variation of \(W\) with \(O_2\) concentration.** To test (6), values of \(W\) were determined from the observed signal intensity by means of (7), and plotted against \([O_2]\). Two such plots are shown in Fig. 6 for data taken at two different \(N\) atom concentrations. The pressure was 2.1 torr. The linearity of these plots shows that (6) does represent the dependence of \(W\) on \([O_2]\) in this range. The intercepts gave values of \(W_0\) which agreed with those determined from the signal versus flow data. The increase in \(W_0\) with \([N]\) was again apparent. Since the slopes appeared to be the same in both plots, we concluded that \(Q\) does not vary noticeably with \([N]\) in this range. These experiments were also repeated at a pressure of 1 torr. There was no noticeable difference between the values of \(Q\) observed at 1 and 2 torr.
Signal versus $[O_2]$ data at 2.1 torr are shown in Fig. 8. The points are the observed values of $\Delta N/0.5[N]_0$; the curve was calculated from (3) and (6) using $Q = 4.5 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$, $W_0 = 15 \text{ sec}^{-1}$, and $t_m = 0.0058 \text{ sec}$. The calculated curve fits the observed points satisfactorily.

Summary of results of experiments at low power. Values of $W_0$ and $Q$ determined in the foregoing experiments are presented in Table I., along with conditions of pressure, flow, and $[N]$.

Determination of a spin exchange cross section for $N-O_2$ collisions. Any spin orientation possessed by the N atoms should be rapidly transferred to $O_2$ via spin exchange collisions. If we assume a cross section of $5 \times 10^{-16}$ cm$^2$ for such collisions, the number of these collisions in a system having $[N] = 3 \times 10^{14}$ and $[O_2] = 3 \times 10^{11}$, (which is typical of our experimental conditions) would be $1.5 \times 10^{17} \text{ cm}^{-3} \text{ sec}^{-1}$. On the basis of arguments given by McNeal et al., one would expect that every collision of an $O_2$ molecule with a $N_2$ molecule would disorient the $O_2$ spin. Assuming a cross section of $1.2 \times 10^{-15}$ (gas kinetic) for these collisions, and taking $[O_2] = 3 \times 10^{11}$ and $[N_2] = 6.7 \times 10^{16} \text{ cm}^{-3}$ we get $51 \times 10^{17} \text{ cm}^{-3} \text{ sec}^{-1}$ for the number of these collisions. Thus, the number of disorienting collisions for $O_2$ should be considerably greater than the number of $N-O_2$ exchange collisions. In this case, the N atom relaxation rate should be limited by exchange collisions with $O_2$. Any spin orientation which had been transferred to the $O_2$ would be rapidly lost to the surrounding heat bath. It should therefore be possible to relate the measured parameter $Q$ to a cross section $\sigma$ for $N-O_2$ spin exchange through the kinetic theory relation $Q = \sigma (8\pi RT/\mu)^{1/2}$.
where $R$ is the gas constant ($\text{ergs deg}^{-1} \text{mole}^{-1}$), $T$ is the absolute temperature, and $\mu$ the reduced mass of the colliding particles ($\text{g mole}^{-1}$). For $Q = 5 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$, we get $\sigma = 1.5 \times 10^{-15} \text{ cm}^2$. This interpretation requires that $Q$ be independent of $[N]$ and total pressure. For the rather small ranges of these variables studied, these criteria were found to be satisfied. Since the main purpose of this work was to explain the effect of $O_2$ on the $N$ atom EPR signal and not to obtain an accurate value for $\sigma$, no attempt was made to refine estimates of flow rate, $O_2$ concentration, length of high field region, etc. The uncertainties in these various factors put the uncertainty in $\sigma$ at about $\pm 200\%$.

Saturation Experiments

As discussed earlier, when saturation studies are made with the double attenuator technique, the signal intensity may be taken to be proportional to $\Delta N$ as given by the reciprocal of (5). A plot of the reciprocal of the signal intensity vs microwave power incident on the cavity is shown in Fig. 9. Experimental conditions are given in the figure caption. No $O_2$ was added. A large number of such plots were made with and without added $O_2$, at different pressures, $N_2$ flows, and $N$ atom concentrations. Within the estimated experimental uncertainties, all of these plots were linear, indicating that (5) is a good representation of the effect of power saturation.

The intercept to slope ratios of a number of plots, made under the conditions given in Fig. 9, are shown in Fig. 10 where they are plotted
against the quantity \( W_0 + \frac{1}{t_c} \). The expected proportionality of these ratios to \( W_0 + \frac{1}{t_c} \) is evident, as is the zero intercept. No dependence of these intercept to slope ratios on \([N]\) or pressure was noticed. When \( O_2 \) was added, these ratios were found to increase linearly with \([O_2]\) within experimental error.

**Miscellaneous Observations**

**Changes in the line width of the N atom resonance.** Increasing the microwave power from 0.006 to 0.6 \( \mu W \) caused a 22% increase in the line width, showing that inhomogeneities of the magnetic field did not account entirely for the observed line width.\(^{16}\) The line width (under low power conditions) was also found to increase with increasing \([N]\). Over the range \([N] = 5 \times 10^{13} \) atoms \(cm^{-3} \) the increase was approximately 8%. The fact that these line width changes were observed indicates that the natural line width under the conditions of our experiment was close to the observed width of 103 KHz (0.037G). (This width was taken as the separation between the derivative maxima; see Fig. 1) Assuming a lorentzian line shape and using this observed width to estimate the relaxation time \( T_2 \) according to the relation \( T_2 = \frac{2(2\pi\Delta\nu)^{-1}}{\text{see Ref. 11, p. 29}} \), we get \( T_2 = 3 \times 10^{-6} \) sec, which is probably a lower limit since the line was almost certainly broadened by field inhomogeneities. Anderson, Pipkin, and Baird\(^{18}\) have calculated a value of \( 4.5 \times 10^{-16} \) cm\(^2\) for the spin exchange cross section for collisions between N atoms at 400°K. Assuming that this
cross section is the same at 300°K and taking \([N] = 3 \times 10^{14} \text{ atoms cm}^{-2}\),
we calculate a value of \(2.5 \times 10^{-6} \text{ sec}\) for \(T_2\), in good agreement with the
observed value. Thus, \(N-N\) spin exchange collisions could account for our
observed line width. Although no change in the line width was observed for
additions of \(O_2\) up to 50 p.p.m., one would expect \(O_2\) to affect the width
only when its concentration became comparable to that of \(N\), so that \(N-O_2\)
spin exchange collisions began to compete with the \(N-N\) collisions.

*Production of the pink nitrogen afterglow.* This afterglow was observed
roughly 10 cm downstream from the discharge at pressures above about 3 torr.
Small amounts of \(O_2\) added to the \(N_2\) upstream from the discharge greatly
increased its intensity and also made it possible to obtain it at lower
pressures. This enhancement by \(O_2\) has been observed elsewhere.\(^{17}\) At a
pressure of 2 torr, where this afterglow was not normally evident in the
purified \(N_2\), shutting off the upstream \(O_2\) supply did not cause its immediate
disappearance. During the course of several minutes the pink region slowly
moved downstream from the discharge, without any noticeable change in
intensity. When it reached a point corresponding to about 14 cm away from
the discharge it suddenly vanished. This behavior was reproducible. We
made no attempt to study this problem.

*Production of electrons.* Under certain conditions, the electron
cyclotron resonance absorption was observed when either \(O_2\) or \(NO\) was added
downstream. These conditions appeared to be the same as those which gave
the pink afterglow suggesting that one might try searching for some
relationship between the two phenomena. Below 3 torr (no noticeable pink
afterglow in purified N₂), no electron signal was detected even for large downstream O₂ additions. At 2 torr, addition of NO occasionally gave rise to the electron signal, but not always. No attempt was made to determine the causes of this variable behavior. To avoid complicating the N atom relaxation process by the presence of electrons, practically all of the measurements reported here were done under conditions in which there was no noticeable pink afterglow or electron resonance signal. This meant working at rather low pressures.

By comparison of our electron and N atom signals with those shown by Bayes, Kivelson, and Wong,¹⁸ it was possible to estimate an upper limit for the electron concentration under conditions in which we could detect no electron resonance. The limit obtained was ~10⁷ cm⁻³. The results of these workers also show that there should have been no rf heating of any electrons present at the power levels used in our work. Dehmelt¹⁹ has shown that spin exchange cross sections for electron-atom collisions are of the order of 23 x 10⁻¹⁶ cm². If the electron concentration were as high as 10⁷ cm⁻³, a N atom would experience several exchange collisions per second with 300°K electrons. This would not be enough to account for the observed relaxation rates. Under conditions in which an electron resonance was observed, however, this additional relaxation would probably have to be considered.

**Effect of NO on the N atom relaxation.** Because the electron spin in NO is strongly coupled to its rotational angular momentum, this molecule should relax the N system in the same manner as O₂. In this case, however,
there is a competing mechanism in the form of the rapid reaction \( N + NO = N_2 + O \), which forms the basis of the N atom titration.\(^{10}\) Phillips and Schiff\(^{20}\) report a value of \( 2.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \) for the rate constant for this reaction. From this we can calculate how fast the NO is converted to O atoms. For \([N] = 3 \times 10^{14} \text{ atoms cm}^{-3} \) and \([NO]_o \ll [N]\), where \([NO]_o \) is the NO concentration in the flow tube at the point of addition, then in only \(0.7 \times 10^{-3} \text{ sec} \), \([NO]/[NO]_o = 10^{-2}\). In our system this will happen before the N atoms reach the high field region. Therefore, any relaxing effect of NO will actually be caused by O atoms. Because of the coupling between the spin and electronic angular momentum in this atom, it should be easily relaxed by collisions with the buffer gas,\(^{21}\) in the same fashion as would \( O_2 \). We neglected to carry out the simple experiment of measuring the N atom EPR signal as a function of \([NO]\) (and consequently \([O]\)), in order to estimate a spin exchange rate constant as we did for \( O_2 \). However, the observed qualitative effects of NO appeared to be the same as those of \( O_2 \). Small amounts of NO (of the order p.p.m.) produced the expected increase in the EPR signal, with no noticeable change in the afterglow intensity. Larger amounts (approaching \([N]\)) decreased both the afterglow intensity and the EPR signal showing the N was being consumed through the titration reaction.

Experiments with He or Ar as buffer gases. The effects of adding \( O_2 \) to a discharged mixture of 1\% \( N_2 \) in He or Ar were found to be similar to those observed for pure \( N_2 \). Therefore, no detailed measurements were made for those systems.
Addition of $O_2$ before the discharge. Roughly $1/3$ less $O_2$ was required upstream to produce the same amount of relaxation as when added downstream. Upstream addition also produced appreciable increases in the Lewis-Rayleigh afterglow intensity (accompanied by appropriate increases in the EPR signal), and as mentioned earlier, enhanced the pink afterglow intensity.

DISCUSSION

The main observation of this work was an increase in the N atom EPR absorption intensity when traces of $O_2$ were added to the active nitrogen downstream from the discharge. Two pieces of experimental evidence indicated that $[N]$ was not changed by the $O_2$ addition. (Ref. 6 gives results of some spectrometric work on the effect of $O_2$ addition.)

a) The Lewis-Rayleigh afterglow intensity remained constant.

b) There was no noticeable change in the N atom line width. Since line width changes were observed on power saturation, it appeared that the natural width was not completely determined by field inhomogeneities. The observed width was comparable to that expected if N-N exchange collisions were the determining factor. One might therefore expect the line width to depend somewhat on $[N]$. The observed increase in width with increasing afterglow intensity was consistent with this view.

We can think of only two explanations for this increase in the signal; either power saturation was occurring, or because of a naturally long spin relaxation time and short residence time in the magnet, the atoms arrived
at the cavity before achieving an equilibrium magnetization. In both cases
the addition of O₂ should relax the N spin system and produce an equilibrium
magnetization.²²

The possibility that we were working under a condition of power
saturation was eliminated by the results of several experiments.

a) Measurements of χ'' by the double attenuator method showed that
saturation was only barely noticeable at a power level 10 db above our
normal operating level of 0.006 μW. The plot shown in Fig. 9 demonstrates
how the reciprocal of χ'' increases with increasing power. Notice that
under these particular conditions even a 20 db increase in the power level
decreased χ'' only by a factor of 0.8.

b) In another test, the flow rate was adjusted so that the addition
of excess O₂ increased the signal by a factor of two. Suppose that the
signal were initially too small by this amount because of power saturation.
If the power level were then increased by a factor of 10, we see from (5)
that the addition of excess O₂ would now produce (by making W large) an
11-fold change in the signal. The observed change was, however, again only
a factor of two showing that power saturation was not responsible for the
effect.

c) If power saturation were involved, increasing the flow rate, while
maintaining constant afterglow intensity and thus constant [N], would pro-
duce an increase in the signal since unsaturated atoms would be entering the
cavity at a higher rate. The opposite effect was observed, however. Increas-
ing flow rate produced a decrease in the signal.
The second explanation is favored by the results of a number of experiments. These have been interpreted on the basis of a two level spin model whose behavior is described by (3). This equation contains a parameter $W$. In this two level scheme, $W = 1/2T_1$. The observed functional dependence of the signal intensity on flow rate at constant [N] (monitored by the afterglow intensity) was found to be quantitatively represented by (3). A fit of the data to this equation yielded values of $T_1$. In the absence of added $O_2$, $T_1$ was of the order 25 msec. $T_1$ did not vary noticeably with pressure. It did decrease somewhat with increasing [N] and discharge power.

This rather long relaxation time seems consistent with optical pumping studies which have shown that disorientation of N by $N_2$ is inefficient. Although spin exchange collisions between N atoms are frequent and appear to account for at least part of the observed line width, they do not produce a change in the net magnetization in the direction of the magnetic field and thus do not contribute to relaxation.\textsuperscript{23, 24} The observed relaxation time could be accounted for by wall collisions and by collisions with paramagnetic impurities, present initially in the $N_2$ or generated in the discharge or from N atom recombination. It was not determined which of these processes were operative.

When small amounts of $O_2$ were added to the discharged $N_2$, the resulting increase in the N atom EPR signal was found to be satisfactorily accounted for by (3) if $W$ increased according to the relation $W = W_0 + Q [O_2]$. We assumed that any orientation transferred to $O_2$ from N by spin exchange
collisions would be rapidly lost through collisions with the surrounding heat bath molecules because of the coupling between the O₂ molecule's electron spin and its rotational angular momentum. This enabled us to relate the quantity Q to an exchange cross section for N-O₂ collisions. This analysis of O₂ effects also indicated the N₂ initially contained less than 1 p.p.m. O₂. (See Figs. 7 and 8.)

The rate at which microwave energy can be absorbed without resulting in saturation depends on the time the atoms spend in the cavity as well as collisional relaxation processes. Relaxation rates estimated from power saturation measurements should be of the order \( W + \frac{1}{t_c} \), where \( t_c \) is the average residence time of an atom in the cavity. For flow conditions given in Fig. 9, \( \frac{1}{t_c} \) was around 800 sec⁻¹, considerably greater than \( W \) observed in the absence of added O₂. An estimate of \( W + \frac{1}{t_c} \) was made from saturation experiments according to the procedure outlined in Ref. 15 p. 132. The value obtained, 1800 sec⁻¹, is probably in satisfactory agreement with the expected value in view of the uncertainties involved in such an estimate. Figure 10 shows that the power required to saturate the lines did decrease with flow rate as expected.
CONCLUSIONS

On the basis of these experiments it is evident that N atoms have rather long spin relaxation times when produced by discharges through relatively pure nitrogen. This relaxation can be so slow that atoms arrive at the cavity before they have reached their equilibrium magnetization. As a result the EPR signal can be abnormally small. Unless traces of O₂ or other suitable paramagnetic species are present or are added, large errors can arise when EPR is applied to quantitative detection of N atoms. In the absence of added O₂, the amount of power required to saturate the lines was determined primarily by the time the atoms spent in the cavity and not by collision relaxation processes. Under these conditions, one should test for power saturation at the lowest flow rate anticipated for a particular experiment.
TABLE I.

Results of experiments carried out at a low microwave power level (0.006 μW).

<table>
<thead>
<tr>
<th>Pressure (torr)</th>
<th>t_m (sec)</th>
<th>[N] (atoms cm⁻³)</th>
<th>W₀ (sec⁻¹)</th>
<th>Q (cm³ sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1b</td>
<td>varied</td>
<td>1.6x10¹⁴±10%⁸</td>
<td>20±15%⁸</td>
<td></td>
</tr>
<tr>
<td>6.5b</td>
<td>varied</td>
<td>1.6</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>2.1c</td>
<td>varied</td>
<td>1.8</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>2.1d</td>
<td>varied</td>
<td>0.64</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>2.1e</td>
<td>0.012</td>
<td>varied</td>
<td>variable</td>
<td></td>
</tr>
<tr>
<td>2.1f</td>
<td>0.0058</td>
<td>1.3</td>
<td>15</td>
<td>4.5x10⁻¹⁰ ±10%⁸</td>
</tr>
<tr>
<td>2.1g</td>
<td>0.0058</td>
<td>3.5</td>
<td>35</td>
<td>4.5</td>
</tr>
<tr>
<td>1.2f</td>
<td>0.0077</td>
<td>1.3</td>
<td>18</td>
<td>5.0</td>
</tr>
</tbody>
</table>

a The estimates shown here are relative uncertainties.

b From signal intensity vs flow data; see Fig. 3.

c Also from signal vs flow data; see Fig. 5.

d Eight values of W₀ ranging from 9 to 25 sec⁻¹ were obtained from signal vs [N] data at constant flow; see Fig. 6.

f From signal vs [O₂] at constant flow; see Fig. 7.
5. C. J. Ultee, J. Chem. Phys. 41, 281 (1964); J. Phys. Chem. 64, 1873 (1960). These references contain a discussion of the observed enhancement of saturated N atoms EPR absorption lines by O₂ added to discharged N₂ in a flow system.
12. In $^4S_{3/2}$ ground state N atoms, the relationship of the absorption line intensity to the population differences between Zeeman levels is the following. Because this state has no noticeable second order Zeeman effect, each of the three nuclear hyperfine lines in its EPR spectrum consists of an unresolved triplet corresponding to the three possible transitions between the four Zeeman levels. The intensity
of such a triplet is proportional to the sum of the population differences between adjacent Zeeman levels (weighted by the appropriate transition probabilities) having the same nuclear spin magnetic quantum number.


14. By excess $O_2$ we mean an amount somewhat greater than that which produced no further noticeable increase in the $N$ atom EPR signal. In general, this was of the order 30 to 50 p.p.m.


22. It might be suggested that addition of $O_2$ decreased the wall recombination rate for $N$ atoms. More atoms would reach the cavity and the EPR signal would rise. However, an increase in $[N]$ would also result in
an increase in the afterglow intensity. This was not observed. Furthermore, switching the same $O_2$ flow back and forth between the inlet located 27 cm from the cavity and the inlet located at the light trap produced no change in the EPR signal or the afterglow intensity. If $O_2$ were conditioning the walls, addition of $O_2$ further upstream from the cavity would likely result in a further increase in signal since a longer section of the tube would be affected. This experiment showed, incidently, that mixing was complete at the 27 cm inlet.


FIGURE CAPTIONS

Fig. 1  N atom absorption line. The scale to the left of the line gives the deflection of the strip chart recorder in cm. The total pressure was 2.1 torr and the N atom concentration was $2.5 \times 10^{14}$ atoms cm$^{-3}$. The O$_2$ concentration was $10^{12}$ molecules cm$^{-3}$. Microwave power incident on the cavity was 0.006 $\mu$W. Amplitude of the field modulation was about 0.02 G. The spectrometer time constant was 1 sec.

Fig. 2  Schematic of apparatus showing reaction tube and optical system. Dimensions given are in cm.

Fig. 3  Determination of $W_0$ from signal intensity as a function of N$_2$ flow; no added O$_2$. Shown are plots of the experimental quantity $\log e(1 - \Delta N/0.5[N]^6)$, vs $t_m$ at pressures of 2.1 and 6.5 torr. $t_m$ is the transit time in the 15 cm section of the reaction tube preceding the cavity. Eq. (7) shows that the ordinate should be $2W_0t_m^{-1}$. The slope should give a value of $W_0$. Microwave power was 0.006 $\mu$W. $[N] = 1.6 \times 10^{14}$ atoms cm$^{-3}$ at both pressures.

Fig. 4  Signal intensity vs transit time and flow rate. The points shown are the observed values of $\Delta N/0.5N^6$, which is the ratio of the signal, to its equilibrium value observed when excess O$_2$ (see Ref. 12) was added. The curve was calculated from Eq. (3) using $W_0 = 19.6$ sec$^{-1}$. The pressure was 2.1 torr; $[N] = 1.8 \times 10^{14}$ atoms cm$^{-3}$. Microwave power was 0.006 $\mu$W.
Fig. 5  
Wo at two different values of [N] from signal vs flow data; no added O₂. Pressure was 2.1 torr. The data are plotted according to Eq. (7). Points represented by circles have [N] = 1.8 x 10^{14} atoms cm^{-3}; those by triangles have [N] = 0.64 x 10^{14} atoms cm^{-3}. Microwave power was 0.006 μW.

Fig. 6  
Variation of Wo with [N] from signal versus [N] data at constant flow. Data are plotted according to Eq. (7). t_m = 0.012 sec, corresponding to a N₂ flow of 2.7 cm³ sec⁻¹ at 1 atm and 25°C. Pressure was 2.1 torr; microwave power was 0.006 μW. The two points designated by triangles come from the slopes of the lines shown in Fig. 5.

Fig. 7  
Variation of W with [O₂]. The ordinate is the observed value of the quantity (2t_m)^{-1}log_e(1 - ΔN/0.5[N]θ), which according to Eq. (7) is W. The circles correspond to data taken with [N] = 1.3 x 10^{14} atoms cm⁻³; the triangles to [N] = 3.5 x 10^{14} atoms cm⁻³. t_m = 0.0058 sec; pressure was 2.1 torr; microwave power was 0.006 μW. The dotted lines indicate the estimated error band.

Fig. 8  
Signal intensity vs [O₂]. The points are the observed values of ΔN/0.5[N]θ; the curve was calculated from Eqs. (3) and (6) using Q = 4.5 x 10⁻¹⁰ cm³ sec⁻¹, Wo = 15 sec⁻¹, and t_m = 0.0058 sec. Pressure was 2.1 torr; [N] = 1.3 x 10^{14} atoms cm⁻³. Microwave power was 0.006 μW.
Fig. 9  Reciprocal of EPR signal intensity (arbitrary units) vs microwave power incident on cavity. No added O$_2$. Pressure was 2.1 torr; [N] = 3.2 x 10$^{14}$ atoms cm$^{-3}$; N$_2$ flow was 2.5 cm$^3$ sec$^{-1}$ at 1 atm and 25°C.

Fig. 10 Variation with N$_2$ flow of power required to saturate the N atom absorption. The ordinate gives the intercept to slope ratios of plots like that shown in Fig. 9. These ratios should be proportional to the quantity W$_0$ + 1/t$_0$, which is proportional to the N$_2$ flow. Pressure was 2.1 torr. No O$_2$ was added.
\[ \log_e \left(1 - \frac{\Delta N}{0.5 N_e}\right) = 2 W_0 t_m \]

- ○ 2.1 torr
- △ 6.5 torr
\[
\log_8 (1 - \Delta N / 0.5 N_0) = 2 W_0 t_m
\]
$$(2t_m)^{-1} \log_8^e (1 - \Delta N / 0.5 N\theta) = W = W_0 + Q [O_2] (\text{sec}^{-1})$$
Fig. 10

Graph showing the relationship between the intercept to slope ratio of (Signal)^(-1) vs Power plots and N_2 flow (cm^3 sec^-1 NTP) with the x-axis labeled W_0 + 1/tc and the y-axis labeled (arbitrary units).