Magnetic Resonance Absorption in Nitric Oxide

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The nine-line magnetic resonance spectrum of $N^{14}O^{16}$ is observed at fields in the range of 8600 oersted at a frequency of 9360 megacycle/sec. The spectrum arises from magnetic-dipole transitions between Zeeman levels in the $J=\frac{3}{2}$ state of the $^2\Pi_{3/2}$ spin component. The line positions allow a determination of the magnetic IJ coupling constant, which is 29.8 ± 0.3 megacycle/sec., and the nuclear electric quadrupole coupling, which is -1.7 ± 0.5 megacycle/sec. The line position and triplet spacings, which arise from molecular perturbations, are in good agreement with the theory of Margenau and Henry. The absolute intensity of the three stronger lines is measured to be $\chi''=1.2\times10^{-10}$ which also agrees with theory.

1. INTRODUCTION

THIS paper describes an investigation[1] of the magnetic levels of one of the rotational states of the paramagnetic gas NO. The experiments employ the principle of magnetic resonance and have much in common with other recent applications of this principle.[2] They fall into the general class which is termed magnetic resonance absorption experiments.

When a gas composed of molecules possessing permanent magnetic moments is placed in a magnetic field, the degeneracies associated with the magnetic quantum numbers are removed and the energy levels are split into a number of Zeeman components. Transitions between pairs of these component levels are generally permitted for magnetic-dipole radiation. Since the permanent magnetic moments are of the order of Bohr magnetons, the frequencies of these transitions lie in the microwave region for field strengths of a few thousand oersteds. For such frequencies the Einstein coefficient of spontaneous emission is negligibly small as compared with the equal coefficients of induced emission and of absorption, so that the transition probabilities for absorption and emission are essentially equal. However, molecular collisions bring the gas to an equilibrium state in which there is a preferential population of the less energetic states. Thus there are more absorption than emission transitions, which produces a net absorption of an electromagnetic wave which satisfies the polarization rules and the Bohr frequency condition for the two levels involved. There is also an anomolous dispersion[3] but this is not exploited in the present experiments.

The paramagnetic molecule NO follows Hund's coupling case (a) to a fair approximation.[4] The electronic orbital motion and spin are strongly coupled to the internuclear axis and weakly coupled to the nuclear rotation. In the ground electronic state $\Lambda=1$ and $\Sigma=\frac{1}{2}$. The resulting doublet has a large ($\sim$120 cm^{-1}) separation. The upper or $^2\Pi_{3/2}$ doublet component possesses an electronic magnetic moment and is responsible for the paramagnetism of the gas. At room temperatures ($kT\sim200$ cm^{-1}) a number of rotational

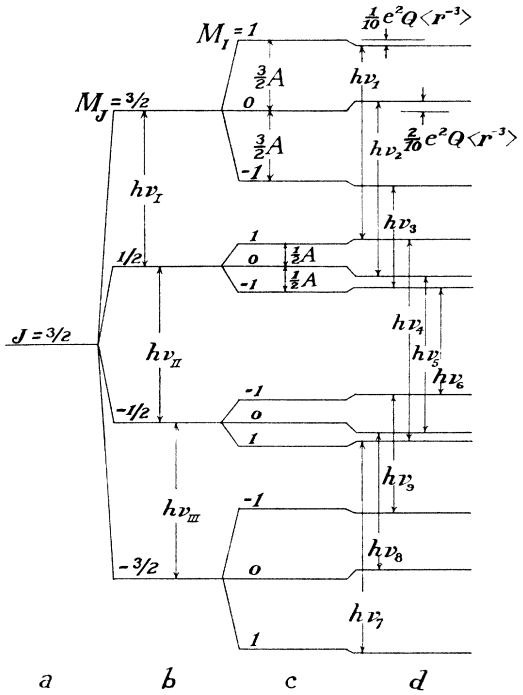

FIG. 1. Energy level diagram of the $J=\frac{3}{2}$ level of the $^2\Pi_{3/2}$ state of $N^{14}O^{16}$. Stage (a) is in the absence of magnetic field. Stage (b) shows the magnetic levels considering only molecular effects. Stage (c) includes the nuclear electric quadrupole IJ coupling. The nine transitions $\Delta M_J=\pm1$, $\Delta M_I=0$ are shown in stage (d). Arabic indices on the transitions correspond to the labeling of the observed absorption lines.

Note: The quadrupole energies labeled $1/10e^2Q\langle r^{-3}\rangle$ and $2/10e^2Q\langle r^{-3}\rangle$ should be written $1/20eQq$ and $2/20eQq$ respectively in accord with Eq. (14) of reference 4a.

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[1] A preliminary report is given by R. Beringer and J. G. Castle, Jr., Phys. Rev. **76**, 868 (1949).

[2] These include the experiments of Purcell, Torrey, and Pound, Phys. Rev. **69**, 37 (1946) on nuclear magnetic resonance absorption; those of Bloch, Hansen, and Packard, Phys. Rev. **69**, 127 (1946) on nuclear induction; those of E. Zavoisky, J. Phys. U.S.S.R. **9**, 211, 245 (1945) on magnetic resonance by paramagnetic ions; and those of J. H. E. Griffiths, Nature **158**, 670 (1946) on ferromagnetic resonance.

[3] The general Kramers-Kronig relation, H. A. Kramers, Atti Congr. Fis., Como (1927) 545 connects the absorption and dispersion.

[4] G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939), pp. 241, 242, 326, 502.

states of this upper component are appreciably populated; of these, the lowest ($J=\frac{3}{2}$) is of concern here.

Vector model considerations[4] give a system of four magnetic levels, $M_J=\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$, spaced by $(\frac{4}{5})H\mu_0$ erg for the $J=\frac{3}{2}$ rotational level of the $^2\Pi_{3/2}$ state; μ_0 is the Bohr magneton $eh/2mc$ and H the applied field in oersted. This level system is shown in stage (b) of Fig. 1. Such a level system would give rise to three coincident transitions of frequency ($4H\mu_0/5h$) cycle/sec. for magnetic-dipole radiation ($\Delta M_J=\pm 1$). As might be expected, however, this coincidence is removed by field-uncoupling in the molecule and the perturbations of nearby states. Thus ν_I, ν_{II}, and ν_{III} of Fig. 1 differ from each other and from $4H\mu_0/5h$. The accompanying paper by Margenau and Henry[4a] sets forth an exact theory of the magnetic energy states in NO.

In addition to these molecular distortions, hyperfine structure is to be expected, since the nucleus N^{14} possesses a spin ($I=1$), a magnetic moment, and an electric quadrupole moment. In distinction to the usual case of molecules in $^1\Sigma$ states the magnetic IJ coupling will be large in this molecule because of the electronic magnetic moment. The nuclear electric quadrupole coupling will add to this. The result of these two interactions is to split each M_J state into three M_I components. A twelve-level pattern results and transitions $\Delta M_J=\pm 1$, $\Delta M_I=0$ give rise to a nine-line absorption spectrum (see stages (c) and (d) of Fig. 1). For pure magnetic IJ coupling and strong magnetic fields the M_I components would be symmetrical around the M_J levels, and the nine-line spectrum would be composed of triplets of constant spacing. Electric quadrupole coupling removes this constant spacing. It should be noted that the spectrum $\Delta M_I=\pm 1$; $\Delta M_J=0$ lies in the radiofrequency range and is not observed here.

2. APPARATUS

The experiment consists in noting the absorption which results from transitions brought about by a microwave magnetic field in a gas-filled resonant cavity when a transverse d.c. magnetic field is adjusted for resonance with one of the transitions.

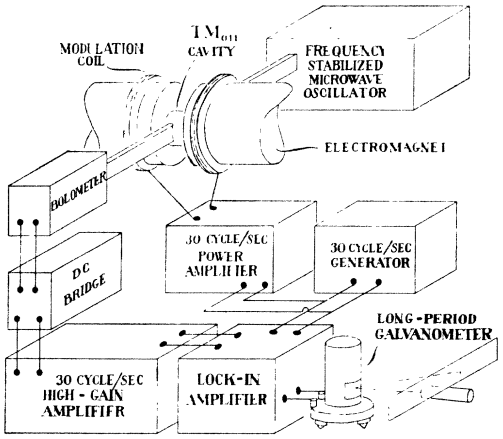

FIG. 2. Schematic diagram of the microwave magnetic resonance absorption apparatus.

The main components of the apparatus are shown in Fig. 2. The oscillator, a 723A/B klystron, is stabilized by a microwave discriminator and d.c. amplifier following the method of Pound.[5] A brass wave guide leads from the oscillator to the circular-cylinder cavity which is resonant at 9360 mc/sec. in the TM_{011} mode. The cavity is machined from commercial copper and is isolated by vacuum-tight mica windows. It is coupled to the incident and emergent wave guides by circular irises of 0.250 inch diameter. The measured loaded and unloaded Q-values at room temperature are 3500 and 8400 respectively. The cavity is placed between the poles of a Weiss design (Société Genevoise) electromagnet with plane parallel pole faces of 5.7 inches diameter spaced by 1.8 inches. The microwave H field in the cavity lies entirely in planes normal to the H field of the magnet.

The wave guide emergent from the cavity goes to a matched bolometer[6] mounted in a tuneable wave guide circuit. This bolometer forms one arm of a high impedance d.c. bridge which is in balance for a bolometer resistance of 200 ohms. In place of the usual balance meter there is connected a high gain (voltage gain of 2.2×10^6) audio amplifier of 2 cycle/sec. noise-band width[7] centered at 30 cycle/sec. The output from this amplifier is impressed on a balanced lock-in[8] mixer which receives its local-oscillator voltage from a small 30 cycle/sec. a.c. generator driven by a synchronous motor. The d.c. output from the lock-in mixer deflects a critically damped galvanometer of 0.04 cycle/sec. band width. A conventional audio power amplifier takes a 30 cycle/sec. signal from the same generator and energizes a pair of modulation coils wound on the magnet poles. These produce a 30 cycle/sec. sinsudoidal modulation of the d.c. magnetic field, uniform in space and variable from 1 to 200 oersted, peak-to-peak.

The main coils of the magnet are energized by a compound-wound d.c. generator which receives its excitation from a conventional degenerative voltage stabilizer using the terminal voltage of the magnet coils as a control voltage. A voltage derived from dry batteries is balanced against the magnet voltage and is used to set the magnet current. The short-term stability of the magnetic field is about one part in ten thousand. The magnet current is monitored with a L and N type-K potentiometer connected across a resistor in series with the magnet coils. Recently we have used an improved current stabilizer of the type described by Lawson and Tyler[9] as modified by Wadey.

In operation the microwave oscillator is tuned to the

[4a] H. Margenau and A. Henry, Phys. Rev. **78**, 587 (1950).

[5] R. V. Pound, Rev. Sci. Inst. **17**, 490 (1946).
[6] Similar to the Sperry No. 921 barretter.
[7] J. M. Sturtevant, Rev. Sci. Inst. **18**, 124 (1947).
[8] Similar to that of R. H. Dicke, Rev. Sci. Inst. **17**, 268 (1946).
[9] J. L. Lawson and A. W. Tyler, Rev. Sci. Inst. **10**, 304 (1939); W. G. Wadey, Thesis, University of Michigan (1948).

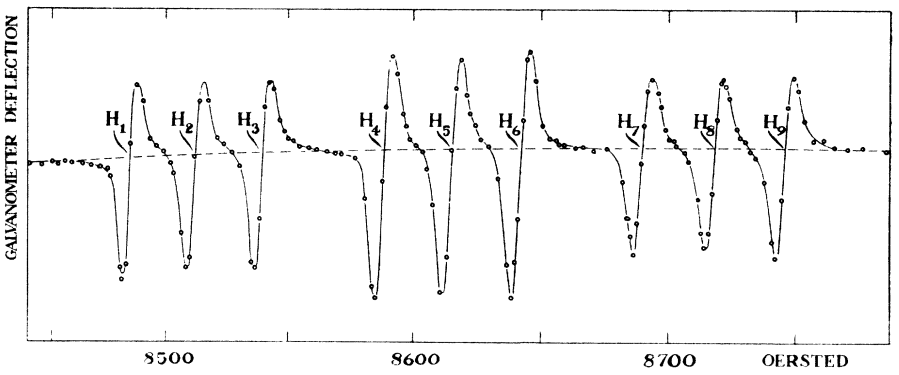

FIG. 3. Observed spectrum of $N^{14}O^{16}$ at a pressure of 1.0 mm Hg. The modulation amplitude is 3.2 oersted peak-to-peak.

cavity resonance where some four milliwatts of microwave power is transmitted to the bolometer. The d.c. magnetic field is then raised to the region of a magnetic absorption line. Modulation of the d.c. magnetic field produces amplitude modulation of the microwave power which modulates the bolometer resistance; hence a 30 cycle/sec. signal appears at the input of the amplifier. As the d.c. magnetic field is increased the galvanometer deflection traces essentially the derivative of the absorption line; phase is preserved by the lock-in mixer.

3. SENSITIVITY

The apparatus described has a high signal-to-noise ratio resulting from the mode of operation of the bolometer and the narrow noise-band width of the amplifying system. Because of the relatively high values of the signal power, it does not suffer from the usual low sensitivity of single-detection receivers.[10] For most microwave spectra these high power levels would not be permissible because of energy saturation of the absorption, and a bolometer system would be quite insensitive. However, the weak magnetic absorption lines require large energy densities for saturation. In contrast to crystal detectors, bolometers do not produce low frequency noise in great excess of thermal noise. In the present system flicker noise in the amplifier is the principal noise contribution.

The resistance-power law for bolometers is given by[11]

$$R-R_0=K(P+i^2R)^n$$

where R is the operating resistance, R_0 the cold resistance, K a constant, P the microwave power, i the bolometer current, and n a constant (<1) describing the deviations from square-law response. A simple analysis shows that for a fixed total power, the sensitivity (idR/dP) of a bolometer in a constant-current circuit is a maximum for equal d.c. and microwave power. For the bolometer used this optimum sensitivity is 46 volt/watt at the bolometer terminals for a total power of 9 milliwatts.

The microwave power absorbed by the bolometer can be written as

$$P+P2(Q_L/Q_A)S\cos\omega_m t$$

where Q_L is the loaded Q of the cavity, Q_A the Q of the absorption line, $\omega_m/2\pi$ the modulation frequency and S a constant depending on the field configuration in the cavity and the value of the magnetic field modulation. In the present case S attains a maximum value of 0.5. Q_A may also be expressed as

$$Q_A=1/(4\pi\chi'')$$

where χ'' is the imaginary part of the magnetic susceptibility describing the absorption. The r.m.s. signal voltage at the bolometer terminals is

$$\epsilon_s=9.0\times10^3\chi''=720/Q_A \text{ volts.}$$

for the present system. The observed r.m.s. noise voltage at the same terminals is 2×10^{-8} volt. Thus for a signal-to-noise ratio of unity χ'' is 3×10^{-12} and Q_A is 3×10^{10}.

4. EXPERIMENTAL RESULTS

The nitric oxide was produced by the slow reaction of metallic copper with dilute nitric acid. The reaction was carried out at 0°C. The gaseous products were purified of nitrogen and the other oxides of nitrogen by fractional distillation at liquid nitrogen temperatures. The resulting NO is believed to be quite pure.

Several runs at different values of NO pressure and modulation amplitude were taken. All showed the characteristic nine-line spectrum shown in Fig. 3.

TABLE I. Values of resonance field in oersted for the nine absorption lines in NO. Observing frequency is 9360 megacycle/sec. The absolute errors in the field values may be as much as 1 oersted.

$H_1=8481.5$	$H_5=8614.2$
$H_2=8508.2$	$H_6=8641.2$
$H_3=8536.8$	$H_7=8689.4$
$H_4=8586.8$	$H_8=8717.5$
	$H_9=8744.4$

[10] The well-known superiority of a superhetrodyne receiver over a single-detection receiver for small signal detection is not carried over to the detection of small modulations of a large signal, since in the latter case the square-law response of the single-detection receiver is no longer operative. The modulation sidebands beat with the strong signal carrier giving a first-order demodulation signal.

[11] Radiation Laboratory Series (McGraw-Hill Book Company, Inc., New York, 1947), Vol. 11, p. 161.

The line locations are described by the numbers giving the field at the center of each line. Table I collects the average values of these data. The arabic indices correspond to those of Figs. 1 and 3.

The magnetic field intensity was measured at the position of the cavity in terms of the magnetic-resonance field of the proton moment. A regenerative detector, whose grid coil contained distilled water, and an audio amplifier were used to display the proton resonance on an oscilloscope.[12] A U. S. Signal Corps BC221 frequency meter was coupled loosely to the regenerative detector and the regeneration frequency located by zero-beat on the oscilloscope. The frequency meter was in turn calibrated against the standard frequency broadcasts of WWV. The conversion formula[13] $H=2.3487\times10^{-4}f$ served to convert the frequency values to field intensities. The principal error in the magnetic field values arises from geometrical uncertainties. The random errors are less than this and result from current fluctuations in the magnet which set a limit of perhaps 0.2 oersted.

The microwave frequency was monitored with a M.I.T. Radiation Laboratory TSX-4SE spectrum analyzer and measured with a TFX-19GA cavity wave meter. The absolute value of the microwave frequency is subject to an unknown calibration uncertainty but is believed to be accurate to 2 megacycle/sec. The cavity was calibrated against a standing wave machine to a precision of 6 megacycle/sec. Unfortunately no crystal-controlled microwave frequency standard was available at the time of the experiments.

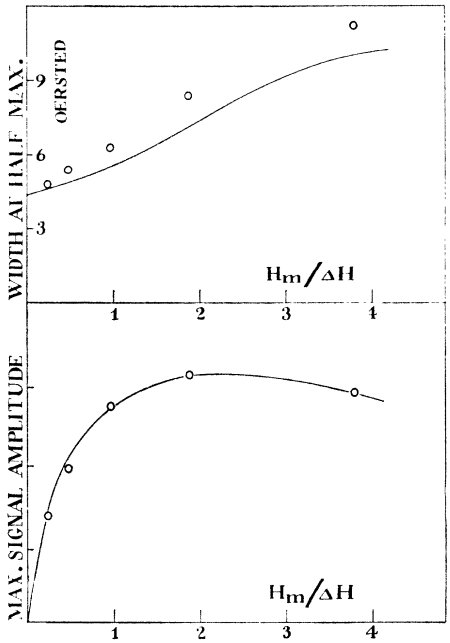

FIG. 4. Variation of line width and amplitude of magnetic resonance lines of NO with modulation amplitude. The pressure is 0.85 mm Hg and the temperature 298°K. $2H_m$ is the peak-to-peak modulation amplitude and ΔH the Van Vleck line half-width. Solid lines are drawn for pure pressure broadening with $\Delta H=3.5$ oersted. The deviations in the upper curve arise from broadening due to magnetic field inhomogeneity.

[12] Similar to that of N. J. Hopkins, Rev. Sci. Inst. **20**, 401 (1949).
[13] Thomas, Driscoll, and Hipple, Phys. Rev. **75**, 902 (1949).

5. LINE WIDTHS

Because of distortions introduced by the large magnetic field modulation, which is required for optimum sensitivity, the output galvanometer deflections do not trace the derivative curve of an absorption line. Actually, one observes the fundamental-frequency Fourier amplitude of the modulated absorption-function of the line.

If one assumes that pressure broadening is the only source of line broadening, then at the low pressures used the Lorentz or Van Vleck-Weisskopf line shape[14] should be correct, and one can write the imaginary part of the magnetic susceptibility (normalized to unity and expressed in terms of field strengths rather than frequencies) as

$$\frac{\Delta H}{(H-H_0)^2+\Delta H^2},$$

where H is the applied d.c. and modulation field and H_0 its value at resonance. Thus

$$H=H_0+H_1-H_m\cos\omega t,$$

where $2H_m$ is the peak-to-peak modulation amplitude and $\omega/2\pi$ the modulation frequency. The coefficient of the signal voltage at the modulation frequency is proportional to

$$\frac{1}{\pi}\int_{-\pi}^{\pi}\frac{\cos\omega t d(\omega t)}{[H_1/\Delta H+H_m/\Delta H-H_m/\Delta H(1+\cos\omega t)]^2+1}.$$

This integral is evaluated[15] for various values of $H_1/\Delta H$ and $H_m/\Delta H$. It is found that the maximum value of the signal voltage occurs for $H_m=2\Delta H$. For higher modulation amplitudes the signal amplitude decreases slowly and the lines are broadened. For smaller modulations the signal amplitude decreases rapidly and assumes the shape of the derivative curve.

The line half-width ΔH may be obtained by plotting certain parameters of the theoretical signal amplitude curves *vs.* the modulation amplitude. Figure 4 shows two such curves drawn for $\Delta H=3.5$ oersted at the pressure 0.85 mm Hg and temperature 298°K. From various line contour measurements it appears that the line shapes cannot be fitted in exact detail by the above procedure. Some other source of broadening is present, probably arising from magnetic field inhomogeneities. This might reduce ΔH by as much as 1.0 oersted. The line width appears to be proportional to pressure in the

[14] J. H. Van Vleck and V. F. Weisskopf, Rev. Mod. Phys. **17**, 227 (1945).
[15] Similar integrals appear in a paper by W. D. Hershberger, J. App. Phys. **19**, 411 (1948).

TABLE II. Formulas for the resonance field values for the nine absorption lines.

$M_J \rightarrow M_J-1$	M_I	Resonance field
$\frac{3}{2}\rightarrow\frac{1}{2}$	1	$H_1 = H_I - H_D + (2/10)H_Q$
	0	$H_2 = H_I - (4/10)H_Q$
	-1	$H_3 = H_I + H_D + (2/10)H_Q$
$\frac{1}{2}\rightarrow-\frac{1}{2}$	1	$H_4 = H_{II} - H_D$
	0	$H_5 = H_{II}$
	-1	$H_6 = H_{II} + H_D$
$-\frac{1}{2}\rightarrow-\frac{3}{2}$	1	$H_7 = H_{III} - H_D - (2/10)H_Q$
	0	$H_8 = H_{III} + (4/10)H_Q$
	-1	$H_9 = H_{III} + H_D - (2/10)H_Q$

range around 1 mm Hg. This proportionality has not been checked at higher pressures because of overlapping of the lines. Assuming that the line width is proportional to pressure it becomes 0.11 cm^{-1} at 76 cm Hg and 25°C.

6. LINE INTENSITIES

The intensities of the transitions, $\Delta M_J = \pm 1$, observed can be calculated from radiation theory using the matrix elements derived in the accompanying paper of Margenau and Henry. We will follow a scheme similar to that used by Bloembergen, Purcell, and Pound[16] in their calculation of the intensity in nuclear magnetic-resonance absorption.

Consider a system of N nitric-oxide molecules per cm^3 characterized by quantum numbers M_J; the hyperfine splitting will be neglected at this stage of the calculation. The molecules are in a d.c. and modulation field along z represented by H and a microwave field of frequency $\omega/2\pi$ given by

$$H_x = 2H_1 \cos\omega t,$$

which, near resonance, can be replaced[17] by a rotating field

$$H_x = H_1 \cos\omega t \quad H_y = H_1 \sin\omega t.$$

The probability per sec. of a transition $M_J \rightarrow M_J - 1$ for a single molecule is given by radiation theory as

$$W_{M_J \rightarrow M_J-1} = (8\pi^3/3h^2)\,|\,(M_J|\mathfrak{M}|M_J-1)\,|^2 \rho_\nu$$

where $\rho_\nu d\nu$ is the isotropic energy density and $\mathfrak{M}$ the magnetic moment operator producing the transition.

In this case the local energy density is replaced by

$$\rho_\nu = (3H_1^2/4\pi) g(\nu),$$

where $g(\nu)$ is a shape factor of the line normalized so that

$$\int_0^\infty g(\nu)\,d\nu = 1.$$

In contrast to optical absorption, the observing frequency is sharp and the dispersion in final states arises from the breadth of the line.

[16] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).
[17] F. Bloch and A. Siegert, Phys. Rev. **57**, 522 (1940).

TABLE III. Comparison of theoretical and experimental resonance field values in the absence of hyperfine splitting.

	H_{II}	$H_{II}-H_I$	$H_{III}-H_{II}$
Theory	8619.5	105.5	103.1
Meas.	8614.1	105.3	103.0

In the Margenau and Henry paper the square of the matrix elements for the transition is shown to be (see Eq. (15) of that paper).

$$0.386(\tfrac{3}{2}+M_J)(\tfrac{5}{2}-M_J)\mu_0^2$$

for the $J=\frac{3}{2}$ states.

For a Lorentz line shape

$$g(\nu) = \frac{1}{\pi}\,\frac{\Delta\nu}{(\nu_0-\nu)^2+\Delta\nu^2}$$

so that, at resonance

$$W_{M_J \rightarrow M_J-1} = 0.772\pi \frac{H_1^2\mu_0^2}{\Delta\nu h^2}(\tfrac{3}{2}+M_J)(\tfrac{5}{2}-M_J).$$

This probability, when multiplied by $h\nu$ and by the excess of upward over downward transitions per sec., gives the absorbed power per cm^3.

The population in the $J=\frac{3}{2}$ level of the $^2\Pi_{3/2}$ state is computed using the case (a) energy function[4]

$$B[J(J+1)-\Omega^2] \pm A\Lambda\Sigma.$$

We define f to be the fractional number of molecules in the J level of the $^2\Pi_{3/2}$ state. At room temperatures

$$f \cong \frac{(2J+1)\exp\{-BJ(J+1)hc/kT\} \times \exp\{-(A+2B)hc/kT\}}{(kT/hcB)[1+\exp\{-(A+2B)hc/kT\}]}.$$

With $J=\frac{3}{2}$, $T=293$°K, $B=1.70$ cm^{-1}, $A=120$ cm^{-1} we find that $f=0.011$.

In the $J=\frac{3}{2}$ state there are four M_J levels. The difference in population of two adjacent M_J levels is

$$fN h\nu/4kT$$

and the energy absorbed per cm^3 per sec. in the gas is

$$\frac{fN(h\nu)^2}{4kT} W_{M_J \rightarrow M_J-1}$$

for one M_J transition.

The absorption Q of the transition is defined by

$$Q_A = 2\pi\nu \frac{\text{energy stored per cm}^3}{\text{energy absorbed per cm}^3 \text{ per sec.}}.$$

Evidently the energy stored per cm³ is

$$(1/8\pi)(2H_1)^2.$$

Thus at resonance for a M_J transition

$$\frac{1}{Q_A}=\frac{0.606fN\mu_0^2\nu}{kT\Delta\nu}(\tfrac{3}{2}+M_J)(\tfrac{5}{2}-M_J).$$

Because of the hyperfine structure an individual absorption line has a Q three times as large as this.

For a pressure of 0.85 mm Hg and a temperature 298°K, $\nu/\Delta\nu=8620/3.5$, $N=0.30\times10^{17}$, and $f=0.011$. For one of the individual lines of the central triplet ($M_J=\frac{1}{2}\rightarrow M_J=-\frac{1}{2}$) the calculated absorption Q is

$$Q_A=7.0\times10^8.$$

The observed r.m.s. signal referred to the bolometer for one of these lines at optimum modulation is 1.1×10^{-6} volt. This corresponds to a measured Q_A of 6.5×10^8 which agrees with the calculated value to much less than the experimental uncertainty.

The relative intensities are observed as dictated by the term $(\frac{3}{2}+M_J)(\frac{5}{2}-M_J)$ which predicts relative intensities of 3:4:3 for the M_J transitions $\frac{3}{2}\rightarrow\frac{1}{2}$, $\frac{1}{2}\rightarrow-\frac{1}{2}$, $-\frac{1}{2}\rightarrow-\frac{3}{2}$, respectively. The observed intensity ratios are 1.33 ± 0.02.

7. ANALYSIS

The line positions are determined by three splitting energies: (a) the molecular energies neglecting nuclear spin (stage *b* of Fig. 1), (b) the magnetic IJ coupling (stage *c* of Fig. 1), (c) the nuclear electric quadrupole IJ coupling (stage *d* of Fig. 1). Expressions for the molecular energies are given in the paper of Margenau and Henry and are not repeated here. The magnetic IJ energy can be written as

$$AM_IM_J.$$

The electric quadrupole energy[18] for $J=\frac{3}{2}$, $I=1$ is

$$\tfrac{1}{60}eQq[15/4-3M_J^2][2-3M_I^2]$$

Taking account of the three energies, the resonance fields for the nine lines are as given in Table II. H_I, H_{II}, and H_{III} are given by the molecular energies in the absence of nuclear spin and

$$H_Q=-\tfrac{1}{2}eQq(H_{11}/h\nu_0)$$
$$H_D=A(H_{II}/h\nu_0),$$

where ν_0 is the frequency of observation.

The average values of H_D and H_Q are obtained by taking differences of the nine equations. The results are

$$H_Q=0.78\pm0.2 \text{ oersted}$$
$$H_D=27.4\pm0.3 \text{ oersted}.$$

Converting these numbers to "coupling constants" expressed in megacycle/sec., as is the usual practice, the magnetic IJ coupling constant A is 1.98×10^{-19} erg or 29.8 ± 0.3 megacycle/sec. and the nuclear electric "quadrupole coupling" is -1.7 ± 0.5 megacycle/sec. The assignment of a negative quadrupole coupling[19] is unambiguous from the experiment.

The average values of H_{II}, $H_{II}-H_I$, and $H_{III}-H_{II}$ are given in Table III and compared with the theory of Margenau and Henry.

The agreement between the theoretical field values of Margenau and Henry and the experiments is quite good. The general features of the interpretation are supported by this agreement and also by the relative intensities of the nine absorption lines. Recently we have observed the corresponding spectrum $N^{15}O$, which further verifies the interpretation. A six-line spectrum is observed with pairs of lines centered at field values slightly lower than H_I, H_{II} and H_{III}; the pairs arising from magnetic IJ coupling with the N^{15} nucleus ($I=\frac{1}{2}$). The details of this spectrum will be published elsewhere.

[18] See Eq. (14) of reference 4a.
[19] The notation is that of B. T. Feld, Phys. Rev. **72**, 1116 (1947).