PHYSICAL REVIEW VOLUME 99, NUMBER 2 JULY 15, 1955

Atomic Phosphorus Paramagnetic Resonance Experiment Employing Universal Dissociator*

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(Received March 29, 1955)

A simple spectrometer for the observation of paramagnetic resonance of free atoms near 9000 Mc/sec is described. This is followed by a detailed discussion of a new dissociation technique employing a carrier gas and a high-temperature arc which is shown to be effective enough to allow oscilloscopic observation of the atomic nitrogen spectrum, previously reported by Heald and Beringer. This dissociation technique which is believed to have universal applicability has been used to produce atomic phosphorus. The spectrum due to its ${}^4S_{\frac{3}{2}}$ ground state has been observed. It consists of a narrow doublet which arises from magnetic hfs interaction due to the P^{31} nucleus. The separation has been measured as

$$\delta\nu(P^{31}, {}^4S_{\frac{3}{2}}) = 56.2\pm1.5 \text{ Mc/sec},$$

and the g_J factor for the ground state has been obtained as

$$g_J(P, {}^4S_{\frac{3}{2}}) = 2.0019\pm0.0004,$$

which is only slightly smaller than the free-electron g value. The occurrence of a hfs in the supposedly symmetric ${}^4S_{\frac{3}{2}}$ ground state as well as the small g_J factor indicate the presence of higher state admixtures. The effects of beginning *jj* coupling in group V elements are briefly discussed and a sizeable electric quadrupole term in the ground state hfs of Sb and Bi is predicted.

INTRODUCTION

In the last few years, an appreciable number of free atoms[1–3] has been studied by Beringer and coworkers using microwave paramagnetic resonance techniques. A similar microwave absorption experiment on Cs vapor[4] had been performed earlier. If there are no complications in such paramagnetic resonance experiments the static magnetic field, H_0, the resonance frequency, ν_0, and g_J, the gyromagnetic ratio of the free-atom state of total angular momentum, J, are connected by the well-known relation,

$$\nu_0 = (g_J\beta/h)H_0,$$

β denoting the Bohr magneton. Of the atoms H, O, and N studied so far, only H had been investigated previously by atomic beam resonance deflection techniques.[5] The g_J factor results on the two populated states of O, and the hyperfine structure observed for atomic N, provided interesting information on the higher order interactions of the electrons in these atoms.

The difficulties which have to be overcome in the extension to other atoms of this, in comparison with other methods experimentally easy, technique for the study of magnetic properties of atoms, consisted mainly in getting the free atoms into the microwave cavity in a sufficient concentration to give a detectable absorption. One elegant solution[6] has been suggested by Gordon *et al.* In this method a beam of atoms is magnetically focused[7] into a microwave cavity. As the focuser at the same time rejects the higher or lower of the two states between which transitions take place, a gain of the order of $kT/h\nu$ in intensity in an absorption or stimulated emission experiment can be realized which then offsets the loss in intensity due to the low density which can be used in atomic beams. However, there still remains the problem of dissociation.

In Beringer's experiments, the approach was simply to pass the usually wet molecular gases through a high-voltage discharge at pressures around 0.1 mm Hg, and then pumping the appreciably dissociated discharge products through a short section of tubing whose insides had been poisoned with a suitable anticatalyst to prevent recombination on the walls. Since at these low pressures the diffusion speed, with which the atoms reach the walls, is much greater than practical flow speeds and dissociation rates, this wall poisoning is absolutely necessary to maintain a sufficient concentration of free atoms at a reasonable distance from, and even in, the discharge tube.[8]

On the other hand, the actual mechanism of this wall poisoning is little understood. It has been possible to find suitable anticatalysts for H, O, and N but even for other gases like the halogens, not much success has been reported. As for substances like C, which in the form of gaseous compounds like CO can easily be introduced into the discharge but have an extremely low vapor pressure at practical wall temperatures, it is at least highly unlikely that a suitable poisoning agent will ever be found. Furthermore, it is not at all easy to break up tightly bound molecules like N_2 in a low-pressure discharge and special techniques may have to be employed.

For these reasons, it appeared desirable to test a dissociation technique in which the active component at a pressure between 0.01 and 0.1 mm Hg is added to an inert gas carrier of the comparatively high pressure of 10–100 mm Hg. As at these pressures it is possible to maintain high temperature arcs with gas temperatures up to 6000°K, the simple *thermal* dissociation of *any*

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* This work has been supported by a contract with the Office of Ordnance Research, Department of the Army. A short account has already appeared in Bull. Am. Phys. Soc. **30**, No. 1, 42 (1955).

[1] R. Beringer and M. A. Heald, Phys. Rev. **95**, 1474 (1954).

[2] E. B. Rawson and R. Beringer, Phys. Rev. **88**, 677 (1952).

[3] M. A. Heald and R. Beringer, Phys. Rev. **96**, 645 (1954).

[4] Roberts, Beers, and Hill, Phys. Rev. **70**, 112 (1946).

[5] Koenig, Prodell, and Kusch, Phys. Rev. **83**, 687 (1951).

[6] Gordon, Zeiger, and Townes, Phys. Rev. **95**, 282 (1954).

[7] H. Friedburg, Z. Physik **130**, 493 (1951).

[8] R. W. Wood, Phil. Mag. **44**, 538 (1922).

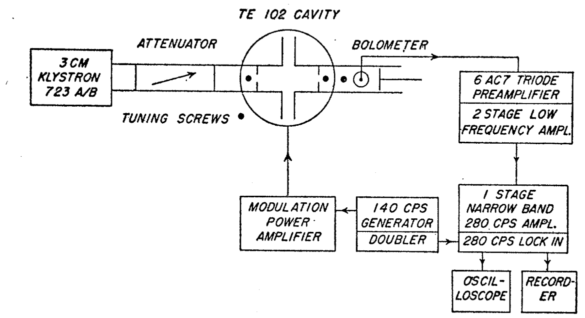

FIG. 1. Block diagram of paramagnetic resonance spectrometer.

molecule into atoms is assured. At the same time the carrier greatly reduces the diffusion speed of the free atoms and thereby effectively eliminates the wall effects. An experiment on atomic phosphorus along these lines shall now be described in some detail.

SPECTROMETER

The paramagnetic resonance spectrometer used, see Fig. 1, was essentially a simplified version of the one described by Beringer *et al.*[1] It operated at a frequency around 9000 Mc/sec. A 723*A*/*B* klystron was used as the power source and great care was taken to reduce the ripple and jitter on the cathode and reflector voltages as far as possible. The reflector voltage was obtained from batteries through a low impedance dividing network. In this simple way it was possible to keep the spurious frequency modulation of the klystron low enough that no significant decrease in noise was noticed for identical power incident upon the bolometer if the power was fed directly from the klystron into the bolometer instead of through the cavity. A rather-low-*Q* rectangular transmission cavity made from standard *X*-band wave guide and silvered afterwards was used. The gas stream entered and left the λ length (TE102) cavity through short tubular sections acting as below-cutoff attenuators.

The use of the rectangular cavity was dictated by the fact that only a magnetron electromagnet of 3-in. diameter and $\frac{5}{8}$-in. gap was available. Consequently the homogeneity over the largest dimension of the sample, 1 in., was rather poor, namely of the order of 1 oersted. The magnet was powered from 16 ordinary 6-volt car batteries. Mainly in order to increase the ease of field measurements, a proton resonance stabilization system was installed. Simply by changing the frequency of the proton stabilizer, the field at its usual value, around 3300 oe, could be pulled ±200 oe. By mechanically ganging the stabilizer control with the recorder drive, field reproducibility on the recording tape was achieved, which greatly helped with the identifications of weak lines. The magnetic field was modulated by conventional circuits at 140 cps, this frequency being derived from the 60-cps main by dividing and multiplying circuits.

The transmitted microwave power was detected by a commercial (Sperry 821) bolometer. Application of the microwave power increased the Johnson noise of the dc biased bolometer more than would have been due to its corresponding temperature and resistance increase. This indicates some amplitude noise in the klystron output. Provided one considers a factor of 2 or 3 worthwhile, a balanced bolometer circuit would have merits. In such a circuit, one bolometer would obtain its power through the cavity, while the other one would get an equal amount directly from the klystron. The amplitude modulation noise of the klystron could then be cancelled out by bucking the two bolometers against each other. The ac output of the bolometer was fed through a large dc blocking capacitor and over a well-shielded step-up transformer (Thermador TG1) applied to the grid of a triode connected 6AC7 input stage. Tests by grounding the grid of this input stage showed that the Johnson noise of the hot bolometer easily swamped the tube noise a few times. After further amplification by two penthode stages, the signal had to pass a single twin *T* negative feedback narrow band stage tuned to 280 cps before it reached a Schuster-type lock-in detector[9] employing a reference voltage of 280 cps. The lock-in output, which was displayed on a recording milliammeter, corresponded essentially to the second derivative of the absorption lines. The doubling technique greatly enhanced the narrow lines of interest here over broad absorptions due to various spurious causes like free electron cyclotron resonances, etc. It also reduced the pick-up and flicker noise problems. These advantages easily outweigh the inherent loss in modulation efficiency of about 30 percent, as compared with detection at the modulation frequency itself. The spectrometer sensitivity was optimized with the help of a diphenyl-picryl-hydrazil test sample. Peak-to-peak signal-to-noise ratio at 1-sec time constant for a sample of this substance containing 3×10^{15} free electron spins was found to be better than 200 for a line width of about 6 Mc/sec.

DISSOCIATOR AND CARRIER GAS SYSTEM

The helium-argon carrier was supplied in the form of commercial compressed gases (Matheson) of better than 99.9 percent purity. The pressure was reduced to about 1 atmosphere with the usual automatic regulators, followed by small needle valves (Hoke) for further reduction down to the 10–100 mm Hg range. A finer adjustment for partial pressures below 1-mm Hg could be obtained with the Matheson 51 needle valve, which was used for the N_2 addition. It was found that the expensive argon could be replaced by the cheaper helium to a large extent. Pure helium operation led to overheating of the quartz tube. The carrier then passed over white phosphorus contained in a flask which could be heated to cover a P_4 partial pressure range of

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[9] N. A. Schuster, Rev. Sci. Instr. 22, 254 (1951).

0.02–1 mm Hg, see Fig. 2. The dissociator consisted essentially of a 15-mm o.d. quartz tube containing two tungsten electrodes. In order to sustain the desired high current arc, the cathode has to get hot enough to thermally emit an electron current of several amperes, which is the case at about 3000°K. To start the arc an ac voltage of more than 800 volts had to be applied in series with the dc operating voltage of 130–250 volts. A choke limited the ac current to 4 amp. After about a minute of high-voltage operation at 100–200 mm Hg the electrodes became suddenly white hot, emitting an intense light, and the gap voltage dropped to a low value. After removal of the ac voltage the arc then operated on the dc supply. The starting procedure was aided by a high-frequency high voltage from a Tesla transformer. The gap voltage in argon for a gap distance of 40 mm in the pressure range of 10–200 mm Hg was around 40–50 volts and was rather independent of the current, which could be raised up to 8 A without melting the electrodes.

In the pressure range of interest, 10–100 mm Hg, it is still not a bad assumption that electron and gas temperature in the arc plasma are nearly equal, and that the current is mainly carried by the electrons. The gas temperature then must be large enough to provide by thermal ionization a sufficient positive ion concentration to neutralize the heavy space charge associated with the large observed electron current densities. Calculations along these lines, as well as experiments, establish gas temperatures[10,11] up to 6000°K. At these temperatures all molecules at the low partial pressures of interest here will be completely dissociated into their atomic constituents. This expectation was tested by adding up to 1-mm N_2, dissociation energy 9.8 ev, to argon and helium-argon mixtures around 50-mm Hg. The well-known active nitrogen afterglow appeared strongly, and the hfs triplet of the atomic $^4S_{\frac{3}{2}}$ ground state was observed in the paramagnetic resonance spectrometer, compare Fig. 3. Resonance due to atomic hydrogen also was detected with this arrangement.

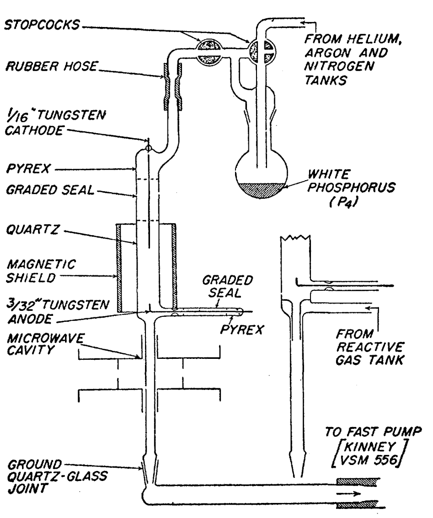

FIG. 2. Universal dissociator employing helium-argon carrier.

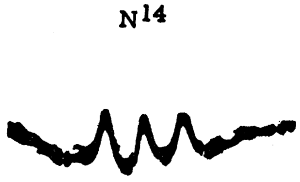

FIG. 3. Atomic N^{14} hfs triplet. Broad-band oscilloscopic display and field modulation at 15 cps were used. The dissociator was an earlier Pyrex water-cooled version.

After these early tests proved successful, attempts were made to obtain the paramagnetic resonance spectrum of atomic phosphorus. Phosphorus was chosen for various reasons: (1) its hfs had not been measured; (2) the dissociation technique could be tested on polyatomic molecules, P_4, which could also be easily admixed to the carrier; (3) its atomic ground state, $^4S_{\frac{3}{2}}$, has no orbital angular momentum. So far a certain setback of the carrier technique has not been discussed. While collisions of the inert nonmagnetic carrier atoms will not broaden resonance lines of S-states, since there is no interaction with the sole contributor to the total angular momentum, the electron spin resultant, they will broaden non-S-states at a likely rate of 1 Mc/sec/mm Hg carrier pressure. For these states, the electron orbitals of nonvanishing angular momentum provide the handle by which the total angular momentum can be turned over by an impinging carrier atom. Fortunately for a sizeable group of atoms where the orbital momentum carrying electrons are shielded by outer inert shells, like in the $4f^n6s^2$ states of the rare earth elements, this broadening may be appreciably reduced. Even though the associated intensity loss may not be prohibitive, it was clearly desirable to avoid non-S atoms at this stage. In spite of these precautions, the early attempts did not meet with success. It was, therefore, decided to have a closer look at the processes by which the free atoms do recombine which definitely have been generated in the arc. It is well known that two single atoms which collide in the gas phase will not stay together long unless the resulting collision complex has a way to get rid of the recombination energy which, of course, is also sufficient for dissociation. To stabilize the collision complex, a third body has to be present to absorb part of the recombination energy. This now may be another molecule or the wall of the container. Triple collisions in the gas phase are too rare and can be neglected here. The worst assumption concerning the wall effect is that every free atom hitting the wall recombines. It follows then that the carrier pressure in a flow system like ours should be high enough to prevent appreciable diffusion to the tube wall before the cavity

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[10] W. Elenbaas, *The High Pressure Mercury Vapor Discharge* (Interscience Publishers, Inc., New York, 1951).

[11] J. P. Cobine, *Gaseous Conductors* (McGraw-Hill Book Company, Inc., New York, 1941).

is reached. By demanding that the average time, t, an atom travels the arc-cavity distance, S, should be half its diffusion time to the wall, a relation between the necessary pumping speed V in cm^3/sec and the diffusion constant D in cm^2/sec can be formulated:

$$V \approx 40SD.$$

The tube diameter has conveniently dropped out. As a practical example, we take $V=6000$ cm^3/sec and $S=6$ cm and obtain $D_{\max}=25$ cm^2/sec. If we assume a diffusion coefficient for atomic P into argon of about 0.3 cm^2/sec at atmospheric pressure and at room temperature, this calls for a minimum carrier pressure of 10 mm Hg. Because of the much higher temperatures in and immediately after the arc region, this estimate may be considerably too low unless one uses water-cooling of the arc housing. In this way, one shields the dissociator wall with a dense layer of cooler gas. The just-obtained relation should be satisfied in any case unless one wants to rely on wall poisoning. However, in the general case it is not the only condition which has to be satisfied in order to assure a sufficient free atom concentration in the cavity. While for atoms forming only diatomic molecules gas phase losses are completely in the background, this is by no means so when polyatomic molecules are formed.[12] Even though not much will happen if one P atom collides with another one, there will always be an appreciable fraction of fragments P_2, P_3, and also impurities at hand which have not passed through the hottest zone of the dissociator. If a P atom now hits such a fragment, say P_3, the recombination energy in the resulting excited P_4 molecule can spread over many degrees of freedom, which gives the complex a sufficiently long life to be deactivated by a collision with a carrier atom, or it may also break up into two P_2 molecules. Fortunately, not every collision between a free atom and a polyatomic fragment leads to the formation of an excited molecule, as it must clearly make a difference if the fragment can form a bond at the spot where it is hit or not. The whole matter gets rather involved, and the gist of all this is that one may hope for an atom to live over 10 to 100 collisions with polyatomic groups. This places a limit on the partial pressure of the active component which is likely to give an optimum concentration of free atoms. One may arrive at a rough estimate by demanding that a P atom should not collide with more than 10–100 other P atoms during the transit time, t, from the arc to the cavity. With a tube cross section of $\frac{1}{2}$ cm^2 and the same values for V and S as in our above example, t comes out 5×10^{-4} sec. If one assumes a collision time for P at atmospheric pressure and room temperature of 4×10^{-10} sec, this optimum P pressure will be $10^{-2}-10^{-1}$ mm Hg which should lead to a well-observable paramagnetic resonance signal. It might be emphasized here that the rather stringent general conditions to assure a sufficient free atom concentration can be met in a practical arrangement. Therefore, the carrier dissociation and transport technique should be quite universally applicable. Besides, for H and N, this has so far also been demonstrated for atomic P, whose paramagnetic resonance spectrum was observed after a sufficiently fast pump (Kinney, VSM 556, preceded by 35 l ballast volume) was installed.

The arc may also be used to evaporate metals into the carrier gas. Preliminary experiments employing a graphite anode supporting a ball of molten Cu indicate that even *excited or metastable* Cu atoms are present as far as 20 cm downstream from the arc, as evidenced by the emission of the characteristic green Cu spectrum. The formation of metallic mirrors on the tube wall inside the cavity poses a problem which, however, can be overcome by the design shown in the insert of Fig. 2. Here the carrier stream is sheathed by a thin lamina of reactive gas like Cl_2 or air which reacts with the metal atoms diffusing into it.

ATOMIC P SPECTRUM

It was originally planned to measure the P spectrum, which consists of a narrow doublet (see Fig. 4) centered around roughly the free electron g value, by simultaneously observing it with the atomic N spectrum. The g_J factor of atomic N had been measured with high precision by Heald and Beringer,[3] and this procedure would have eliminated the need for precise measurements of the microwave frequency and the magnetic field at the exact site of the free-atom sample. Unfortunately, however, it was not possible with the present equipment to achieve a suficient concentration of P, as well as N atoms, by simultaneously charging the carrier with P_4 and N_2. Therefore, an intermediate standard in the form of the center high-field line, Mn_{+1}, of the hfs sextet of Mn^{++} in the cubic ZnS host lattice (line width 3 oe was employed. The procedure now was to alternate recordings of the Mn_{+1} line and the N spectrum with recordings of the Mn_{+1} and the P spectrum a few times while the geometrical arrangement of free atom cavity Mn^{++} sample and proton resonance coil was left unchanged. The average proton resonance frequency differences with respect to the Mn_{+1} line as zero are

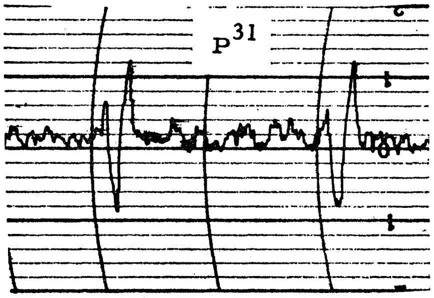

FIG. 4. Hfs doublet of atomic P^{31}. A 1-sec time constant was used in the recording circuit.

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[12] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

given in Table I. The proton frequencies were measured with a direct reading frequency meter (Gertsch FM3). The limit of error in these frequencies was about 2 kc or half the observed line width. The spectrum was proven to be independent of the carrier pressure in the region of 20–40 mm Hg. This includes the line width which was found to be 1 oe between zero deflection points and which was exclusively due to the inhomogeneity of the available field. From the values in Table I one calculates for the P^{31} hfs separation 20.0±0.5 oe or

$$\delta\nu(\mathrm{P}^{31})=56.2\pm1.5\ \mathrm{Mc/sec.}$$

TABLE I. Proton frequency differences for measured resonance peaks, in kc/sec.

Mn_{+1}	P_{+1}	N_0	P_{-1}
0	−74	−118	−159.5

The proton frequency corresponding to the center of the P spectrum is only 1.3 kc/sec lower than that of the N center line, N_0, which is less than the assigned limit of error. With Heald and Beringer's value $g_J(\mathrm{N})=2.0021$, we consequently obtain

$$g_J(\mathrm{P})=2.0019\pm0.0004,$$

neglecting small correction terms, as the Paschen-Back effect is very nearly complete.

In order to explain the observed splitting as magnetic hfs due to the P^{31} nucleus of nuclear spin $I=\frac{1}{2}$, one has to assume small admixtures of excited states to the predominantly $3s^23p^3\,{}^4S_{\frac{3}{2}}$ ground state, since this state in pure *LS* coupling cannot couple to the nuclear magnetic moment. The admixtures most effective in producing a magnetic hfs interaction will be the ones of the type $3s3p^3ns$ $(n=4, 5\cdots)$, in which one of the $3s$ electrons has been promoted to a higher *s* orbital and the two *s* electrons have parallel spins.[13,14] A total of such admixtures of the order of 1 percent is sufficient to account for the observed hfs in P. For the last members of the series N, P, As, Sb, Bi, however, there will be sizeable contributions from the ground state *p* electrons to the hfs. This can easily be seen since in pure *jj* coupling the $J=\frac{3}{2}$ ground state is made up of two antiparallel $p_{\frac{1}{2}}$ electrons and one $p_{\frac{3}{2}}$ electron and, therefore, effectively behaves like a single $p_{\frac{3}{2}}$ electron. Consequently, in *jj* coupling one will find not only sizeable magnetic dipole and electric quadrupole interactions for the ground state but also a g_J factor of 1.333 instead of 2. There is little doubt that beginning *jj* coupling is the essential cause for the small g_J values of the last members of the series. While a look at Table II shows that extreme *jj* coupling is not even reached in Bi, there are definitely observable quadrupole terms to be expected in the ground state hfs of at least Sb and Bi.

TABLE II. Ground state g_J-factors for group *V*-atoms.

Free electron	N	P	As[a]	Sb[b]	Bi[b]
2.0023	2.0021	2.0019	1.994	1.967	1.65

[a] J. B. Green and W. M. Barrows, Phys. Rev. **47**, 131 (1935).

[b] D. R. Inglis and M. H. Johnson, Phys. Rev. **38**, 1642 (1931).

It is a pleasure to express my thanks to Professor Beringer for stimulating discussions during a visit at Yale University and to Professor Gordy for the use of the facilities of the Duke Microwave Laboratory.

My thanks further go to Mr. H. Mortenson for the construction of the proton resonance field stabilizer system, and I should like to mention the friendly cooperation of Mr. Thomas Henson in building the various quartz dissociators.

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[13] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

[14] G. F. Koster, Phys. Rev. **86**, 148 (1952).