

One-to-Two Millimeter Wave Spectroscopy. V. PH_3 and PD_3 †

CHARLES A. BURRUS,* ALBERT JACHE, AND WALTER GORDY
 Department of Physics, Duke University, Durham, North Carolina
 (Received April 19, 1954)

The $J=0\rightarrow 1$ rotational transition of PH_3 has been measured at $\nu_0=266\,944.0\pm 1.0$ Mc/sec ($\lambda=1.12$ mm). With $D_J=3.15$ Mc/sec from infrared spectroscopy, this measurement yields $B_0=133\,478.3$ Mc/sec. Similarly, the $0\rightarrow 1$ transition of PD_3 was measured at $\nu_0=138\,937.98\pm 0.30$ Mc/sec ($\lambda=2.16$ mm) and $B_0=69\,470.41$ Mc/sec was obtained by using $D_J=0.71$ Mc/sec from infrared spectroscopy. The bond lengths in the two isotopic forms were found to be slightly different with $d_{\text{PH}}=1.4206\pm 0.005$ Å and $d_{\text{PD}}=1.4166\pm 0.005$ Å.

THE present paper on PH_3 and PD_3 is one of a series¹ reporting measurements in the newly opened one-to-two millimeter wave region on molecules which do not have rotational transitions occurring at the lower microwave frequencies. The first rotational line ($J=0\rightarrow 1$ transition) of PH_3 , observed in the present work, occurs at 1.12-mm wavelength, and thus the second (the $J=1\rightarrow 2$ not yet measured) should fall at 0.556 mm (556 microns) in what can be appropriately called the infrared region.

As early as 1933 pure rotational lines of PH_3 down to the $J=9\rightarrow 10$ transition were measured by Wright and Randall² with purely infrared-optical methods. More recently these measurements have been extended by Stroup, Oetjen, and Bell³ to the $J=5\rightarrow 6$ transition. Thus the rotational spectrum of PH_3 has now been measured by both microwave-electronic and infrared-optical methods. Although it has not yet been achieved, it seems probable that soon the same transition can be measured by both methods. It is an evidence of careful work by Wright and Randall that the $0\rightarrow 1$ transition was found to occur within 220 Mc/sec of the frequency predicted from their infrared measurements made some 21 years ago.

The mixed isotopic forms of phosphine PHD_2 and PH_2D are asymmetric rotors, and these have rotational transitions occurring in the lower-frequency microwave region. Certain of these have been investigated by Loomis and Strandberg⁴ and by Sirvetz and Weston.⁵ The infrared rotational vibration spectrum of phosphine has been studied by Fung and Barker⁶ and by McConaghie and Nielsen.⁷

† This research was supported by the U. S. Air Force under a contract monitored by the Office of Scientific Research, Air Research and Development Command.

* Shell Company Fellow.

¹ W. C. King and W. Gordy, Phys. Rev. **90**, 319 (1953); **93**, 407 (1954). Charles A. Burrus and W. Gordy, Phys. Rev. **92**, 274 (1953); **92**, 1437 (1953). W. Gordy and Charles A. Burrus, Phys. Rev. **93**, 419 (1954).

² N. Wright and H. M. Randall, Phys. Rev. **44**, 391 (1933).

³ Stroup, Oetjen, and Bell, J. Opt. Soc. Am. **43**, 1096 (1953).

⁴ C. C. Loomis and M. W. P. Strandberg, Phys. Rev. **81**, 798 (1951).

⁵ M. H. Sirvetz and R. E. Weston, Jr., J. Chem. Phys. **21**, 898 (1953).

⁶ L. W. Fung and E. F. Barker, Phys. Rev. **45**, 238 (1934).

⁷ V. M. McConaghie and H. H. Nielsen, J. Chem. Phys. **21**, 1836 (1953).

EXPERIMENTAL ASPECTS

The millimeter wave components employed are those already described by King and Gordy¹ (Parts I and IV of this series). For PD_3 measurements the cell was of K -band guide of one meter length with electroformed tapered sections to match to the smaller guide of the multiplier and detector. For PH_3 a cell of G -band guide of length 15 centimeters and total volume of 0.2 cubic centimeter was employed.

Lines of both PH_3 and PD_3 were observed on the cathode-ray scope with a simple video spectrometer having 60-cps sweep and a P amplifier of 5 kc/sec band width. However, it was found that an improvement in signal-to-noise ratio of about 25 times that of the video signal could be obtained with automatic recording with a phase lock-in detector as described elsewhere.¹ In the present work the receiver was tuned to the second harmonic of the modulation frequency, so that for sufficiently small modulation amplitudes the signal appears as a second derivative of the actual line shape function. The line frequencies were measured in the usual manner with a frequency standard monitored by Station WWV. The PH_3 was prepared by the action of H_2O on Mg_3P_2 , while the PD_3 was made in a similar manner using D_2O instead of H_2O .

SPECTRA AND MOLECULAR STRUCTURE

An automatic recording of the $J=0\rightarrow 1$ transition of PH_3 is shown in Fig. 1 and that of PD_3 in Fig. 2. For reasons already mentioned, the signal of Fig. 1 appears as a second derivative of the actual line shape function, while that of Fig. 2, because of the different

TABLE I. Molecular constants of phosphine.

PD_3	PH_3
$\nu_0(J=0\rightarrow 1)=138\,937.98$ ± 0.30 Mc/sec	$\nu_0(J=0\rightarrow 1)=266\,944.0$ ± 1.0 Mc/sec
$B_0=69\,470.41$ Mc/sec	$B_0=133\,478.3$ Mc/sec
$D_J=0.710$ Mc/sec (from infrared data ^a)	$D_J=3.15$ Mc/sec (from infrared data ^a)
$I_b=12.0758_6\times 10^{-40}$ g cm ²	$I_b=6.28499_7\times 10^{-40}$ g cm ²
$\angle \text{DPD}=93^\circ 10'$ (assumed)	$\angle \text{HPH}=93^\circ 27'$ (assumed)
$d_{\text{PD}}=1.4166\pm 0.005$ Å	$d_{\text{PH}}=1.4206\pm 0.005$ Å

^a See reference 3.

modulation employed, represents approximately a first derivative of the line shape. The line frequencies and other constants are listed in Table I.

The rotational lines of a symmetric top molecule are given by the formula

$$\nu_0 = 2B_0(J+1) - 2D_{JK}(J+1)K^2 - 4D_J(J+1)^3,$$

where J represents the lower rotational quantum number of the transition. Since only the $0 \rightarrow 1$ transitions were observed, D_{JK} and D_J cannot be obtained from the present measurements. In the infrared region, where the second term on the right becomes large, it is possible to obtain D_J with sufficient accuracy to correct for the small stretching effects on the $0 \rightarrow 1$ frequency to the degree of accuracy of our microwave measurements. Stroup, Oetjen, and Bell³ give for PH_3 , $4D_J = 421 \times 10^{-6} \text{ cm}^{-1}$ and for PD_3 , $4D_J = 95 \times 10^{-6}$. When converted to Mc/sec, these become 12.6 and 2.85, respectively, and with our $0 \rightarrow 1$ frequencies yield the B_0 values listed in Table I.

Because the zero-point vibration causes the effective ground-state values of the bond angles and bond lengths to be slightly different for the different isotopic forms, a simultaneous solution of the isotopic equation for PH_3 and PD_3 gives unreliable values for these parameters. For this reason we use information obtained by others on mixed isotopic forms in combination with our data to deduce values of the PH and PD distances. Since the mixed isotopic forms PH_2D and PHD_2 are asymmetric tops, more than one independent spectral constant can be obtained from microwave measurements for each form. Hence, a bond angle and a bond-length value for each species can be calculated if it is assumed that the PH and PD distances and the angle between the three bonds in each species are the same. Such solutions have been obtained by Sirvetz and Weston.⁵ These solutions are shown in Table II. They indicate that the PH and PD distances, as well as the HPH and DPD angles, are measurably

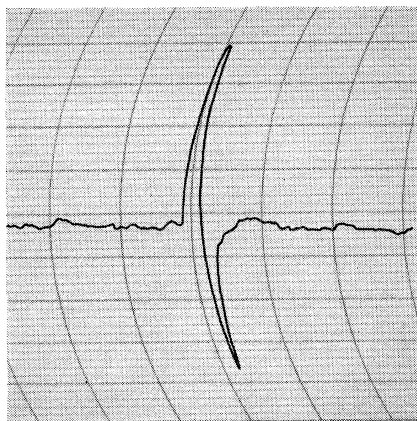


FIG. 1. Recorder tracing of the $J=0 \rightarrow 1$ transition of PH_3 at 1.12-mm wavelength.

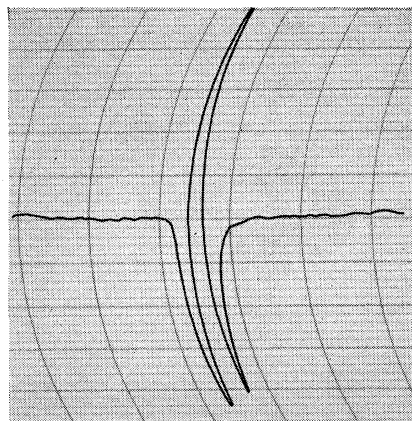


FIG. 2. Recorder tracing of the $J=0 \rightarrow 1$ transition of PD_3 at 2.16-mm wavelength.

different. Although the values given by Sirvetz and Weston are averaged values for the mixed forms, we can assume that those for PH_2D are nearer to the correct values for PH_3 than are those of PHD_2 , and similarly those obtained for PHD_2 are nearer to the correct values for PD_3 than are those of PD_2H . Furthermore, it is evident that the percentage variation for the bond angle in passing from one species to the other is much less than the percentage variation in the distances. For these reasons we assume that a change from PH_2D to PH_3 would cause the same increase in the effective angle as that of PHD_2 to PH_2D , and likewise that the change from PD_3 to PD_2H would cause the same increase as that from PD_2H to PD_3 . Thus are the angles listed for PH_3 and PD_3 in Table II obtained. With these assumed angles we calculated the PH and PD distances given in the same table. They are seen to differ by 0.004 Å. The error limits given for the PH and PD lengths are based on the assumption that the total difference in the bond angles of PH_2D and PHD_2 gives the maximum errors in the "guessed" bond angles for PH_3 and PD_3 .

Because the $K=0$ line is not split, no information could be obtained about the interesting possibility of low-frequency inversion splitting in PH_3 . We are hoping that further development of our generators and detectors may soon make it possible to observe the second rotational transition of PH_3 at 0.55-mm wavelength for which the $K=1$ line should be split

TABLE II. Molecular dimensions of phosphine.

	Bond angle	Bond length	Reference
PH_2D	$93^\circ 21.6'$	1.4177Å	Sirvetz and Weston ^a
PD_2H	$93^\circ 15.4'$	1.4116Å	Sirvetz and Weston ^a
PH_3	$93^\circ 27' \pm 6'$ (assumed)	$1.4206 \pm 0.005\text{Å}$	Present work
PD_3	$93^\circ 10' \pm 6'$ (assumed)	$1.4166 \pm 0.005\text{Å}$	Present work

^a See reference 5.

by inversion. Already submillimeter spectral lines have been observed at wavelengths as low as 0.77 mm.⁸

In collaboration with Dr. Ralph Livingston's group of the Oak Ridge National Laboratory, we are attempting to measure the nuclear moments of P³² by observation on the 0→1 transition of P³²D₃. At present this rotational

⁸ Charles A. Burrus and W. Gordy, Phys. Rev. **93**, 897 (1954).

line is being used as an analytical indicator by Dr. Livingston and Dr. Benjamin in the development of the microchemistry for the radioactive compound. The advantages of the shorter millimeter wave region for the study of moments of radioactive nuclei is obvious from the small cell volume of 0.2 cc employed for observations on PH₃ in the present work.

Spectrometer Studies of the Radiations of Neutron Deficient Isotopes of Cesium and of the *E3* Isomers, Xe^{127m} and Xe^{125m}†

HIRDAYA B. MATHUR* AND EARL K. HYDE

Radiation Laboratory and Department of Chemistry, University of California, Berkeley, California

(Received February 4, 1954; revised manuscript received April 27, 1954)

Cesium isotopes produced by I¹²⁷(α, xn) type reactions in the 60-inch and 184-inch cyclotrons were studied in Geiger counters, a mass spectrometer, beta-ray spectrometers, a sodium iodide crystal scintillation spectrometer, and a gamma-gamma coincidence spectrometer. The mass assignment of 30-minute Cs¹³⁰ was verified. The 6.25-hour Cs¹²⁷ was shown to decay predominantly by electron capture but also by the emission of positrons of 1.063-Mev and 0.685-Mev energy. Prominent gamma rays of 125 and 406 kev are observed. Cs¹²⁷ exhibits branching decay to 75-second Xe^{127m} in about one disintegration in 10⁴. This isomer was isolated and studied in a scintillation spectrometer. *E3* radiation of 175 kev connecting *h*_{11/2} and *d*_{5/2} levels is followed by 125-kev *M1* radiation corresponding to a *d*_{5/2}–*d*_{3/2} transition to the ground state. Forty-five minute Cs¹²⁵ is shown to decay predominantly by electron capture and also by the emission of positrons of 2.05-Mev energy. Other lower energy positron groups are present. A prominent gamma ray of 112 kev is observed. In one disintegration in about 10⁸, Cs¹²⁵ decays to a 55-second Xe^{125m}. This isomer emits gamma rays of 75 and 110 kev which are believed to be *E3* *h*_{11/2}–*d*_{5/2} and *M1* *d*_{5/2}–*d*_{3/2} transitions, respectively. An incomplete study of Cs¹²³ shows it to be a 6-minute positron emitter.

I. INTRODUCTION

THIS report concerns a study of some neutron-deficient isotopes of cesium prepared by bombardment of iodine with high-energy helium ions. The principal emphasis is on Cs¹²⁷ and Cs¹²⁵, although some preliminary data on Cs¹²³ and a confirmation of the mass assignment of Cs¹³⁰ are also reported. The work on Cs¹²⁷ represents a considerable extension of the previous studies of Fink, Reynolds, and Templeton,¹ while that on Cs¹²⁵ and Cs¹²³ represents completely new work. This report also describes a study of some short-lived isomers of Xe¹²⁷ and Xe¹²⁵ which appear in the decay of the cesium activities. The data on Xe^{127m} confirm and extend previous data on this isomer, while Xe^{125m} has not been reported before. Both isomers are probably of the *E3* type.

The experimental results are presented and discussed first, following which a brief account is given of our chemical methods and of the various instruments used to study the radiations.

† This work was carried out with the support of the U. S. Atomic Energy Commission.

* On leave of absence, Department of Chemistry, University of Delhi, Delhi, India.

¹ Fink, Reynolds, and Templeton, Phys. Rev. **77**, 614 (1950).

II. MASS ASSIGNMENT OF Cs¹³⁰

Following the preliminary studies of Risser and Smith² and of Fink, Reynolds, and Templeton¹ on a 30-minute cesium activity produced in bombardments of iodine with low-energy helium ions a careful study of the radiations emitted by this activity was carried out by Smith, Mitchell, and Caird.³ There is little doubt that the activity is produced by the (α, n) reaction and hence that the mass is correctly assigned to mass number 130. Nevertheless, it is probably worth recording the confirmation of this assignment by the use of a mass spectrograph.

Iodine in the form of calcium iodide was bombarded with 20-Mev helium ions in the 60-inch cyclotron. The cesium fraction was isolated in a carrier-free form within 1 hour of the end of the bombardment and run in the time-of-flight mass spectrometer described at the end of the paper. This work was done by Michel and Templeton.⁴ The 30-minute activity was collected in the mass-130 position.

² J. R. Risser and R. N. Smith (private communication from K. Lark-Horowitz, 1948) as reported by Hollander, Perlman, and Seaborg, Revs. Modern Phys. **25**, 469 (1953).

³ Smith, Mitchell, and Caird, Phys. Rev. **87**, 454 (1952).

⁴ M. C. Michel and D. H. Templeton, Phys. Rev. **93**, 1422 (1954).

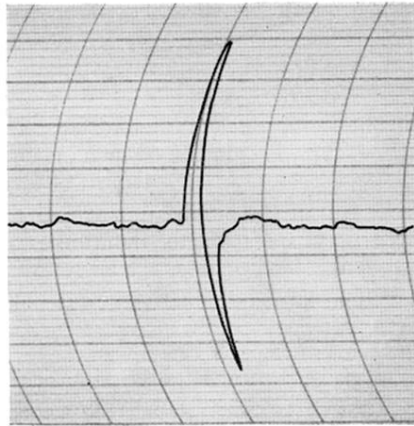


FIG. 1. Recorder tracing of the $J=0 \rightarrow 1$ transition of PH_3 at 1.12-mm wavelength.

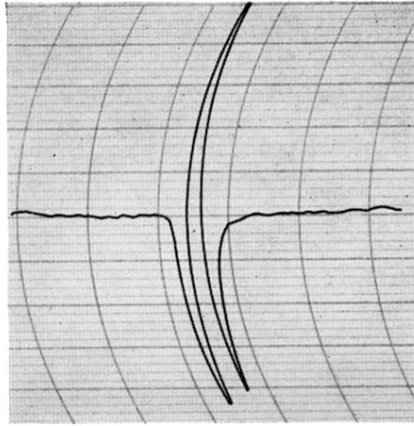


FIG. 2. Recorder tracing of the $J=0 \rightarrow 1$ transition of PD_3 at 2.16-mm wavelength.