

Hyperfine Structure of Atomic Phosphorus*†

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The spin-exchange optical polarization method was used to determine the sign and the magnitude of the hyperfine interaction constant in the ground $(3p)^3\ ^4S_{3/2}$ state of atomic P^{31} . The measurements were made by monitoring the transmission of circularly polarized rubidium D_1 ($5P_{1/2} \rightarrow 5S_{1/2}$) resonance radiation through a flask containing rubidium, atomic phosphorus, and a buffer gas as a function of the frequency of an external radio-frequency field. The value for the hyperfine interaction constant of P^{31} obtained by extrapolation to zero pressure in a helium buffer gas is

$$A(P^{31}) = +(55\,055\,691 \pm 8) \text{ cps/sec.}$$

The pressure shifts in cycles/sec/mm Hg of the phosphorus hyperfine interaction constant for helium and neon buffer gases are $+3.61 \pm 0.23$ and $+6.73 \pm 0.15$, respectively.

INTRODUCTION

IN an LS -coupling scheme the ground-state electronic configuration of atomic phosphorus is $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^3\ ^4S_{3/2}$. The only stable isotope of phosphorus, P^{31} , has a nuclear spin $1/2$ and a nuclear magnetic moment of $+(1.13162 \pm 31)$ nuclear magnetons.^{1,2} If there were no configuration mixing, the electronic g factor would be 2.0023, and there would be no nuclear hyperfine interaction.^{3,4} Dehmelt used a paramagnetic resonance technique to make the first measurements on atomic phosphorus.⁵ He found that the electronic g factor was 2.0019 ± 0.0004 and the magnetic hyperfine interaction constant was 56.2 ± 1.5 Mc/sec. He was not able to determine the sign of the hyperfine interaction constant. Recently, a wide theoretical interest has been expressed in the hyperfine structure of atoms with this type of electronic configuration. It is now believed that most of the hyperfine interaction is due to an exchange polarization of the closed shell core by the unpaired p electrons. The core electrons with spin parallel to that of the unpaired electrons experience stronger exchange forces than the core electrons with the opposite spin orientation. This exchange polarization of the core electrons causes the S -state wave functions at the nucleus for the two-spin orientations to differ and produces a hyperfine interaction through the Fermi contact term. Several approaches are being used to calculate the electron wave functions at the

nucleus.⁶⁻¹⁰ For interpreting these calculations, it is important to know the sign of the hyperfine interaction constant. In this paper we report a measurement of the magnitude and sign of the phosphorus hyperfine interaction constant by the spin-exchange optical polarization method.

METHOD, APPARATUS, AND TECHNIQUE

The measurements were made by the same technique employed in the earlier reported experiments on nitrogen and hydrogen.^{11,12} Rubidium vapor in a 500 cm³ spherical absorption flask was oriented by the absorption of circularly polarized D_1 ($5P_{1/2} \rightarrow 5S_{1/2}$) resonance radiation. The orientation was monitored by observing the light transmitted by the bulb with a 925 vacuum photocell. A small amount of white phosphorus was then allowed to evaporate into the bulb. A radio-frequency discharge between two glass-covered electrodes in the center of the bulb dissociated some of the phosphorus molecules into atoms, and these atoms were polarized by spin-exchange collisions with the rubidium. When a radio-frequency field was applied so as to depolarize the phosphorus, the spin-exchange collisions resulted in a decrease in the rubidium polarization, and an increase of the amount of light absorbed by the bulb.

Most of the apparatus used in this experiment has been described in the papers on the hyperfine splittings of the hydrogen isotopes;^{12,13} only those aspects which are peculiar to this experiment will be discussed here. To excite the phosphorus hyperfine transitions, a simple vacuum tube tripler was employed to multiply the output of the Gertsch AM-1 frequency meter up to the

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¹ M. F. Ashley, *Phys. Rev.* **44**, 919 (1933).

² H. E. Walchli, Oak Ridge National Laboratory Report ORNL-1775, 1954 (unpublished).

³ S. Goudsmit, *Phys. Rev.* **37**, 663 (1931).

⁴ R. E. Trees, *Phys. Rev.* **92**, 308 (1953).

⁵ H. G. Dehmelt, *Phys. Rev.* **99**, 527 (1954).

⁶ T. P. Das and A. Mukherjee, *J. Chem. Phys.* **33**, 1808 (1960).

⁷ D. A. Goodings, *Phys. Rev.* **123**, 1706 (1961).

⁸ N. Bessis, H. Lefebvre-Brion, and C. M. Moser, *Phys. Rev.* **124**, 1124 (1961).

⁹ A. J. Freeman and R. E. Watson (to be published).

¹⁰ W. Marshall, *Proc. Phys. Soc. (London)* **78**, 113 (1961).

¹¹ L. W. Anderson, F. M. Pipkin, and J. C. Baird, Jr., *Phys. Rev.* **116**, 87 (1959).

¹² L. W. Anderson, F. M. Pipkin, and J. C. Baird, Jr., *Phys. Rev.* **120**, 1279 (1960).

¹³ F. M. Pipkin and R. H. Lambert, *Phys. Rev.* **127**, 787 (1962).

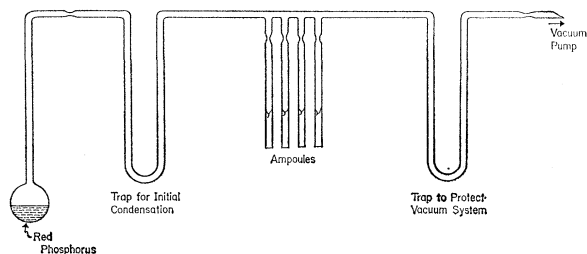


FIG. 1. A diagram of the glass vacuum system employed for preparation of the white phosphorus samples.

desired frequency of 110 Mc/sec. For observing the transitions this frequency was modulated by inserting the *L*-band relay between a 37-Mc/sec amplifier following the Gertsch and the tripler circuit. The frequencies were measured with a Northeastern frequency counter whose time base was derived from a stable 100-kc/sec crystal oscillator maintained and monitored by J. R. Pierce of the Cruft Laboratory.

Early attempts to orient phosphorus by spin-exchange collisions with rubidium revealed that the two could combine chemically. If there were too much phosphorus vapor in the absorption flask, the exposed rubidium rapidly became coated with a reddish scum, and the optical pumping signals disappeared. These experiments also indicated that because of its higher vapor pressure white phosphorus was more suitable than red phosphorus. The following procedure was evolved to overcome the chemical peculiarities of phosphorus.

First, a vacuum system was set up as shown in Fig. 1, and several ampoules of white phosphorus were prepared from a supply of red phosphorus. Each of these ampoules was provided with a break-off seal so that it could be sealed on to another system and then broken open at a later date. When preparing the white phosphorus, a Dewar of liquid nitrogen was placed around the U-tube between the red phosphorus supply and the ampoules. When the red phosphorus was heated, a mixture of red and white phosphorus condensed in the U-tube. The heating was stopped, the nitrogen-filled Dewar removed from the U-tube, and a second nitrogen-filled Dewar placed around the ampoules. As the first U-tube returned to room temperature, the white phosphorus evaporated and recondensed in the ampoules. This operation was repeated several times until each ampoule contained an ample supply of white phosphorus. The ampoules were then sealed off.

The construction of the optical pumping absorption flasks is illustrated in Fig. 2. One of the phosphorus ampoules was attached to each of the flasks. When it was desired to make a run, the bulb was inserted in the apparatus, the discharge turned on, and the rubidium signals optimized. At this point a liquid nitrogen Dewar was placed around the phosphorus ampoule. When the phosphorus was cold, a magnet

and the glass-covered iron slug were used to break open the ampoule. The Dewar was then removed, and as the phosphorus warmed, a search was made for the phosphorus Zeeman transitions. As soon as the phosphorus signals grew to an adequate size, the liquid nitrogen Dewar was replaced to prevent further evaporation of the phosphorus. The signals obtained in this manner were quite stable and maintained their strength for as long as it was desired to make measurements (usually 2 to 3 h). The three helium and the two neon bulbs constructed and operated in this manner worked very well. Three attempts to employ the same technique on bulbs with an argon buffer gas failed.

MEASUREMENTS AND RESULTS

The Hamiltonian for a phosphorus atom in a magnetic field is

$$\mathcal{H} = A\mathbf{I} \cdot \mathbf{J} - g_J \mu_0 \mathbf{J} \cdot \mathbf{H} - g_I \mu_0 \mathbf{I} \cdot \mathbf{H}.$$

Here, *A* is the magnetic hyperfine interaction constant, *g_J* is the gyromagnetic ratio for the electronic ground state, *g_I* is the nuclear gyromagnetic ratio, and *μ₀* is the Bohr magneton. The hyperfine interaction constant is positive for an atom-like hydrogen where the nuclear magnetic moment is positive and the effective magnetic field at the nucleus is antiparallel to the direction of the electron spin. The energy levels for P³¹ in a small magnetic field are shown in Fig. 3.

The first experimental efforts were directed towards the determination of the sign of the hyperfine interaction constant. The dc magnetic field was set at a value such that the phosphorus Zeeman lines in the *F*=2 hyperfine multiplet were resolved. For a known circular polarization of the rubidium light source, measurements were made of the amplitudes of the four Zeeman transitions in the *F*=2 multiplet. If left circularly polarized light is incident on the bulb, only $\Delta m = +1$ optical transitions

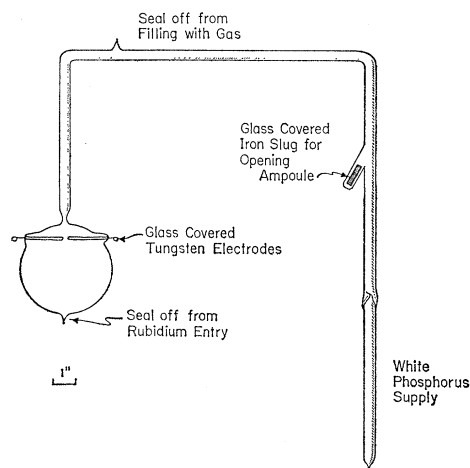


FIG. 2. A drawing illustrating the optical pumping flasks used for the phosphorus measurements.

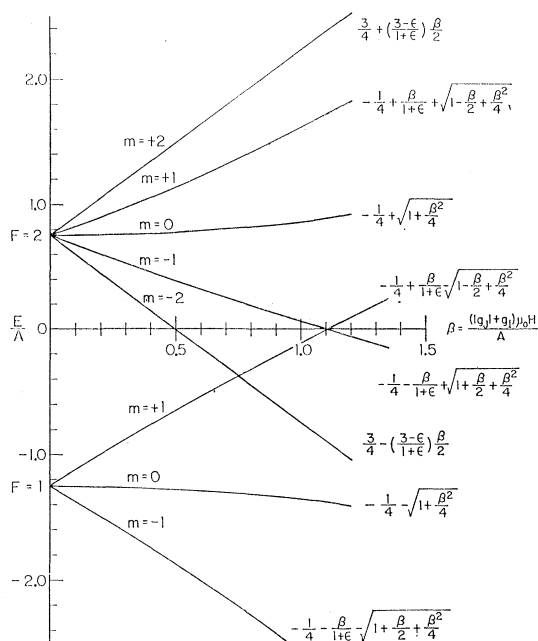


FIG. 3. The energy levels for the ground state of P^{31} in a magnetic field. Here, $\beta = (|g_J| + g_I)\mu_0 H/A$ and $\epsilon = g_I/|g_J|$.

are induced, the population of the $F=2$, $m=2$ state is greater than that of the $F=2$, $m=-2$ state, and the polarization of the phosphorus is sufficiently large that the amplitude of the $(2,2) \leftrightarrow (2,1)$ Zeeman transition is greater than that of the $(2,-2) \leftrightarrow (2,-1)$ transition. If A is positive, the $(2,-1) \leftrightarrow (2,-2)$ transition has the lowest frequency; if A is negative, the $(2,2) \leftrightarrow (2,1)$ transition has the lowest frequency. Thus, the observation of which transition had the smallest amplitude immediately gave the sign of the hyperfine interaction

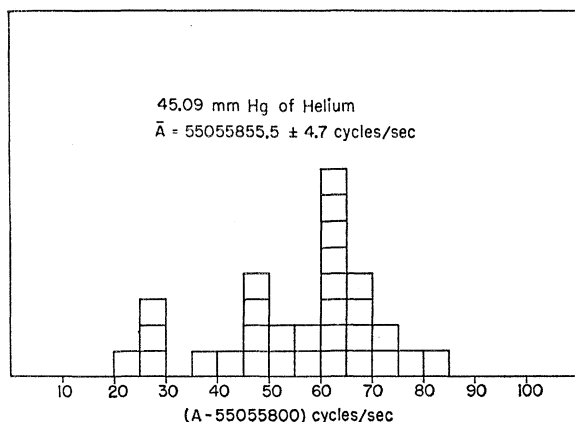


FIG. 4. A histogram of all the values of the phosphorus hyperfine interaction constant obtained for the 45.09 mm Hg helium bulb. For the determination of one value for the hyperfine interaction constant, two measurements were made on each of the $(2,2) \leftrightarrow (1,1)$ and $(2,-2) \leftrightarrow (1,-1)$ hyperfine transitions. Each square designates one value for the hyperfine interaction constant.

constant. This measurement showed that A was positive as in the case of the hydrogen atom.

Careful measurements were then made of the frequencies of the four Zeeman transitions in the $F=2$ multiplet for several magnetic fields in order to obtain a more precise value of the hyperfine interaction constant than that reported by Dehmelt and to reduce the search required to locate the $\Delta F=1$ hyperfine transitions. By this technique, the hyperfine splitting was determined to 100 kc/sec. The six $\Delta F=1, \Delta m=\pm 1$ hyperfine transitions were then searched for and found. The final observations for determining the zero-field hyperfine splitting were made by repeated measurements of the $(2,2) \leftrightarrow (1,1)$ and the $(2,-2) \leftrightarrow (1,-1)$ hyperfine transitions. These lines were selected because

TABLE I. The average hyperfine interaction constants for the phosphorus bulbs. The measurements were usually made in sets of ten and the standard deviation of the mean of each set was calculated. The bulb average is the unweighted average of the various sets taken for a particular bulb. The error quoted for the bulb average is the standard deviation of the distribution of set averages for that bulb. The bulb pressure is the pressure of the gas when the temperature of the bulb is 0°C . The measurements were made in the range 60 to 90°C .

Buffer gas	Pressure (mm Hg at 0°C)	Number of measure- ments in set	Set averages $A - 55\,050\,000$ (cycles/sec)
Helium	17.07 ± 0.10	10	5750.7 ± 4.4
		10	5757.6 ± 6.2
		Mean	5754.2 ± 4.8
Helium	33.62 ± 0.10	6	5816.6 ± 7.2
		10	5808.8 ± 5.0
		10	5814.4 ± 2.2
Helium	45.09 ± 0.10	Mean	5813.3 ± 4.0
		10	5850.3 ± 6.2
		10	5856.6 ± 2.3
Neon	53.91 ± 0.10	10	5859.5 ± 4.9
		10	5855.5 ± 4.7
		Mean	5855.5 ± 4.7
Neon	53.91 ± 0.10	10	6056.2 ± 1.5
		10	6055.4 ± 2.5
		Mean	6055.8 ± 1.3

they have the smallest g factor and consequently a small line width due to field inhomogeneity. The portion of the linewidth due to magnetic field inhomogeneities was 180 cps (0.25 mG). For the measurements, the rf driving field and the discharge were reduced to the point that the full width at half maximum of these hyperfine lines was 400 to 600 cps. The procedure employed in taking the measurements has been described in the paper on the remeasurement of the hydrogen and tritium hyperfine splittings.¹³ The sum of the frequencies of these two transitions depends quadratically on the magnetic field; the quadratic correction was calculated by using the difference of these two frequencies to determine the magnetic field. Figure 4 shows, in the form of a histogram, all the values of the hyperfine

interaction constant obtained for the high-pressure helium bulb.

In order to correct for the dependence of the observed hyperfine splitting upon the pressure of the buffer gas, phosphorus bulbs with three different helium pressures were prepared and measured. A least-squares procedure was used to fit the average hyperfine interaction constants for the various bulbs to a linear function of pressure. In order to determine the dependence of the observed hyperfine splitting upon the polarizability of the buffer gas, measurements were also made for one neon bulb. Three unsuccessful attempts were made to make measurements with an argon buffer gas. The average frequencies for the various bulbs and the number of measurements upon which they are based are summarized in Table I. Figure 5 depicts these

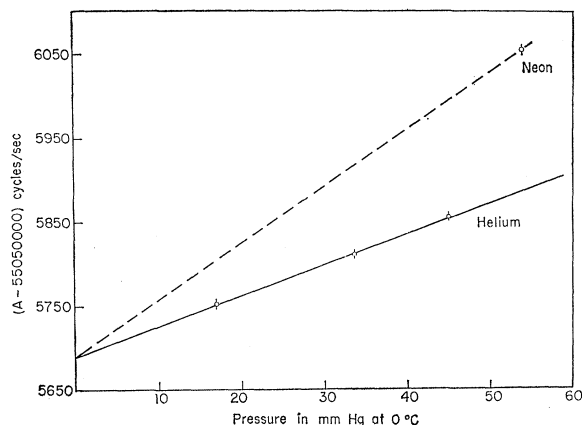


FIG. 5. A plot of the measured values of the phosphorus hyperfine interaction constant vs the buffer gas pressure for the three helium bulbs and the one neon bulb. The straight line through the helium points is the least-squares fit used to determine the zero-pressure hyperfine interaction constant.

same data graphically and shows the least-squares line for helium. The value of the phosphorus hyperfine interaction constant obtained by extrapolation to zero pressure is

$$A(P^{31}) = + (55\,055\,691.0 \pm 8.1) \text{ cps}$$

The quoted error is one standard deviation, and it was calculated by the standard least squares procedure. Previous experience indicates that twice this error usually gives a better estimate of the reliability of the measurement. It has been assumed that the phosphorus concentration was sufficiently small that no correction for the pressure shift due to the phosphorus vapor was

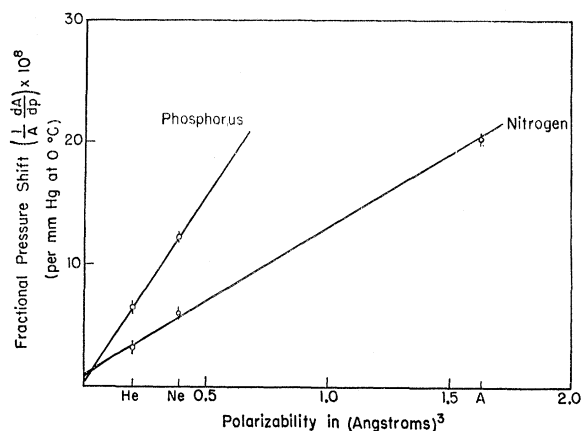


FIG. 6. A plot of the fractional pressure shifts $[(1/A)(dA/dP)]$ for phosphorus and nitrogen vs the polarizability of the buffer gas.

necessary. The pressure shift for the hyperfine interaction constant in helium is

$$dA/dP = + (3.61 \pm 0.23) \text{ cps/mm Hg},$$

and that for neon

$$dA/dP = + (6.73 \pm 0.15) \text{ cps/mm Hg}.$$

For calculating these pressure shifts, the bulb pressures at 0°C have been used. Thus, the density of the gas in the bulb is

$$N/V = p/kT_0,$$

where $T_0 = 273^\circ\text{K}$. The quoted error is the standard deviation, and it was calculated by the least-squares method. Figure 6 is a plot of the fractional pressure shift $[(1/A)(dA/dP)]$ vs the polarizability of the buffer gas for phosphorus and for nitrogen.¹⁴ The fractional pressure shifts for phosphorus and nitrogen depend upon the polarizability of the buffer gas in the same manner. This is the expected behavior if the nitrogen and phosphorus pressure shifts are due principally to the van der Waals interaction with the buffer gas.¹⁵ It is amusing to note that the magnetic field at the phosphorus nucleus is almost the same as that at the nitrogen nucleus: 63.9 kG for phosphorus and 67.9 for nitrogen.

ACKNOWLEDGMENTS

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¹⁴ R. H. Lambert and F. M. Pipkin, *Bull. Am. Phys. Soc.* **7**, 26 (1962).

¹⁵ F. J. Adrian, *Phys. Rev.* **127**, 837 (1962).