ELECTRON PARAMAGNETIC RESONANCE OF NITROGEN AFTERGLOW CONDENSED AT 4.2°K

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TABLE OF CONTENTS.

ABSTRACT

The electron paramagnetic resonance (EPR) spectrum of nitrogen afterglow condensed on the walls of a microwave cavity at $4.2^{\circ}K$ indicates the presence of considerable quantities of ground state nitrogen atoms. The hyperfine coupling constant for the ^4S state is estimated at $A\hbar^2/h = 11.2$ Mc/sec. Frozen dissociation products of ammonia produced the same nitrogen resonance line and, in addition, the resonance spectrum for atomic hydrogen.

I. INTRODUCTION.

A. Historical Summary

Active Nitrogen Gas

When nitrogen gas at a few hundred microns pressure is conducted through a region of electric discharge, a modification is produced known as active nitrogen. Its prominent feature is a yellowish glow which persists up to several hours. Initial investigation, quite naturally, was of a spectroscopic nature. Lewis (1), using a low dispersion instrument, obtained spectra containing the most prominent features of active nitrogen in 1904. It remained for John Strutt, Lord Rayleigh, to demonstrate the extreme chemical activity of the products of the discharge. In a series of definitive experiments, Rayleigh (2) discovered a number of unusual properties of active nitrogen. Intensive investigation and analysis followed these discoveries. What emerged from the results is a fairly complete and consistent description of room temperature nitrogen afterglow which can be summarized as follows:

1. Nitrogen molecules in a variety of excited states exist in the afterglow. Their presence is revealed by characteristic emission bands (3). The yellow glow itself is due to transitions from excited vibrational states of the $^3\Pi$ level to an intermediate metastable level, $^3\Sigma$.

2. Although there is no optical spectroscopic evidence for atomic nitrogen in the gaseous afterglow, the spectrum for ground state N is found from paramagnetic resonance (4). Diffusion experiments (5) indicate considerable quantities of particles lighter than molecular nitrogen, and specifically Mass 14 has been observed in mass spectroscopy (6).

3. The glowing material reacts violently with a number of non-metals, including phosphorus (to form red phosphorus), sulfur, and iodine; in the process it becomes absorbed and the yellow glow is extinguished. An interesting feature is that the reaction with phosphorus proceeds most rapidly after the yellow glow has diminished in intensity. It has no effect on cool metal but an intense flame spectrum is obtained when the glow is passed over metals heated to only 250°C. Similarly, the flame spectra of many compounds are developed when they are vaporized in active nitrogen. In many cases these substances are too unstable to be seen at the temperature of a Bunsen flame. Unsuccessful attempts to condense the glow at liquid air temperature indicate the absence of complex molecules. The chemical activity cannot be ascribed to ions as their removal by electric fields does not alter any of the above properties.

It is of interest to note that originally controversy centered on whether the activity of the afterglow was due to nitrogen itself or to impurities. Very pure nitrogen seemed to give little afterglow, whereas the addition of small amounts of oxygen stimulated the glow considerably. However, it was later discovered that traces of numerous

foreign gases added to nitrogen aided the glow. Since these foreign gases by themselves fail to exhibit the properties of the nitrogen afterglow, it is concluded that impurities are catalytic for a good yield of active nitrogen in the discharge but that they play no role in the properties of the afterglow.

Excited Solid Nitrogen

In 1924, Vegard (7), in an attempt to reproduce the 5577Å green line found in the Auroral spectrum, bombarded solid nitrogen with cathode rays. A layer of luminescent solid nitrogen was thus formed. The same green glow persisted over five minutes after the cathode rays were cut off. A set of three emission spectra was found. The strong yellow-green line of the Aurora appeared in a group of diffuse lines, while a conspicuous line emitted during intense Aurora display was included in a group of sharp blue-green lines clustered about 5230Å. Also, in both cases the spectra were dominated by negative band heads from 4708Å to 3914Å. The slow fading away of the light after an Aurora display corresponded to phenomena observed in solid nitrogen.

Broida and Pellam (8) in 1954 observed the spectrum of nitrogen which they had excited by a microwave electrodeless discharge and then condensed on the walls of a dewar maintained at 4.2°K. The improved technique in the preparation and deposition of the discharge products of nitrogen greatly enhanced the spectrum as obtained by Vegard. Subsequent analysis of the spectrum by Broida and Herzfeld (9), and Broida and Bass (10) produced compelling evidence of the existence of metastable molecules and of considerable quantities of atoms in both the

ground and first excited states. The sharp blue-green lines (α lines; $\frac{1}{2}$ life, 15 sec) are caused by transitions between the first excited state (^2D) and the ground state (^4S) of the atom. These consist of five lines spaced by 20/cm; their center of gravity is shifted 104/cm from the single line observed in the free atom. This ^2D to ^4S transition is highly forbidden in the free atom, which explains its absence in the gaseous glow. The large crystal fields which produce splitting in the solid can stimulate transitions so that the atoms are de-excited by radiation to the ground state rather than by recombination to excited molecular states. The diffuse yellow-green lines (β lines; $\frac{1}{2}$ life, .1 sec) are observable only while active products are being deposited. They are produced by transitions among atomic states with n = 3, 4 and 5. The remaining spectroscopic feature of the condensed glow is the A bands, the first positive bands of molecular nitrogen. These persist faintly for several minutes at 4.2°K, although a blue glow can be restored after periods greater than an hour by heating. Inasmuch as excited states in atoms and molecules have lifetimes much shorter than this, the excited molecular states must arise from recombination of ground state atoms. This then is indirect evidence of the presence of considerable concentration of ground state atoms in the discharge products for appreciable lengths of time.

B. Purpose of Present Investigation

A definitive test for the existence of long-lived atomic species in condensed nitrogen afterglow would clearly be extremely useful in understanding its unusual and spectacular properties. Since the ground

state of atomic nitrogen (^4S) has a net spin, it should exhibit paramagnetic resonance in the vicinity of the resonance expected for a free S electron. Accordingly, we proposed to condense dissociated nitrogen in a microwave cavity and investigate its resonance properties. If the presence of atomic nitrogen were thus revealed through its ground state, it was proposed to search for the EPR spectra of the excited ^2D and ^2P states and also to discover the temperature and time stability of the observable atomic species.

II. EXPERIMENTAL DESIGN.

The experimental problem is essentially this: to produce excitation of molecular gas by electric discharge, to condense the products rapidly before recombination can occur, to introduce the solid sample into a favorable field region of a microwave cavity, and to observe absorption of r-f power by the sample as a function of magnetic field. The sample must be maintained below its condensation temperature while its spectrum is taken.

A Raytheon diathermy (Microtherm) unit operating at 2450 Mc/sec provides the excitation energy to the gas (see figures 1 and 2 for the dissociation apparatus). The diffusing head supplied with the machine for medical purposes is replaced by a tapered resonant cavity with a transverse slot provided for the glass tube which conducts the gas through the dissociating electric fields within the cavity. The gas flows from a tank of commercial compressed gas through a valve system and into the discharge region. A floor pump is used to draw a continuous stream of fresh nitrogen through the discharge and to maintain the pressure of the gas at a few hundred microns. Preliminary investigation showed that the yellow material formed in the discharge (active nitrogen) can be conveyed through glass tubing of greater than a few millimeter bore for distances more than a meter. Smaller bores or the use of metal tubing extinguished the glow in shorter distances.

The method employed in this investigation for collecting a condensed sample in a cavity represents a considerable advance over that previously developed by Jen and co-workers (11). They condensed active

hydrogen on a sapphire rod placed in a stream of yellow glowing gas. The rod was maintained at 4.2°K by contact with a reservoir of liquid helium. The coated rod was then inserted into a cavity. The disadvantages of this approach are the difficulty of manipulating the sample under liquid helium and the necessity of placing the sample in the volume of the cavity rather than on the walls where dielectric losses are zero and magnetic fields strongest.

Our method consists of conducting the glow directly into the sample cavity where it is deposited on the walls at 4.2°K (fig. 1). A length of waveguide (fig. 4-A) enters the cap of a liquid helium dewar (fig. 4-B) and extends down into the constricted portion of the dewar between the pole faces of a magnet. It is terminated by a reflection cavity. The gas is conducted from the discharge through a 9 mm I.D. glass tube entering the length of waveguide a few inches above the dewar cap and traversing within to the cavity. The gas emerges at the bottom of the waveguide through the 4 mm diameter cavity coupling hole or iris, whence it condenses instantly onto the cavity walls. A teflon gasket at the upper end of the section of waveguide permits evacuation of the cavity when a vacuum is drawn on the glass tube. A double dewar system, the outer dewar (fig. 4-C) filled with liquid nitrogen and the inner filled with liquid helium, surrounds the system. Rising vapors from the helium absorb the greatest part of the heat conducted down the waveguide. The loss of helium is less than 200 cc/hour.

A d-c magnetic field plus a radio frequency magnetic field are required for paramagnetic resonance. We employ an Arthur D. Little

electromagnet (fig. 5) powered with three storage batteries in series. Sufficient field homogeneity is obtained through the use of 11" Armco iron pole faces with a gap of $2\frac{1}{4}$". A proton resonance field controller provides time stability plus a means for varying and measuring the field by varying and measuring the proton resonance frequency. See Appendix 1 for details of field calibration. Two 11" coils (fig. 5-D and 5-E) are wound to adapt the ADL magnet to magnetic resonance. One, of 608 turns, provides 400 cps modulation necessary for phase sensitive detection of both the electron and proton signal. The field correction current was fed into a 2000 turn coil.

Consideration of a good signal-to-noise ratio leads to the selection of an r-f field at 9500 Mc/sec; i.e., the 3 cm or X microwave band. (See figure 4 for the microwave system.) A TS 13/AP surplus test set at full output gives 25 milliwatts of microwave power at from 8500 to 9700 Mc/sec. A unidirectional coupler feeds power from the generator through a wavemeter (fig. 2-W) and a tuning stub section to the E arm of a Magic Tee microwave bridge (fig. 2-T) whence the energy divides into two symmetrical H arms of the Tee. Terminating one arm is the sample cavity as described above; a precision attenuator and phase shifter in the other serve to balance the bridge. Any unbalance of power reflected from the H arms is detected by a crystal diode in the fourth arm of the Tee.

The d-c magnetic field is modulated sinusoidally at 400 cps by 1 to 4 x 10^{-4} w/m^2 peak to peak. As the field traverses the resonance region, the crystal diode detects a signal whose component at 400 cps

has an amplitude proportional to the derivative of the resonance line. The signal plus noise is amplified before being fed into a phase sensitive detector which filters out all but the 400 cps components. An absorption spectrum is traced by a Brown chart recorder activated by the rectified output of the detector. An automatic frequency controller serves to lock the klystron to the sample cavity resonant frequency and, incidentally, suppresses the dispersion component of the paramagnetic resonance.

The Varian EPR spectrometer (V-4500)* is a commercially available unit whose operation is sufficiently similar to ours that reference is to be made to it for specifications and circuit diagrams.

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* Available from Varian Associates, 611 Hansen Way, Palo Alto, Calif.

III. EXPERIMENTAL PROCEDURE.

In the experiments described for nitrogen and ammonia, the following procedure is followed:

1) Evacuate inner dewar, test for leaks, and fill with helium gas to 1 atm. Evacuate dissociation apparatus including tube to sample cavity.
2) Fill outer dewar with liquid nitrogen. Precooling takes at least one and one-half hours.
3) During precooling insure that the spectrometer is functioning. Greater stability is obtained by giving the electronics time to reach thermal equilibrium.
4) Transfer liquid helium into inner dewar.
5) Obtain the cavity resonance by varying the frequency of the klystron. This condition is most easily observed by modulating the repeller voltage of the klystron with the linear sweep from an oscilloscope and watching the output of the diode in arm four of the Magic Tee on the oscilloscope.
6) Isolate the sample cavity from the dissociation circuit.
7) With the diathermy power at about 50 watts (half power), adjust the flow and pressure of nitrogen gas until a spark coil triggers a continuous discharge. Adjust pressure further until a strong yellow afterglow appears in the gas issuing from the dissociation region. (Ammonia gives no afterglow; adjust for a bright discharge.) Now open valve leading to cavity and condense discharge products for two to five minutes. It is

well to observe the cavity resonance during this time to prevent lowering its Q too greatly. Finally, isolate the cavity and stop discharge.

8) Observe cavity resonance on scope and adjust attenuator and phase shifter on Tee until the resonance curve is completely suppressed. Then unbalance attenuator slightly to allow diode to operate in more linear region of its characteristics. Measure frequency of klystron with wavemeter and switch klystron to automatic frequency control.

9) Sweep magnetic field through region where resonance is expected from knowledge of magnetogyric ratio of paramagnetic species. This is .34 w/m^2 for an S state. The Brown recorder side marking pen is used to record the proton resonance frequency for field calibration.

IV. RESULTS.

A. Nitrogen

Using condensed nitrogen afterglow as a sample, we observed the paramagnetic resonance spectrum illustrated in figure 7. Several such spectra were obtained, all showing the same features: three distinct lines whose center values are marked A, B, C, plus two weak satellites at points 1 and 2. The spectroscopic splitting factor, $g_,$, for the central line is 2.0013 ± 0.0005 while for free spin resonance $g_s = 2.0023$ (12). The splittings from the center line of the triplet are each 0.0004 weber/meter^2 and of the satellites, 0.0014 and 0.0016 w/m^2 for 1 and 2 respectively. A long lived species is indicated inasmuch as the resonance signal did not diminish noticeably in intensity in spectra taken several hours apart.

The spectrum obtained is the one expected from ground state atomic nitrogen (see Appendix 2). The observed splittings for the triplet yield a value for the hyperfine coupling constant, A, of $A\hbar^2/h$ = 11.2 Mc/sec. This compares closely with 10.45 Mc/sec found by Heald and Beringer (4) in the EPR of nitrogen afterglow at room temperature. A can be calculated for a given configuration, and for a pure $1s^2, 2s^2, 2p^3, {}^4S_{3/2}$ state (very nearly the ground state of a nitrogen atom), the result is zero (13). A treatment involving configuration interaction would be necessary to confirm the experimental A.

The significant difference between these results for condensed afterglow and the data of Heald and Beringer on the EPR spectrum of

room temperature afterglow consists in linewidths of the members of the triplet. They report a linewidth of 0.00009 w/m^2 in the gas, whereas we observe almost 0.0004 w/m^2 in the solid. On the assumption that this broadening was due to dipole-dipole interaction between atoms in the solid, we expected that dilution of the afterglow with inert gas would decrease the linewidths. Precisely the opposite result was obtained from a 10/1, argon/nitrogen mixture which was dissociated and condensed at 4.2°K. The spectrum is shown in figure 8 and it is seen that, although the splitting is unchanged, the lines are about twice as wide as for pure nitrogen. The explanation may well be that the N atoms act as lattice defects in a closely packed molecular matrix. Argon may form a smaller crystal structure than N_2 with a greater overlap of molecular and atomic electron wavefunctions.

Experiments are in progress to obtain additional information on the stability of the frozen active nitrogen. The equipment is being modified to permit operation at temperatures above 4.2°K.

No explanation is offered for the satellites 1 and 2 except that impurities are suspected since the intensity varies from one run to another.

B. Ammonia

The discharge products of ammonia were produced and condensed by the same method used for nitrogen. Figure 9 shows the EPR spectrum obtained for NH_3. The components of a doublet lie 0.02729 weber/meter^2 below and 0.02355 w/m^2 above the position where a free S electron resonance would appear. In frequency units the separation of the

doublet is 1433 Mc/sec. A triplet spanning 0.0008 w/m^2 with its center line satisfying the free electron resonance condition appears between the doublet.

There are two main facts that serve to identify the doublet: 1. The hyperfine splitting of the ground state of hydrogen amounts to 1420 Mc/sec. 2. Jen et al (11) have observed a similar EPR signal from pure hydrogen under the same experimental conditions and have identified the source as atomic hydrogen (see Appendix 2 for analysis of EPR data on solid hydrogen).

Likewise, the triplet is identical to the spectrum reported in the previous section for pure nitrogen. Accordingly, it must be concluded that both atomic nitrogen and atomic hydrogen are present in the frozen dissociation products of ammonia.

V. SPECULATIVE COMMENTS.

A. Nitrogen

If the explanation of the α lines in the condensed afterglow is correct, one should expect to find measureable quantities of ^2D atoms persisting for 15 seconds after the discharge has ceased. The fact that Heald and Beringer (4) were unsuccessful in their attempt to find the EPR of the ^2D state does not necessarily mean that its magnetic resonance is actually unobservable, either because of extreme line broadening or large zero field splitting, particularly since both of these effects are usually of small magnitude in a gas. More likely, the number of ^2D atoms available in a cavity full of gaseous afterglow is simply too small to produce a detectable signal. On the other hand, it may be possible to collect a sufficient number of ^2D atoms in a condensed afterglow, but in this case there is evidence for considerable zero field splitting, namely the 20/cm splitting of the ^2D - ^4S optical transitions. Thus, even in fields of 1 weber/meter^2 complete quenching of the orbital angular momentum occurs. The resulting paramagnetic resonance should differ from a pure spin resonance only to the extent determined by spin-orbit interaction and would thus serve to establish the spin-orbit interaction energy for the ^2D levels. This is an experiment worth trying.

B. Ammonia

In addition to N and H, there are other possible dissociation products from NH_3: NH, NH_2, N_2H_4. The configuration of NH is known ($^3\Sigma$ ground state) and a spin resonance should be expected. None, however, is observed. If an accurate ratio of N atoms to H atoms, N_N/N_H, in the discharge products were known, the presence of other species could be inferred. For example, if $N_N/N_H = 1/3$, it could be reasonably inferred that the dissociation process was exclusively $NH_3 \rightarrow N + 3H$, particularly since recombination into molecules is evidently slow for these species. N_N/N_H can be determined to the accuracy with which the relative integrated EPR absorption signals, A_N/A_H, are known. If the magnetogyric ratio, γ, and the spin angular momentum, $J\hbar$, are known for each, the ratio of nitrogen to hydrogen is $A_N\gamma_H^2 J_H(J_H + 1) / A_H\gamma_N^2 J_N(J_N + 1)$. Zero drift and noise in the EPR detector makes an estimate from our data of

$$N_N/N_H \cong 1$$

uncertain within a 300% error. With care, much greater accuracy could be obtained. The experiment will be performed again with more adequate equipment.

VI. CONCLUSIONS.

In conclusion, the results to be drawn from this research include:

1) Atomic nitrogen can be collected within a solid matrix of molecular nitrogen by freezing out the products of a nitrogen discharge at liquid helium temperature.
2) This atomic species may be detected by EPR methods. It is identified with a high degree of reliability from the character of the absorption spectrum.
3) Permanance of the observed atomic nitrogen signal suggests a high degree of stability, at least in the concentrations obtained. Thus far no observable decrease in the signal has been observed over periods of several hours.
4) Similar experiments with ammonia in place of nitrogen have shown the presence of both atomic nitrogen and atomic hydrogen. (The spectrum of the latter is known from other EPR work.) No direct evidence for other dissociation products is apparent.

Two additional experiments are suggested. Stability of condensed nitrogen atoms should be investigated at temperatures between 4.2°K and the condensation point. In addition to indicating at what temperature recombination takes place, valuable information on the crystal structure may be obtained from line-width measurement. Another interesting possibility is to attempt to find the low field resonance of the quenched ^2D levels of atomic nitrogen.

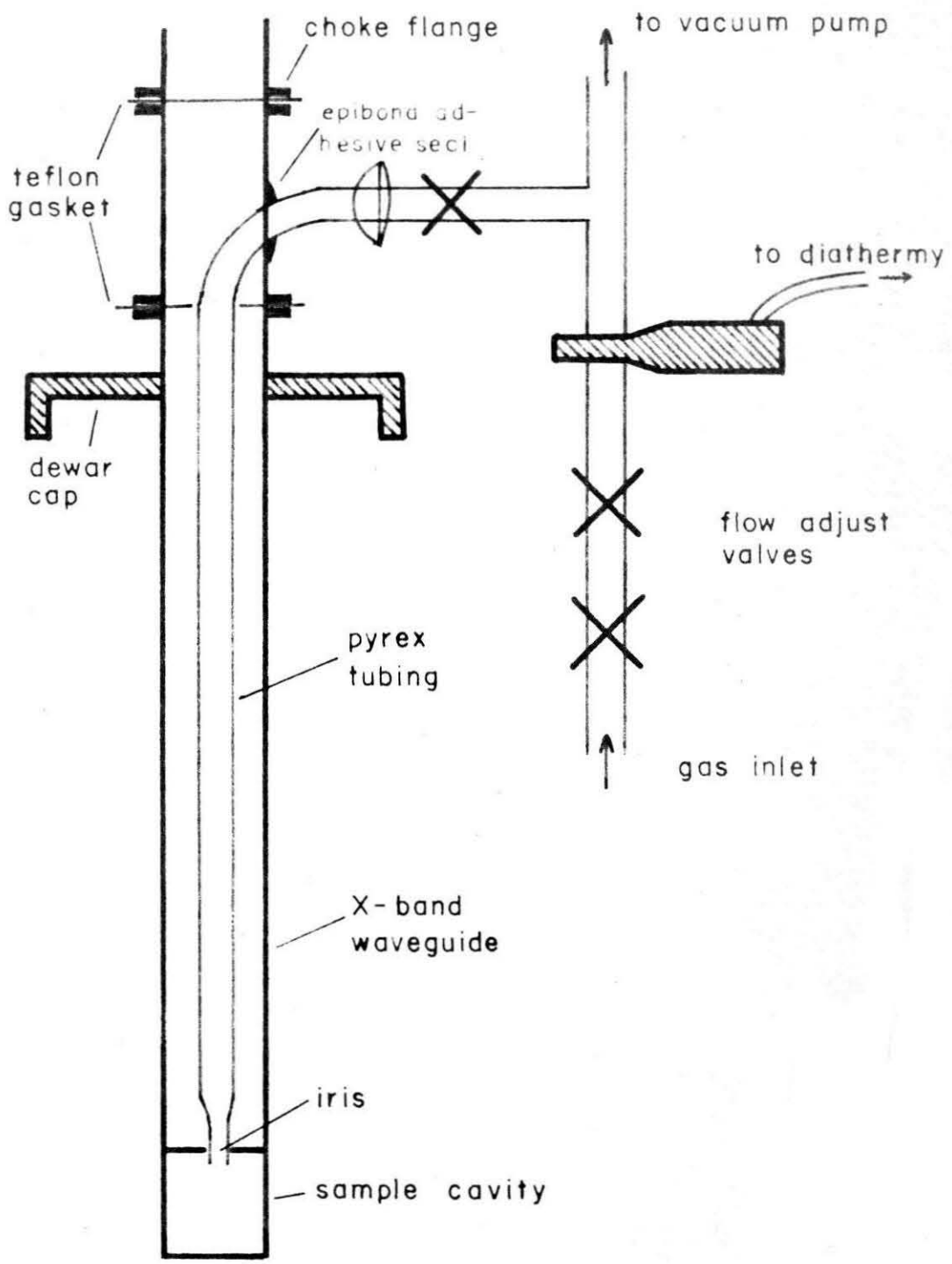

Fig. I GAS DISSOCIATION AND CONDENSATION APPARATUS

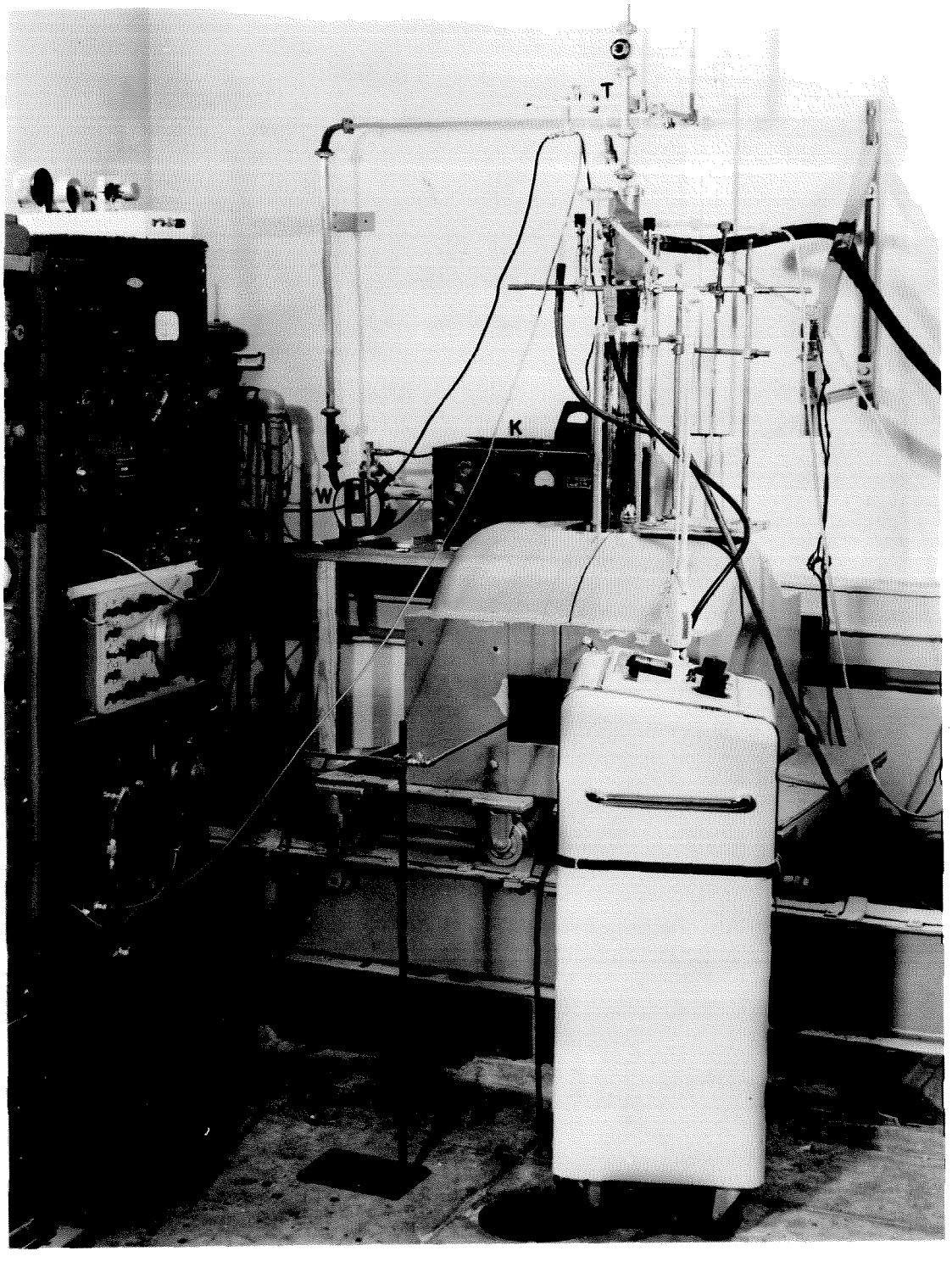

Fig. 2 GENERAL VIEW OF EQUIPMENT

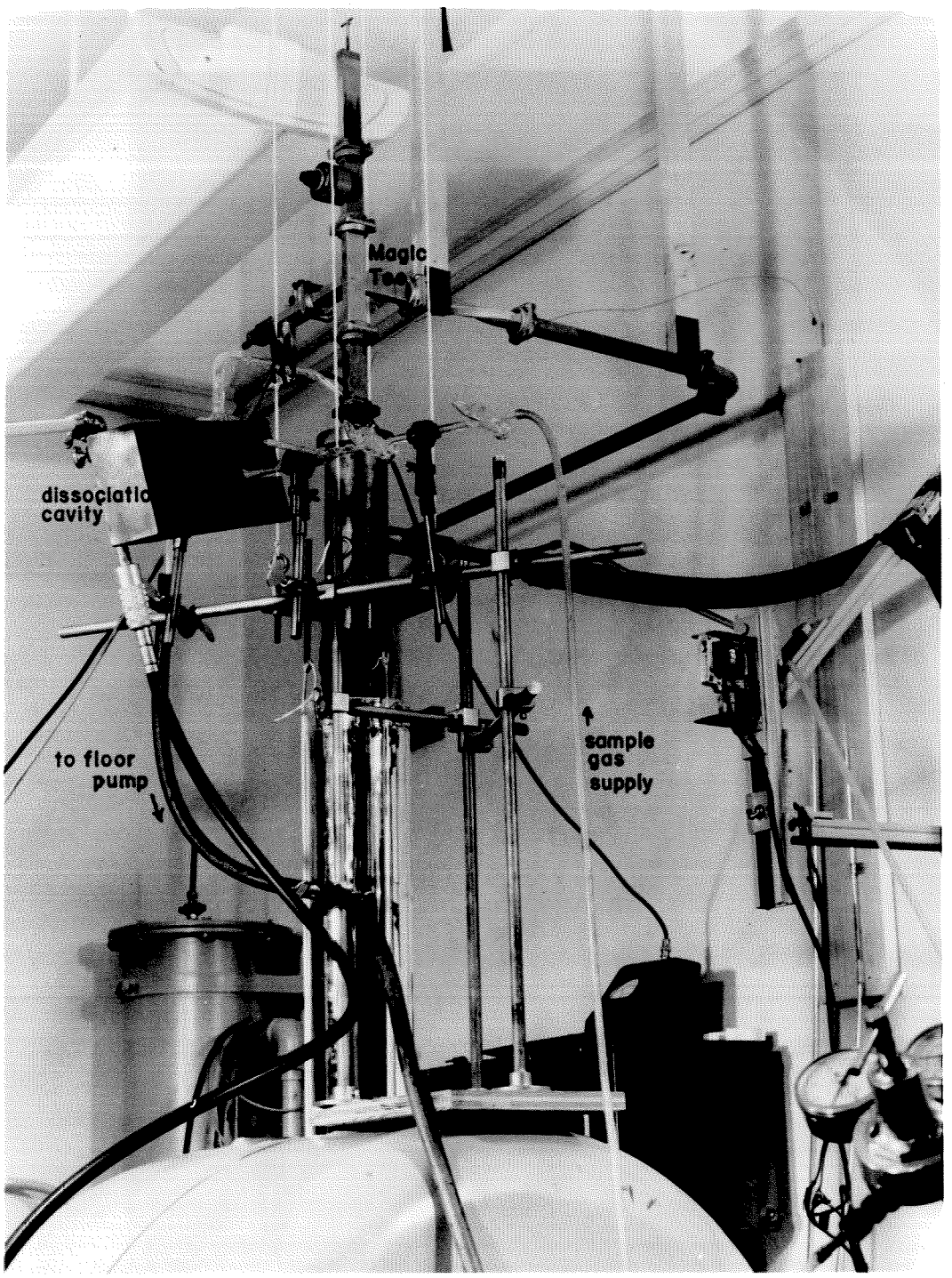

Fig. 3 CLOSEUP OF DISSOCIATION APPARATUS

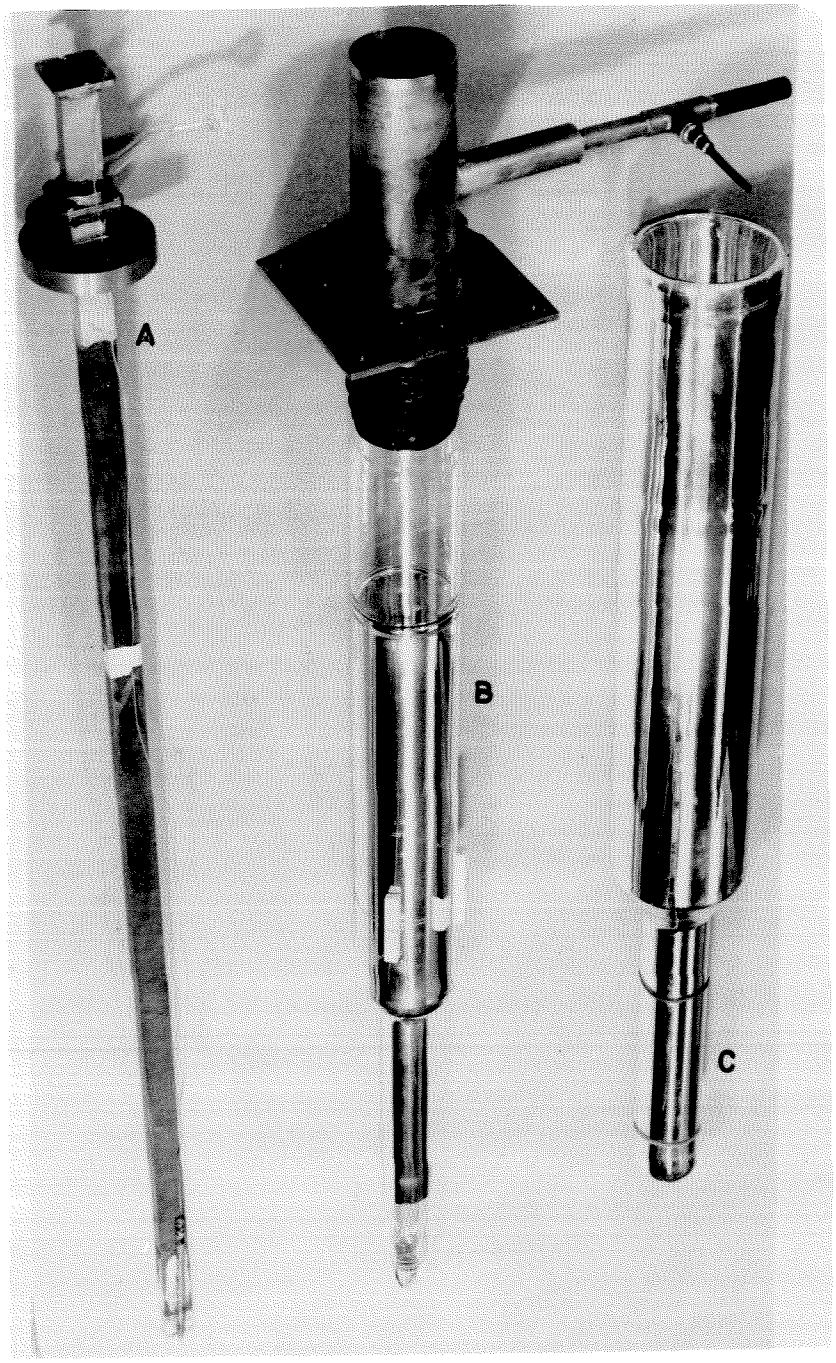

Fig. 4 LOW TEMPERATURE SYSTEM

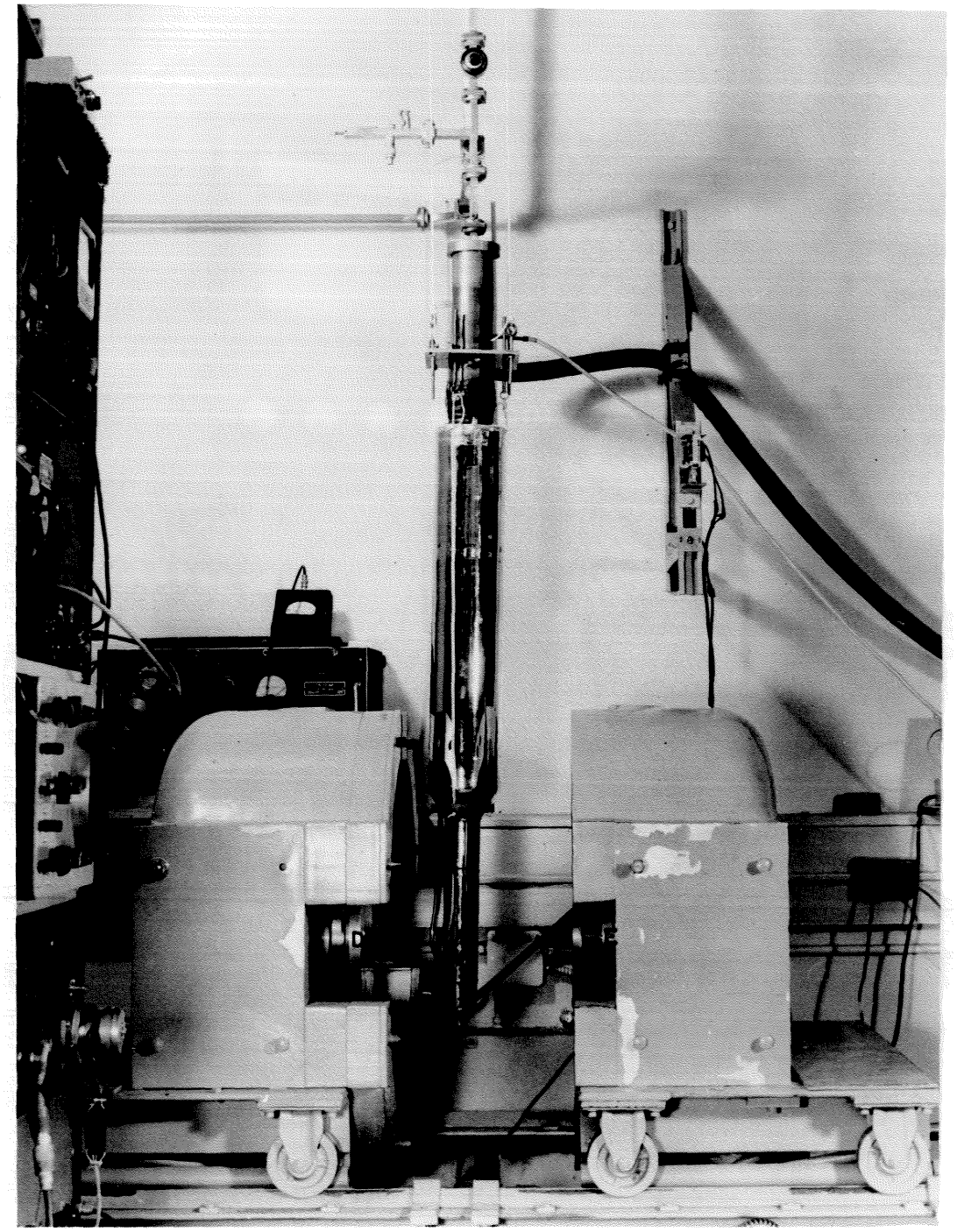

Fig. 5 DEWAR SYSTEM BETWEEN POLES OF ADL MAGNET

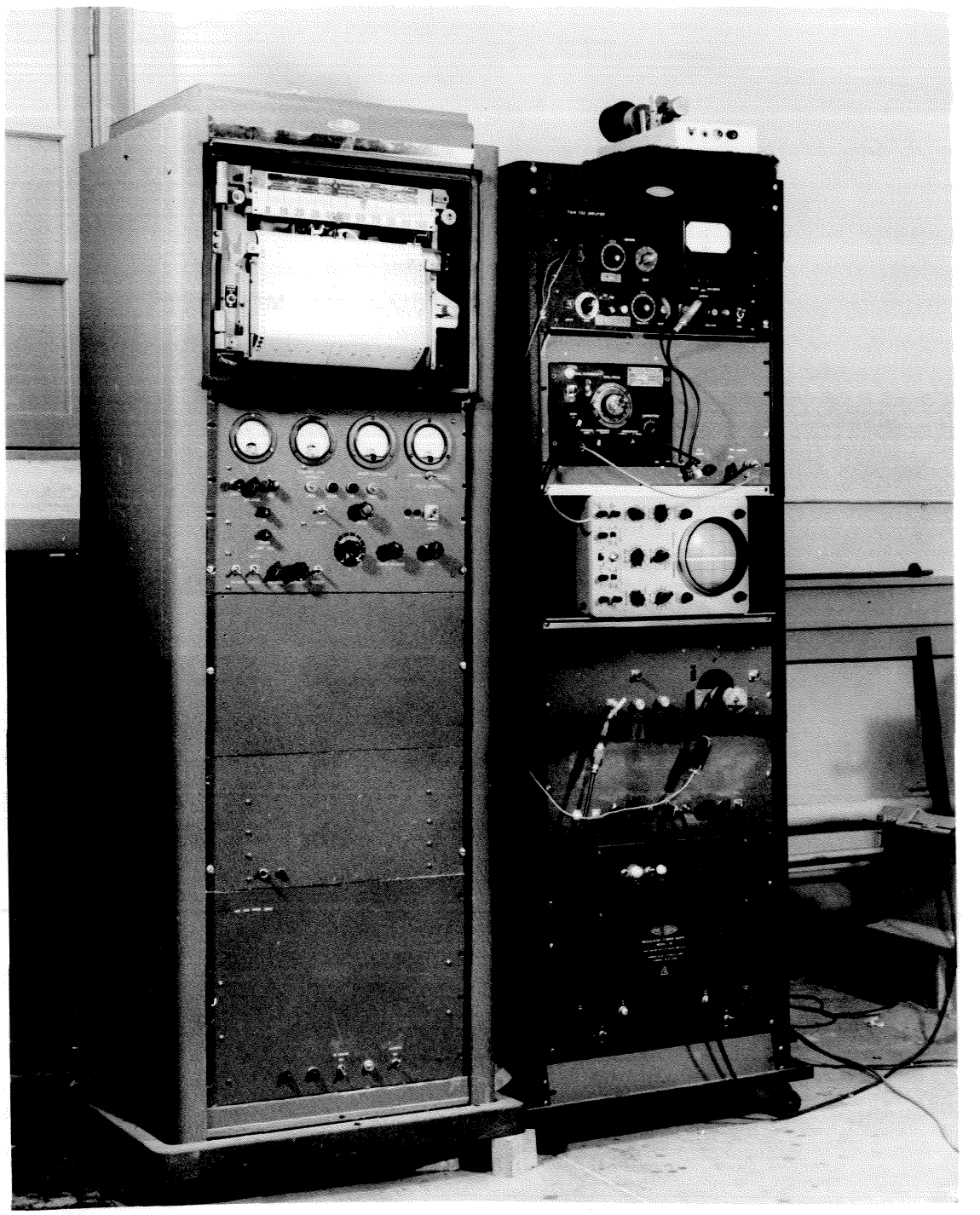

Fig. 6 ELECTRONICS: PROTON CONTROLLER AND EPR SPECTROMETER

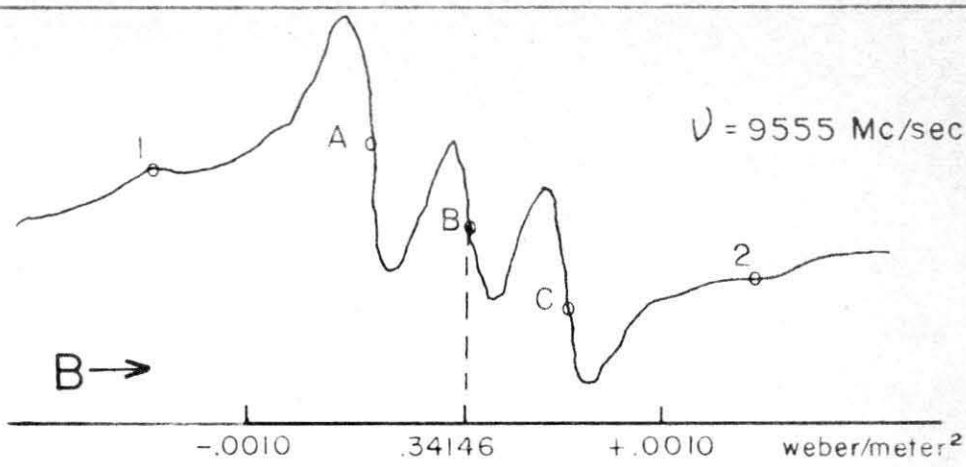

Fig. 7
EPR SPECTRUM OF CONDENSED NITROGEN AFTERGLOW

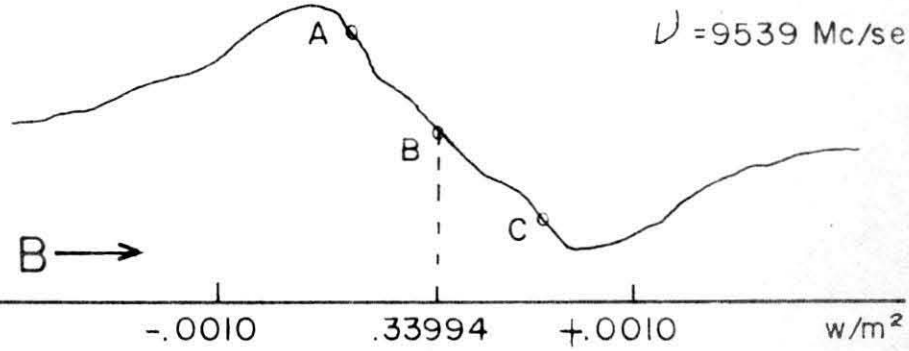

Fig. 8
EPR SPECTRUM OF
NITROGEN DILUTED WITH ARGON

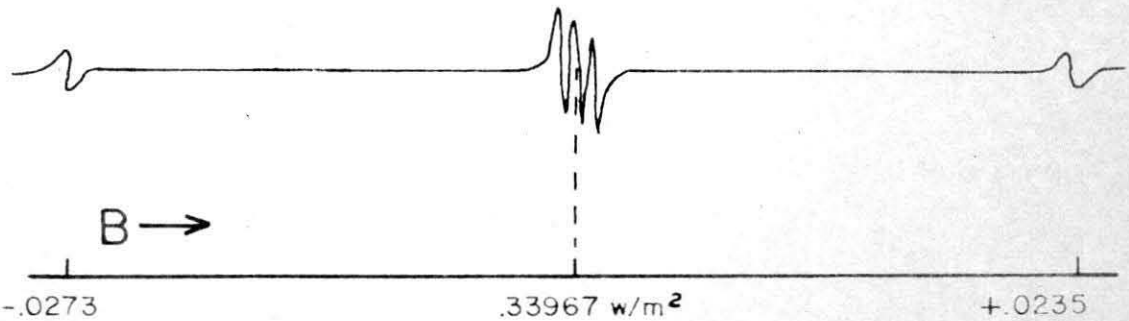

Fig. 9
EPR SPECTRUM OF CONDENSED DISSOCIATED AMMONIA

APPENDIX I.

Magnetic Field Calibration

The use of a proton resonance field controller greatly facilitates highly accurate measurements of magnetic fields. The proton reference sample used here was a 1% molar $Fe(NO_3)_3 \cdot 6H_2O$ solution in water. Using the value for the magnetogyric ratio given by Thomas (14),

$$\gamma_{proton} = 2.67530 \pm 0.00006 \times 10^8 m^2/weber\text{-}sec,$$

one obtains the field in terms of the proton resonance frequency,

$$B(weber/meter^2) = 234.859\ \nu\ (Mc/sec).$$

APPENDIX II.

Calculation of the EPR Spectra for Hydrogen and Nitrogen

If it is desired to evaluate the effect of a magnetic field, B, on the energy levels of an atom, it is necessary to know the quantum mechanical analog of the classical magnetic moment, μ, inasmuch as the addition to the Hamiltonian is $-\mu \cdot B$. The atomic magnetic moment operator can be written:

$$\underline{\mu} = \gamma_j \underline{J} \quad , \quad \underline{\mu}_z = \gamma_j \underline{J}_z ,$$

where $\underline{J}$ is the angular momentum operator and γ is the magnetogyric ratio. For pure orbital angular momentum,

$$\underline{J} = \underline{L} \quad , \quad \gamma_\ell = 1 \text{ Bohr Magneton}/\hbar ,$$

while for pure spin,

$$\underline{J} = \underline{S} \quad , \quad \gamma_s = 2 \text{ (actually 2.0023) Bohr Magneton}/\hbar .$$

Intermediate cases depend on the specific configuration. In a like manner, the nuclear magnetic moment depends on the spin operator:

$\underline{\mu} = \gamma_i \underline{I}$, where $\gamma_i = 2.6753 \times 10$ meter^2/weber-sec (14) for protons.

A given configuration possesses $(2J + 1)(2I + 1)$ degenerate magnetic sublevels. Inasmuch as each of these levels is an eigenstate of the operators $\underline{J}_z$ and $\underline{I}_z$, the effect of a magnetic field is to remove the degeneracy by adding an energy

$$\Delta E = -(\gamma_j m_j + \gamma_i m_i)\hbar B$$

to a state with $\underline{J}_z$ and $\underline{I}_z$ eigenvalues, m_j and m_i. Selection rules for transitions stimulated by radiation permit only those of the form:

$$\Delta m_j = \pm 1 \, , \; \Delta m_i = 0 \quad \text{or} \quad \Delta m_i = \pm 1 \, , \; \Delta m_j = 0$$

The first corresponds to transitions responsible for paramagnetic

resonance absorption and the latter for nuclear resonance absorption. It is to be observed that transitions can occur for only two radiation frequencies, namely:

$$h\nu_{EPR} = \gamma_j \hbar B \qquad \text{or} \qquad h\nu_{NMR} = \gamma_i \hbar B.$$

Consider the effect of hyperfine interaction between the nuclear and electronic magnetic moments. The interaction term which must be added to the Hamiltonian for the system will be proportional to the cosine of the angle between $\underline{I}$ and $\underline{J}$ and may be written:

$$V = A\, \underline{I} \cdot \underline{J}$$

where A, the hyperfine coupling constant, depends on the configuration.

The second order formula for the perturbed energies,

$$\Delta E_i = V_{ii} + \sum_j{}' |V_{ij}|^2 / (E_i - E_j),$$

is utilized once the matrix elements, the V_{ij}'s, of the perturbation energy in the unperturbed representation are calculated. It simplifies the calculation of V_{ij} to note that,

$$\underline{I} \cdot \underline{J} = \underline{I}_z \underline{J}_z + \tfrac{1}{2}\left(\underline{I}^+ \underline{J}^- + \underline{I}^- \underline{J}^+\right),$$

where, $\underline{J}^+ = \underline{J}_x + i\,\underline{J}_y$, $\underline{J}^- = \underline{J}_x - i\,\underline{J}_y$ etc.

These are the spin raising and lowering operators since,

$$\underline{J}^+ \psi(J, m_j) = \sqrt{(J - m_j)(J + m_j + 1)}\ \psi(J, m_j + 1),$$
$$J^- \psi(J, m_j) = \sqrt{(J + m_j)(J - m_j + 1)}\ \psi(J, m_j - 1).$$

To illustrate the calculation, consider a ground state hydrogen atom ($^2S_{\frac{1}{2}}$, I = 1) in a magnetic field. There are four degenerate substates:

1. $m_j = m_s = \frac{1}{2}$, $m_i = \frac{1}{2}$ 2. $m_s = -\frac{1}{2}$, $m_i = \frac{1}{2}$

3. $m_s = \frac{1}{2}$, $m_i = -\frac{1}{2}$ 4. $m_s = -\frac{1}{2}$, $m_i = -\frac{1}{2}$.

Then $$V_{ii} = -\hbar(\gamma_s m_s + \gamma_\lambda m_\lambda)B + m_M A\hbar^2$$

and $$V_{23} = \tfrac{1}{2}A\hbar^2$$

Note that all elements between states of differing $m_J + m_I$ must be zero because internal forces cannot change the net vector angular momentum.

The new energies are:

1. $\Delta E_1 = V_{11} = -\tfrac{1}{2}\hbar(\gamma_s + \gamma_\lambda)B + \tfrac{1}{2}M$,
2. $\Delta E_2 \approx V_{22} + \frac{\frac{1}{4}(A\hbar^2)^2}{V_{22} - V_{33}} = -\tfrac{1}{2}\hbar(-\gamma_s + \gamma_\lambda)B - \tfrac{1}{2}M + N$,
3. $\Delta E_3 \approx V_{33} + \frac{\frac{1}{4}(A\hbar^2)^2}{V_{33} - V_{22}} = -\tfrac{1}{2}\hbar(\gamma_s - \gamma_\lambda)B - \tfrac{1}{2}M - N$,
4. $\Delta E_4 = V_{44} = -\tfrac{1}{2}\hbar(\gamma_s - \gamma_\lambda)B + \tfrac{1}{2}M$.

$$M = \tfrac{1}{2}A\hbar^2, \quad N = M^2/\hbar(\gamma_s - \gamma_\lambda)B \approx M^2/\hbar\gamma_s B$$

since $$\gamma_s/\gamma_\lambda \approx 600.$$

Paramagnetic transitions can occur between states 1 and 2, and between states 3 and 4, with,

$$h\nu_{2-1} = \hbar\gamma_s B - M + N,$$
$$h\nu_{4-3} = \hbar\gamma_s B + M + N.$$

Most EPR spectra are observed as a function of field with ν held fixed. In terms of B, the resonance condition is:

$$B\pm = (h\nu \pm M - N(B))/\hbar\gamma_s.$$

Thus, the hyperfine coupling serves to split the paramagnetic resonance line. To first order in A, this splitting,

$$\Delta B = 2M/\hbar\gamma_s,$$

is symmetrical about the free electron value ($A = 0$), but to second order there is a displacement of the lines by an amount,

$$(\tfrac{1}{2}\Delta B)^2/\tfrac{1}{2}(B_+ + B_-),$$

toward lower fields.

Jen et al (11) observed two lines in the EPR spectrum of condensed hydrogen dissociation products. One lay 0.02746 weber/meter^2 below the free electron spin resonance position, and the other 0.02341 w/m^2 above. The field averaged .324 w/m^2. The theory predicts a displacement of the center of gravity of the doublet by,

$$-\tfrac{1}{4}\,(0.2341 + 0.02746)^2/.324 = -.0020 \text{ w/m}^2$$

The experimental value,

$$(-0.02746 + 0.02341)/2 = -.00202 \text{ w/m}^2,$$

differs by 1%.

The same technique used for hydrogen is readily applied to the ground state of nitrogen ($1s^2$, $2s^2$, $2p^3$, $^4S_{\frac{3}{2}}$, I = 1). There are twelve degenerate substates, which makes the calculations lengthy. The results give (2I + 1)(2J) = 9 paramagnetic transitions yielding five distinct lines, at,

$$\hbar\gamma_s B = (h\nu \pm A\hbar^2 - \tfrac{3}{2}D), (h\nu \pm A\hbar^2), (h\nu - D)$$

$$D \cong (A\hbar^2)^2/\hbar\gamma_s B.$$

If we assume that the natural EPR line-widths are much greater than $D/\hbar\gamma_s$, the spectrum is a triplet. From the separation, ΔB, of its extremities, we can calculate the hyperfine coupling constant. The triplet spectrum described under results on nitrogen gives the value,

$$\Delta B = 2A\hbar^2/\hbar\gamma_s = 8 \times 10^{-4} \text{ w/m}^2 \text{ @ } 9500 \text{ Mc/sec.}$$

With $\gamma_s/2\pi = 2.80 \times 10^4 \frac{\text{Mc/sec}}{\text{w/m}^2}$,

the hyperfine coupling constant is given by,

$$A\hbar^2/h = \frac{\Delta B}{2}(2.8 \times 10^4) = 11.2 \text{ Mc/sec},$$

and thus,

$$D/\hbar\gamma_s = \frac{(A\hbar^2/\hbar\gamma_s)^2}{B} = \left(\frac{A\hbar^2/h}{\gamma_s/2\pi}\right)^2 \frac{1}{.34} = 5\times 10^{-7}\ w/m^2,$$

far below our limit of resolution.

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